

Near-surface Stratification Due to Ice Melt Biases Arctic Air-Sea CO₂ Flux Estimates

Yuanxu Dong^{1,2}, Mingxi Yang², Dorothee C. E. Bakker¹, Peter S. Liss¹, Vassilis Kitidis²,
Ian Brown², Melissa Chierici^{3,4}, Agneta Fransson⁵ and Thomas G. Bell²

¹Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University
of East Anglia, Norwich, UK

²Plymouth Marine Laboratory, Prospect Place, Plymouth, UK

³Institute of Marine Research, Fram Centre, Tromsø, Norway

⁴Department of Arctic Geophysics, University Centre in Svalbard, Longyearbyen, Norway

⁵Norwegian Polar Institute, Fram Centre, Tromsø, Norway

Correspondence to: Yuanxu Dong (Yuanxu.Dong@uea.ac.uk)

Key points:

- Seawater CO₂ fugacity ($f\text{CO}_{2w}$) vertical gradients are generated by fresh and cold sea-ice melt water, which lowers surface $f\text{CO}_{2w}$
- Air-sea CO₂ fluxes are biased when estimated using $f\text{CO}_{2w}$ observations from the subsurface (6 m depth) in sea-ice melt areas
- Summertime sea-ice melt could result in a 6–17% (with high uncertainty) underestimate of annual Arctic Ocean CO₂ uptake

29 **Abstract** Air-sea carbon dioxide (CO₂) flux is generally estimated by the bulk method using
30 upper ocean CO₂ fugacity measurements. In the summertime Arctic, sea-ice melt results in
31 stratification within the upper ocean (top ~10 m), which can bias bulk CO₂ flux estimates when
32 the seawater CO₂ fugacity is taken from a ship's seawater inlet at ~6 m depth ($f\text{CO}_{2w_bulk}$).
33 Direct flux measurements by eddy covariance are unaffected by near-surface stratification. We
34 use eddy covariance CO₂ flux measurements to infer sea surface CO₂ fugacity ($f\text{CO}_{2w_surface}$) in
35 the Arctic Ocean. In sea-ice melt regions, $f\text{CO}_{2w_surface}$ values are consistently lower than
36 $f\text{CO}_{2w_bulk}$ by an average of 39 μatm . Lower $f\text{CO}_{2w_surface}$ can be partially accounted for by
37 fresher ($\geq 27\%$) and colder (17%) melt waters. A back-of-the-envelope calculation shows that
38 neglecting the summertime sea-ice melt could lead to a 6–17% underestimate of the annual
39 Arctic Ocean CO₂ uptake.

40

41 **Plain language summary** The Arctic Ocean is considered to be a strong sink for atmospheric
42 CO₂. The air-sea CO₂ flux is almost always estimated indirectly using bulk seawater CO₂
43 fugacity measured from the ship's seawater inlet at typically ~6 m depth. However, sea-ice
44 melt results in near-surface stratification and can cause a bias in air-sea CO₂ flux estimates if
45 the bulk water CO₂ fugacity is used. The micrometeorological eddy covariance flux technique
46 is not affected by stratification. Here for the first time, we employ eddy covariance
47 measurements to assess the impact of sea-ice melt on Arctic Ocean CO₂ uptake estimates. The
48 results show that the summertime near-surface stratification due to sea-ice melt could lead to
49 an ~10% (with high uncertainty) underestimation of the annual Arctic Ocean CO₂ uptake.

50

51 **1. Introduction**

52 The Arctic Ocean is a strong sink of atmospheric CO₂ due to the active biological production
53 and high CO₂ solubility in cold waters (Anderson et al., 1998; Takahashi et al., 2009). While
54 only accounting for 4% of the world ocean by area and seasonally covered by sea ice, the Arctic
55 Ocean contributes 5–14% (66–199 Tg C yr⁻¹, Bates & Mathis, 2009; Yasunaka et al., 2018) of
56 mean global atmospheric CO₂ removal every year (~1400 Tg C yr⁻¹, Takahashi et al., 2009;
57 Landschützer et al., 2014). However, this Arctic carbon sink is rapidly changing due to climate
58 change. The Arctic warming rate has been more than twice as fast as the global average over
59 the past 5 decades (Romanovsky et al., 2017). The sea-ice extent in the Arctic Ocean in
60 September decreased at a rate of 13.1% decade⁻¹ during 1979–2020 relative to the 1981–2010

61 average (Perovich et al., 2020). Sea-ice loss reinforces upper ocean warming due to reduced
 62 surface albedo and increased shortwave penetration, which in turn inhibits sea-ice formation in
 63 winter and allows for acceleration of summertime sea-ice loss (Perovich et al., 2007). The
 64 reduction in sea-ice coverage in polar regions is expected to increase CO₂ uptake due to larger
 65 sea-ice free area, longer sea-ice free period, more freshwater at the surface and greater
 66 biological primary production (Bates & Mathis, 2009; Arrigo & van Dijken, 2015; McPhee et
 67 al., 2009; Perovich et al., 2020). However, sea-ice melt also causes near-surface stratification
 68 and suppresses water mixing between the surface and sub-surface, which likely generates
 69 upper-ocean gradients in temperature, salinity, dissolved inorganic carbon (DIC), total
 70 alkalinity (TA) and thus seawater CO₂ fugacity (Rysgaard et al., 2007; Li et al., 2009;
 71 Yamamoto-Kawai et al., 2009; Fransson et al., 2009, 2013; Cai et al., 2010; Else et al., 2013;
 72 Calleja et al., 2013; Miller et al., 2019; Ahmed et al., 2020).

73 The air-sea CO₂ flux (F_{CO_2} , mmol m⁻² day⁻¹) is generally estimated indirectly by the bulk
 74 equation as the product of the gas transfer velocity and the air-sea gas concentration difference.
 75 Accounting for near-surface temperature gradients, Woolf et al. (2016) recommended:

$$76 \quad F_{\text{CO}_2} = K_{660}(Sc/660)^{-0.5} (\alpha_{ss}f\text{CO}_{2w} - \alpha_s f\text{CO}_{2a}) \quad (1)$$

77 where K_{660} (cm h⁻¹) is the gas transfer velocity at a Schmidt number (Sc) of 660 (Wanninkhof
 78 et al., 2009). K_{660} is usually parameterized as a function of wind speed (e.g. Nightingale et al.,
 79 2000). α_{ss} and α_s are the CO₂ solubility (mol L⁻¹ atm⁻¹, Weiss, 1974) in the subskin and skin
 80 seawater, respectively (Woolf et al., 2016). $f\text{CO}_{2w}$ and $f\text{CO}_{2a}$ are the CO₂ fugacity (μatm) near
 81 the sea surface and in the overlying atmosphere, respectively. Similarly, the air-sea sensible
 82 heat flux can be estimated by the bulk method using a parameterized sensible heat transfer
 83 velocity and the sea-air temperature difference (Text S1).

84 Air-sea exchange of sparingly soluble gases (e.g. CO₂) is limited mostly by transport within
 85 the waterside molecular diffusive layer (MDL, 20–200 μm depth; Jähne, 2009) just beneath
 86 the water surface (Liss & Slater, 1974). Thus, $f\text{CO}_{2w}$ represents the CO₂ fugacity at the base of
 87 MDL ($f\text{CO}_{2w_surface}$). In practice, $f\text{CO}_{2w}$ measurements are generally made on bulk seawater
 88 from the ship's underway inlet (~ 6 m depth, $f\text{CO}_{2w_bulk}$). For convenience, the upper several
 89 meters of the ocean are assumed to be homogeneous in bulk flux calculations (i.e. $f\text{CO}_{2w} =$
 90 $f\text{CO}_{2w_surface} = f\text{CO}_{2w_bulk}$).

91 However, incidences of near-surface stratification call into question the vertical homogeneity
 92 assumption. In the Arctic, three sea-ice related mechanisms likely drive near-surface vertical

93 gradients in CO₂: 1) Brine drainage. When sea ice forms, carbonate species and salt are ejected
94 into the water under the sea ice as part of brine drainage (e.g. Fransson et al., 2013), which
95 depletes the CO₂ within the sea ice. The salty, dense water sinks and is eventually sequestered
96 in the deep ocean (Rudels et al., 2005). 2) Surface photosynthesis. Phytoplankton are often
97 found in the bottom ice or beneath the Arctic sea ice and their photosynthetic activity further
98 reduces the CO₂ concentration within the sea ice (Assmy et al., 2017; Fransson et al., 2013,
99 2017). 3) Ikaite dissolution. Dissolution of sea-ice derived ikaite will consume CO₂ in Arctic
100 surface waters (Fransson et al., 2017; Chierici et al., 2019). The latest measurements in the
101 Arctic coastal waters show significant vertical $f\text{CO}_{2w}$ gradients in the upper ocean (Ahmed et
102 al., 2020; Miller et al., 2019). Miller et al. (2019) show both positive and negative $f\text{CO}_{2w}$
103 gradients without separating the contributions of sea-ice melt and river runoff. Ahmed et al.
104 (2020) show consistently negative gradients (i.e., $f\text{CO}_{2w_surface} < f\text{CO}_{2w_bulk}$) in the sea-ice melt
105 regions. Vertical gradients, if left unaccounted for, will result in a bias in bulk air-sea CO₂ flux
106 estimates.

107 The micrometeorological eddy covariance (EC) method derives CO₂ fluxes directly and
108 represents an alternative approach for understanding Arctic air-sea CO₂ exchange. EC does not
109 rely on seawater measurements (Text S2), and thus EC fluxes are not affected by near-surface
110 vertical variation in seawater properties. However, polar oceans are a hostile environment and
111 reliable direct CO₂ flux measurements by EC are scarce (Butterworth & Miller, 2016; Prytherch
112 et al., 2017; Butterworth & Else, 2018; Prytherch & Yelland, 2021). This paper presents EC
113 CO₂ and sensible heat flux data from two Changing Arctic Ocean Programme cruises. Directly
114 measured fluxes were used to compute the implied sea surface $f\text{CO}_{2w}$ and water temperature
115 ($f\text{CO}_{2w_surface}$, $T_{w_surface}$). Comparisons of implied surface values with bulk measurements enable
116 us to assess the impact of vertical gradients on bulk air-sea CO₂ flux estimates. We further
117 speculate on the influence of near-surface stratification on bulk air-sea CO₂ flux estimates for
118 the entire Arctic Ocean.

119

120 **2. Methods**

121 **2.1 Description of Cruises**

122 Cruise tracks of JR18006 and JR18007 (on RRS *James Clark Ross*, *JCR*) and FS2019 (on RV
123 *Kronprins Haakon*) are shown in Figure S1. JR18006 visited the Barents Sea between 28 June
124 and 1 August 2019. JR18007 targeted the Fram Strait region within the Greenland Sea between

125 4 and 30 August 2019. DIC and TA were not measured during JR18006 and JR18007.
 126 Measurements taken between 2 and 5 September 2019 (between 0°W and 10°W) on cruise
 127 FS2019 were used to constrain the upper ocean carbonate system. Methods for DIC and TA
 128 measurements can be found in Chierici et al. (2019). The EC system on *JCR*, processing and
 129 quality control of fluxes, underway measurements and the meteorological observations are
 130 detailed elsewhere (Dong et al., 2021) and are briefly described in the supporting information
 131 (Text S3). $f\text{CO}_{2w}$ measurements were only available during ice-free periods of JR18007.

132 2.2 Implied Surface Variables From Eddy Covariance Fluxes

133 We use Brunt–Väisälä frequency (N^2) threshold to identify stratified waters. N^2 at ~6 m depth
 134 is calculated from the CTD (conductivity, temperature, depth) profiles ($N^2 = -g(\rho_{7m} -$
 135 $\rho_{5m})/(2 * \rho_{7m})$) with gravitational acceleration g and seawater density ρ). Fischer et al. (2019)
 136 used $N^2 \geq 10^{-4} \text{ s}^{-2}$ in upwelling waters, but we expect the threshold for near-surface stratification
 137 to be more evident in regions with sea- ice melt, so use a more robust threshold of $N^2 \geq 10^{-3} \text{ s}^{-2}$.
 138 Measurements in waters without a CTD cast and salinity below 34.5 are marked as having
 139 an ‘unknown’ stratification status.

140 The derivations of EC air-sea CO_2 flux ($F_{\text{CO}_2_EC}$) and sensible heat flux (H_{S_EC}) are detailed
 141 in the supporting information (Text S2). The gas transfer velocity (hourly) is computed by
 142 replacing the bulk flux with the hourly EC flux in a rearrangement of Equation 1:

$$143 \quad K_{660} = \frac{F_{\text{CO}_2_EC}}{(Sc/660)^{-0.5} (\alpha_{ss} f\text{CO}_{2w_bulk} - \alpha_s f\text{CO}_{2a})} \quad (2)$$

144 In regions with near-surface stratification, $f\text{CO}_{2w_bulk}$ may not be representative of the surface
 145 (i.e. $f\text{CO}_{2w_bulk} \neq f\text{CO}_{2w_surface}$). Therefore, to derive a wind speed (U_{10N}) dependent
 146 parametrization of K_{660} from this project (K_{660_u}), only data from non-stratified waters are
 147 considered. K_{660_u} and the EC CO_2 flux observations are then used to compute the implied
 148 $f\text{CO}_{2w_surface}$ for all water types (non-stratified and stratified):

$$149 \quad f\text{CO}_{2w_surface} = \frac{F_{\text{CO}_2_EC}}{K_{660_u}(Sc/660)^{-0.5} \alpha_{ss}} + \frac{\alpha_s}{\alpha_{ss}} f\text{CO}_{2a} \quad (3)$$

150 A similar approach is used to derive sensible heat transfer velocity (K_H) and compute the
 151 implied surface seawater temperature ($T_{w_surface}$):

$$152 \quad K_H = \frac{H_{S_EC}}{\rho_a c_{pa}(T_{w_bulk} - dT - T_a)} \quad (4)$$

153
$$T_{w_surface} = \frac{H_{S_EC}}{\rho_a c_{pa} K_{H_u}} + T_a \quad (5)$$

154 where K_H (cm h^{-1}) is parametrized with U_{10N} (K_{H_u}) using data from non-stratified waters
 155 (Figure S2). Here, ρ_a (kg m^{-3}) is the mean density of dry air, c_{pa} ($\text{J kg}^{-1} \text{K}^{-1}$) is the heat capacity
 156 of air and T_a (K) is the air temperature. The temperature offset due to the cool skin effect, dT
 157 (K), is estimated using the COARE 3.5 model (Edson et al., 2013; Fairall et al., 1996).

158

159 **3. Results and discussion**

160 **3.1 CO₂ flux time series**

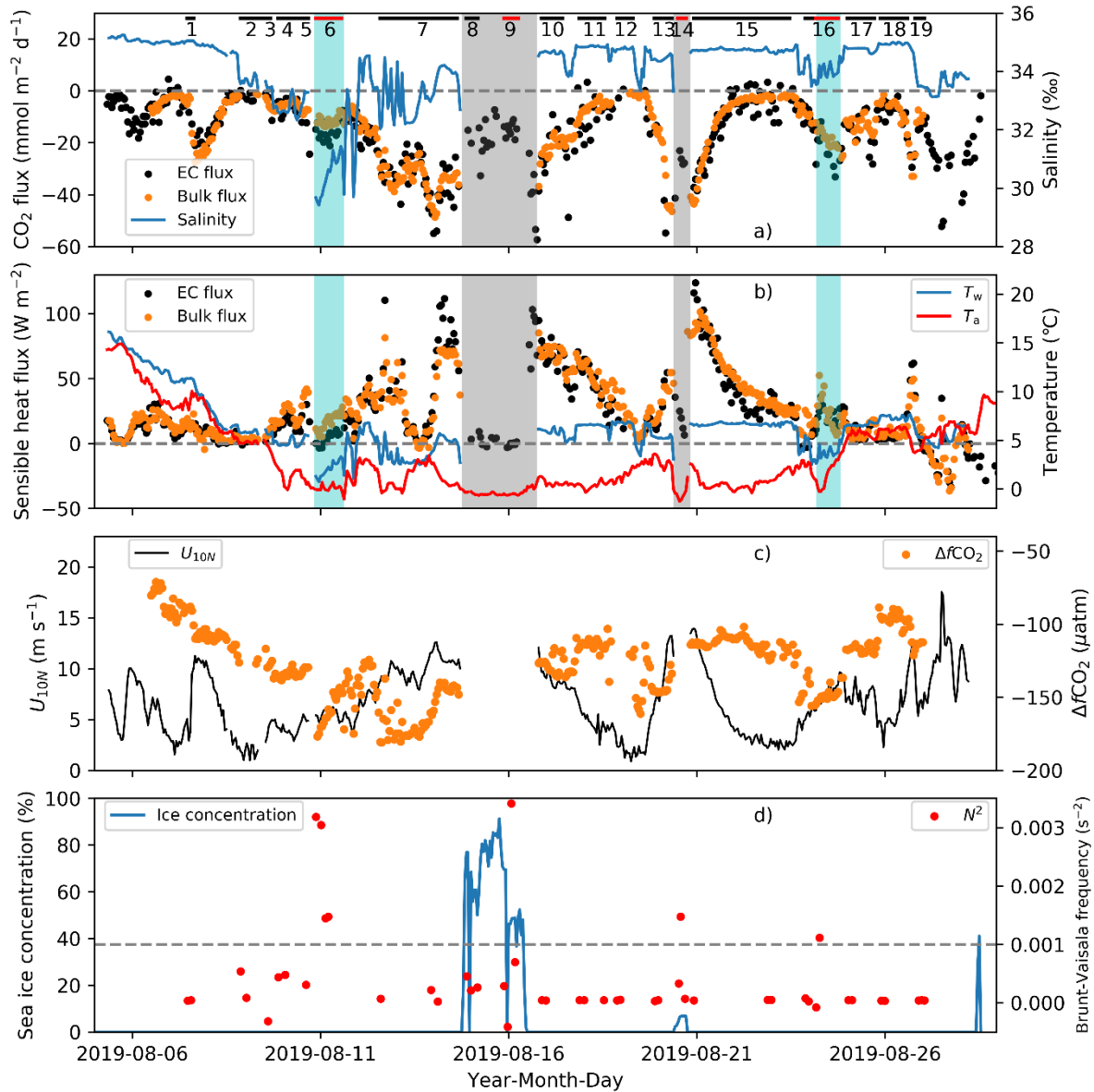
161 The time series of hourly averaged EC and bulk fluxes for CO₂ and heat are shown for cruise
 162 JR18007 (Figure 1). The bulk CO₂ flux is calculated from $f\text{CO}_{2w_bulk}$, $f\text{CO}_{2a}$ and T_{w_bulk}
 163 measurements using the gas transfer velocity parametrisation from Nightingale et al. (2000).
 164 The bulk sensible heat flux is computed using the COARE 3.5 model (Edson et al., 2013). The
 165 sea ice concentration (Figure 1d) is derived from the Advanced Microwave Scanning
 166 Radiometer-Earth Observing System (AMSR-E, daily and 3.125 km resolution; Spreen et al.,
 167 2008).

168 Stratified areas were located at the edge of or within the sea ice (Figure S1), with relatively low
 169 near-surface salinity and temperature (Figure 1) suggesting that sea-ice melt is the principal
 170 reason for near-surface stratification. Terrestrial runoff as a source of freshwater is unlikely
 171 because the ship was far from land (> 50 km) in the stratified stations (Figure S1). Furthermore,
 172 there were no significant precipitation events during the cruise, ruling out surface freshening
 173 due to precipitation.

174 The relatively good agreement between EC fluxes and bulk air-sea CO₂ fluxes in non-stratified
 175 regions (Figure 1a and S3) suggests that the data (EC fluxes and underway $f\text{CO}_{2w_bulk}$) are
 176 reliable and that the Nightingale et al. (2000) gas transfer velocity parameterization is
 177 reasonable for this study region. In areas with near-surface stratification (stations 6 and 16),
 178 bulk CO₂ fluxes are consistently less negative (lower in magnitude) than EC CO₂ fluxes (Figure
 179 1a). Meanwhile, bulk sensible heat fluxes are slightly higher than EC fluxes in stratified regions.

180 Another intriguing feature is that EC sensible heat fluxes were close to zero during sea ice
 181 stations 8 and 9, but EC CO₂ fluxes were still significant. The sea ice concentration data (Figure
 182 1d) show that the sea surface was not fully ice-covered in this region. One possible reason for

183 near-zero sensible heat flux but detectable CO₂ flux is that the surface (seawater or sea ice)
 184 temperature was close to the air temperature, while an $f\text{CO}_2$ gradient existed across the sea
 185 surface. Also, air-sea CO₂ exchange is mainly controlled by waterside processes (Liss & Slater,
 186 1974), whereas the air-sea heat exchange is controlled by airside processes (Yang et al., 2016).
 187 It is possible that the impact of sea ice on waterside controlled gases (e.g. CO₂) is different to
 188 the impact on airside controlled gases and heat.



189

190 **Figure 1.** Time series of hourly fluxes and environmental variables on JR18007. Negative (positive)
 191 fluxes represent ocean sinks (sources): a) EC and bulk air-sea CO₂ fluxes, and salinity at 6 m depth.
 192 Light blue shading shows near-surface stratification (identified from CTD profiles). Grey shading
 193 indicates ice-covered waters where the underway seawater system was shut off. Dashes on the top axis
 194 correspond to CTD stations. Stations with near-surface stratification are in red. Dash length represents

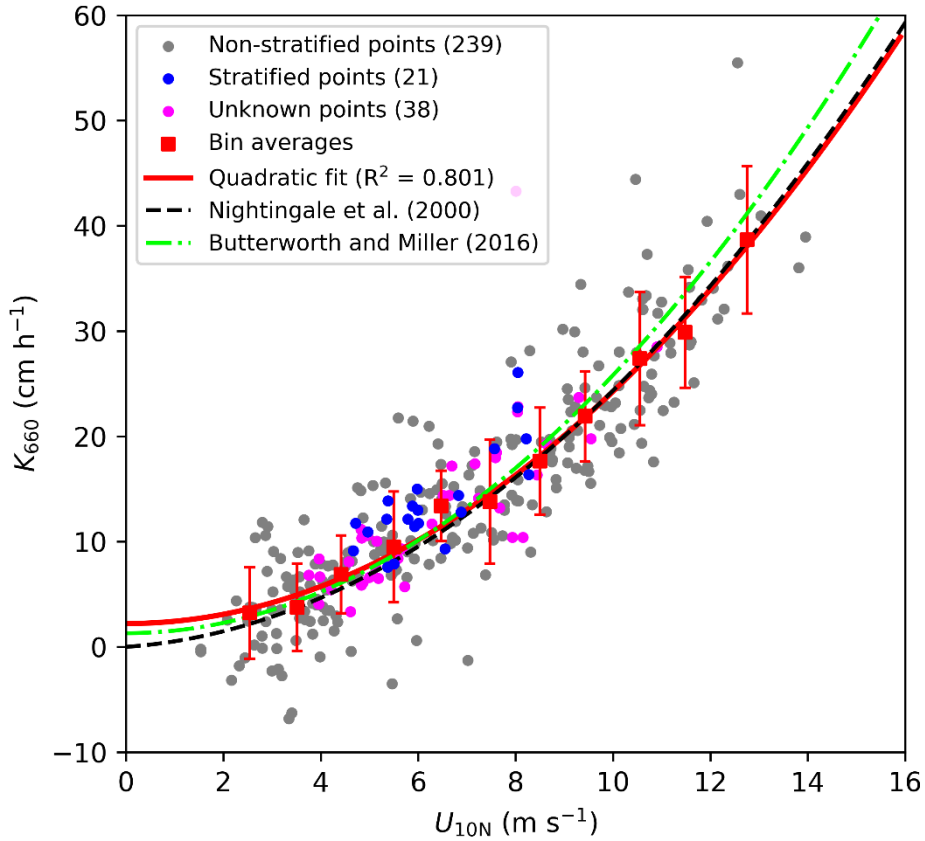
195 the duration on station; b) EC and bulk sensible heat flux, seawater temperature (T_w) at 6 m depth and
196 air temperature (T_a); c) 10-m neutral wind speed and air-sea CO_2 fugacity difference ($\Delta f\text{CO}_2 = f\text{CO}_{2w_bulk}$
197 $- f\text{CO}_{2a}$); d) Sea ice concentration (Spren et al., 2008) and Brunt–Väisälä frequency (N^2) at 6 m depth.

198

199 **3.2 Gas Transfer Velocity**

200 Dong et al. (2021) show that the hourly EC air-sea CO_2 flux relative uncertainty is $\sim 20\%$ on
201 average during JR18007. The $\Delta f\text{CO}_2$ ($= f\text{CO}_{2w_bulk} - f\text{CO}_{2a}$) ranges from -181 to -71 μatm (-
202 130 μatm on average, Figure 1c) during JR18007. The relatively low flux uncertainty and large
203 $\Delta f\text{CO}_2$ values enable us to estimate the gas transfer velocity (K_{660}) with high accuracy. Figure
204 2 shows K_{660} derived from quality-controlled EC CO_2 fluxes and $\Delta f\text{CO}_2$ observations, plotted
205 against 10-m neutral wind speed (U_{10N}); the latter is determined from measurements of wind
206 speed adjusted to U_{10N} using the COARE 3.5 model (Edson et al., 2013). There are 298 hourly
207 averaged K_{660} values. 239 hourly K_{660} values from non-stratified waters are binned in wind
208 speed intervals of 1 m s^{-1} and the bin averages (red squares) are used to derive a least square
209 quadratic fit. The fit ($K_{660_u} = 0.220 U_{10N}^2 + 2.213$) agrees fairly well with a widely-used K_{660}
210 parameterization based on dual tracer results (Nightingale et al., 2000) and a more recent
211 parameterization derived from EC air-sea CO_2 flux measurements (Butterworth & Miller,
212 2016).

213 The K_{660} data in stratified waters (21 hourly K_{660}) are consistently higher than the parameterized
214 K_{660_u} curve. Including data from stratified waters and waters with unknown stratification status
215 (38 hourly K_{660}) decreases the strength of the quadratic fit between hourly K_{660} and U_{10N} from
216 $R^2 = 0.801$ to $R^2 = 0.777$ (Table S1). This is most likely due to a vertical gradient in $f\text{CO}_{2w}$,
217 where $f\text{CO}_{2w_bulk}$ systematically exceeds $f\text{CO}_{2w_surface}$ (see Section 3.3).



218

219 **Figure 2.** Relationship between the CO₂ gas transfer velocity (K_{660} , derived from hourly EC air-sea CO₂
 220 flux measurements) and wind speed (U_{10N}) during JR18007. Grey dots represent K_{660} in non-stratified
 221 waters, blue dots correspond to K_{660} in stratified waters, and magenta dots indicate data with unknown
 222 stratification status. Red squares are 1 m s⁻¹ bin averages of the non-stratified values, with error bars
 223 representing 1 standard deviation. The red curve is a quadratic parameterization ($K_{660,u} = 0.220 U_{10N}^2 +$
 224 2.213 ; $R^2 = 0.801$). The K_{660} parameterizations of Nightingale et al. (2000) (black dashed) and
 225 Butterworth & Miller (2016) (green dot dashed) are also shown.

226

227 3.3 Implied Sea Surface CO₂ Fugacity and Temperature

228 The K_{660} parameterization in Figure 2 and the K_H parameterizations (Figure S2) are used for
 229 estimating $f\text{CO}_{2w_surface}$ (Equation 3) and $T_{w_surface}$ (Equation 5). Data at low wind speeds (U_{10N}
 230 < 4 m s⁻¹) are excluded from these calculations because of the low signal-to-noise ratios of EC
 231 fluxes and larger relative uncertainties in transfer velocities during calm conditions (Dong et
 232 al., 2021).

233 Figure 3 shows the comparison between hourly averages of the bulk seawater measurements
 234 ($f\text{CO}_{2w_bulk}$ and, in the case of temperature, adjusted for the cool skin: $T_w - dT$) and the implied

235 surface values ($f\text{CO}_{2\text{w_surface}}$ and $T_{\text{w_surface}}$). In non-stratified waters (grey dots in Figure 3a), the
236 means of the two $f\text{CO}_{2\text{w}}$ values compare reasonably well, even though the $f\text{CO}_{2\text{w_surface}}$ values
237 have a larger range than $f\text{CO}_{2\text{w_bulk}}$ due to variability in the EC CO_2 flux observations and the
238 uncertainty in the K_{660} parameterization. In stratified waters (blue dots in Figure 3a), the
239 implied $f\text{CO}_{2\text{w_surface}}$ values are consistently lower than $f\text{CO}_{2\text{w_bulk}}$, indicating that bulk
240 measurements are not representative of the surface. Similarly, EC implied $T_{\text{w_surface}}$ values are
241 consistently lower than the bulk water temperature in low salinity areas (≤ 32 , Figure 3b). These
242 data corroborate the CTD profiles from JR18007 (Figure S4) and suggest that the surface water
243 is colder and fresher than bulk water in regions with sea-ice melt.

244 Within the stratified areas during JR18007, $f\text{CO}_{2\text{w_surface}}$ (mean = $208 \mu\text{atm}$) is on average $39 \pm$
245 $39 \mu\text{atm}$ lower than $f\text{CO}_{2\text{w_bulk}}$ (mean = $247 \mu\text{atm}$), while $T_{\text{w_surface}}$ is on average $0.7 \pm 0.8 \text{ }^\circ\text{C}$
246 below $T_{\text{w_bulk}} - dT$. A temperature change of $0.7 \text{ }^\circ\text{C}$ should reduce $f\text{CO}_{2\text{w}}$ by $7 \mu\text{atm}$ according
247 to the Takahashi et al. (1993) empirical temperature relationship (Equation S5), suggesting that
248 the temperature effect accounts for 18% of the vertical $f\text{CO}_{2\text{w}}$ gradient within the stratified area.

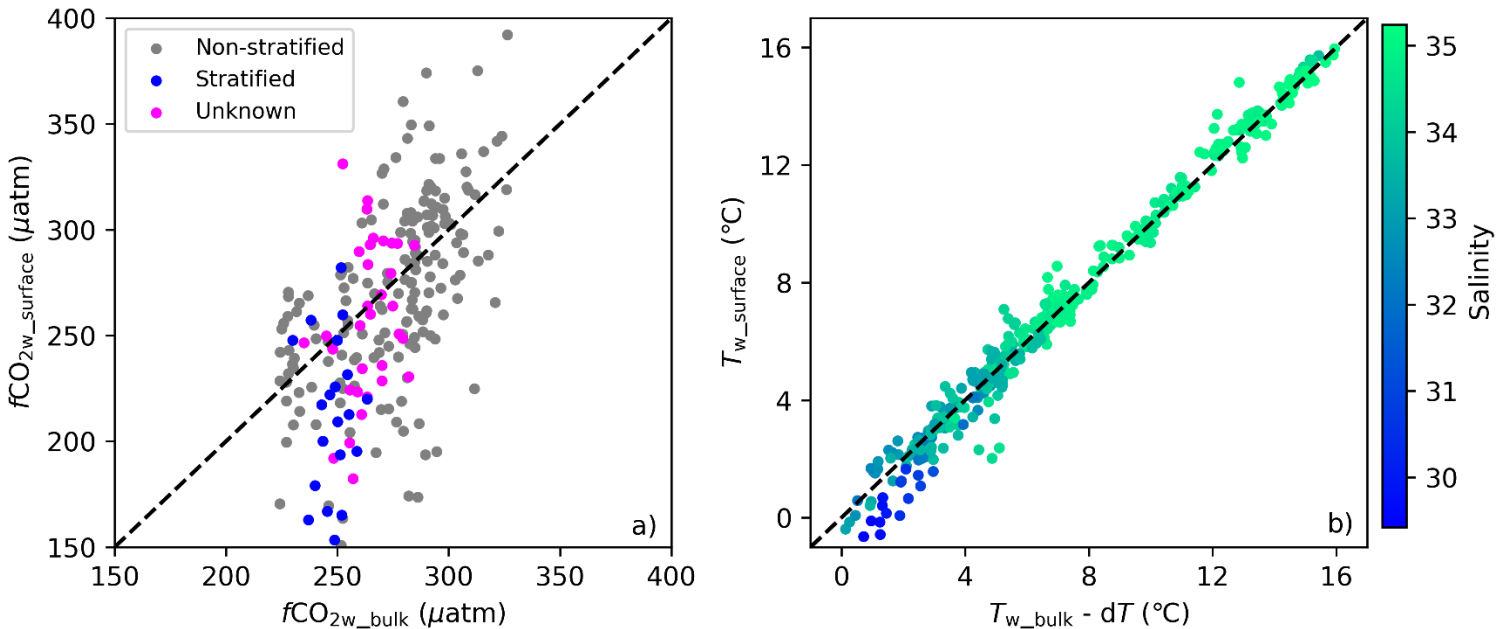
249 Although the top 4 m depth CTD data have been removed due to ship interferences and rough
250 sea state, CTD profiles still indicate that seawater at 4 m depth is fresher than the 5–10 m water
251 at the stratified stations (Figure S4). The shapes of near-surface salinity profiles generally
252 mirror those of temperature profiles (i.e. the vertical salinity gradient is nearly the same as the
253 temperature gradient in magnitude; Figure S4). Here we crudely assume that the salinity
254 difference between the sea surface and 6 m depth is 0.7 (i.e. corresponding to the temperature
255 difference of $0.7 \text{ }^\circ\text{C}$). Variations in near-surface salinity alter carbonate chemistry and influence
256 $f\text{CO}_{2\text{w}}$. We use bulk water (~ 6 m depth) DIC and TA measurements (Table S2) collected a
257 month later from 9 stations in the nearby Fram Strait (Figure S1, the sea ice concentration had
258 decreased from $\sim 50\%$ to $\sim 0\%$ during a previous week of the cruise) to estimate the influence
259 of salinity change on the vertical $f\text{CO}_{2\text{w}}$ gradient. The average DIC, TA and salinity were 1974
260 $\pm 19 \mu\text{mol kg}^{-1}$, $2100 \pm 22 \mu\text{mol kg}^{-1}$, and 30.6 ± 0.6 , respectively.

261 Bulk water DIC and TA are corrected to a sea surface salinity by dividing by bulk salinity and
262 multiplying by surface salinity (= bulk salinity - 0.7). The calculated surface and measured
263 bulk water DIC and TA are used to estimate the sensitivity in $f\text{CO}_{2\text{w}}$ to salinity change (Lewis
264 & Wallace, 1998; Van Heuven et al., 2011). We estimate that the vertical salinity gradient can
265 explain a $f\text{CO}_{2\text{w}}$ gradient of on average $10.6 \pm 1.1 \mu\text{atm}$. This salinity-related decrease in $f\text{CO}_{2\text{w}}$
266 accounts for 27% of the near-surface vertical $f\text{CO}_{2\text{w}}$ gradient. Considering that the surface

267 seawater is expected to be rapidly warmed by solar radiation, whereas salinity is less affected
 268 by surface warming, the temperature effect will be more transitory than the salinity effect. Thus,
 269 the estimated salinity effect is likely conservative, i.e. greater than 27%.

270 Sea-ice-related plankton metabolism might be another reason for lower $f\text{CO}_{2w}$ in the surface
 271 stratified layer. The CTD oxygen profiles show that the oxygen concentration increases close
 272 to the surface in the stratified stations (Figure S4). Chierici et al. (2019) observed meltwater-
 273 induced phytoplankton production in the marginal ice zone near Fram Strait in May 2019,
 274 which continued until the end of August. Photosynthesis in the upper few meters of the water
 275 column could reduce $f\text{CO}_{2w}$.

276 Air-sea gas exchange cannot be the cause of the lower surface $f\text{CO}_{2w}$ observed in stratified
 277 waters because the influx of CO_2 would have not help to explain the observations, increasing
 278 $f\text{CO}_{2w}$ at the surface. The results presented here demonstrate that near-surface stratification due
 279 to sea-ice melt generates a strong near-surface $f\text{CO}_{2w}$ gradient ($f\text{CO}_{2w_surface} < f\text{CO}_{2w_bulk}$),
 280 which causes a bias in bulk air-sea CO_2 flux estimates when $f\text{CO}_{2w_bulk}$ from ~ 6 m depth is
 281 used. In the next section, we estimate the impact of such a bias would have on CO_2 uptake by
 282 the entire Arctic Ocean.



284 **Figure 3.** Measurements at 6 m depth of seawater CO_2 fugacity ($f\text{CO}_{2w_bulk}$) and temperature (corrected
 285 for the cool skin effect, i.e. $T_{w_bulk} - dT$) versus eddy covariance implied sea surface CO_2 fugacity
 286 ($f\text{CO}_{2w_surface}$) and temperature ($T_{w_surface}$): a) $f\text{CO}_2$ values from cruise JR18007. Grey dots are values in
 287 non-stratified waters, blue dots are in stratified waters and magenta dots are in waters for which the

288 stratification status could not be determined; b) Seawater temperature for JR18006 and JR18007 with
289 the dots colour-coded by salinity at 6 m depth.

290

291 **3.4 Potential Impact on Arctic Ocean CO₂ Uptake Estimates**

292 Here we speculate on the potential impact of near-surface stratification due to summertime sea-
293 ice melt on estimates of CO₂ uptake for the entire Arctic Ocean.

294 We make the following crude assumptions: 1) bulk $f\text{CO}_{2w}$ measurements overestimate the
295 surface $f\text{CO}_{2w}$ in all regions with sea-ice melt; 2) the $f\text{CO}_{2w}$ overestimation ($-f\text{CO}_{2w}$ offset,
296 μatm) decreases with wind speed for $U_{10N} > 3 \text{ m s}^{-1}$ ($f\text{CO}_{2w}$ offset = $-408 U_{10N}^{-1} + 27$, Figure
297 S5) (Fischer et al., 2019; Miller et al., 2019; Ahmed et al., 2020) and is assumed to be constant
298 ($109 \mu\text{atm}$) at $U_{10N} \leq 3 \text{ m s}^{-1}$; 3) surface seawater temperature and salinity are 2°C and 31 within
299 the stratified areas, respectively (average of the EC implied $T_{w_surface}$ and surface salinity in the
300 stratified waters during JR18007).

301 The 6-hour Cross-Calibrated Multi-Platform (CCMP) Wind Vector Analysis (Atlas et al., 2011)
302 at a height of 10 m above mean sea level is used to calculate K_{660} and to estimate the $f\text{CO}_{2w}$
303 offset. The flux offset is calculated with Equation 1 (replacing $\Delta f\text{CO}_2$ with $f\text{CO}_{2w}$ offset), and
304 the result from each grid cell is linearly scaled using the sea ice concentration. The AMSR-E
305 (Spren et al., 2008) daily sea ice concentration (SIC) data (3.125 km grid resolution) are used
306 to determine the extent of stratified areas. There are two scenarios when a grid cell is deemed
307 to contain near-surface stratified water: 1) the ice-free proportion of the grid cell is considered
308 to be stratified when SIC is between 0% and 100%; 2) SIC of a grid cell has declined to 0%
309 during the last 10 days (assuming that near-surface stratification lasts for 10 days, within the
310 indicated duration time indicated by Ahmed et al., 2020), the whole cell is considered to be
311 stratified.

312 We focus on the summertime (June to August inclusive) Arctic Ocean in 2019. The result
313 shows that the largest area with near-surface stratification and the greatest underestimation of
314 CO₂ uptake occur in July (Figure S6). K_{660} increases with the wind speed, while the magnitude
315 of $f\text{CO}_{2w}$ offset decreases with wind speed, so the wind speed effect on the variability of the
316 flux offset is almost cancelled out and the estimated bulk flux variability is mainly related to
317 the size of the stratified area. The integrated summertime underestimation of Arctic Ocean CO₂

318 uptake due to sea-ice melt is estimated to be 11 Tg C, which is comparable with the back-of-
319 the-envelope calculation (9.3 Tg C yr⁻¹) of Ahmed et al. (2020)

320 The above estimate is based on assumptions that the $f\text{CO}_{2\text{w}}$ offset is wind speed dependent and
321 the shallow stratification lasts for 10 days. High wind speed enhances the near-surface seawater
322 mixing and weakens the shallow stratification. We do not have a robust relationship between
323 $f\text{CO}_{2\text{w}}$ offset and wind speed because our measurements in stratified waters only span a small
324 range of wind speeds ($6 \pm 1 \text{ m s}^{-1}$) and the data are quite scattered (Figure S5). If we do not
325 consider the influence of wind speed on the $f\text{CO}_{2\text{w}}$ gradient and assume a constant $f\text{CO}_{2\text{w}}$ offset
326 of $-39 \mu\text{atm}$ in the sea ice melt region, then the underestimation of Arctic Ocean CO_2 uptake is
327 reduced to 6 Tg C. Another major uncertainty is inherent in our assumption that near-surface
328 stratification lasts for 10 days. If we assume that the near-surface stratification lasts 7 days or
329 14 days, the underestimation of Arctic Ocean CO_2 uptake is 10 Tg C and 13 Tg C, respectively
330 (using the wind speed dependent $f\text{CO}_{2\text{w}}$ offset).

331 The underestimation of 11 Tg C in 2019 corresponds to 6–17% of annual Arctic Ocean carbon
332 uptake (66–199 Tg C yr⁻¹, Bates & Mathis, 2009). Note that the CO_2 sink estimate by Bates &
333 Mathis (2009) was a decade ago, so the percentage of this underestimate may have slightly
334 changed.

335

336 **4. Conclusions**

337 This study reports direct and indirect estimates of air-sea CO_2 and sensible heat fluxes from
338 shipboard campaigns in the summertime Arctic Ocean. Direct fluxes by eddy covariance are
339 used to compute the implied sea surface $f\text{CO}_{2\text{w}}$ and T_{w} . Comparisons of implied surface values
340 with bulk water measurements at 6 m depth help to identify possible vertical $f\text{CO}_{2\text{w}}$ gradients
341 in the upper ocean. Implied surface $f\text{CO}_{2\text{w}}$ is on average $39 \mu\text{atm}$ lower than bulk $f\text{CO}_{2\text{w}}$ in
342 regions with near-surface stratification due to sea ice melt. EC-derived gas transfer velocities
343 (K_{660}) using bulk seawater measurements in non-stratified regions agree well with previous
344 parameterizations. However, in stratified regions, EC-derived K_{660} is higher at a given wind
345 speed because of the near-surface $f\text{CO}_{2\text{w}}$ gradient.

346 Cooling and freshening due to sea-ice melt in the Arctic summer accounts for 18% and at least
347 27% of the near-surface $f\text{CO}_{2\text{w}}$ gradient during cruise JR18007, respectively. Enhanced

348 photosynthesis in the stratified layer may also have contributed to the near-surface $f\text{CO}_{2w}$
349 gradient.

350 The Arctic Ocean is an important CO_2 sink, but this ocean carbon uptake may have been
351 underestimated previously due to near-surface $f\text{CO}_{2w}$ gradients induced by sea-ice melt. A
352 simple calculation for the summertime Arctic Ocean suggests that near-surface stratification
353 due to sea-ice melt could lead to an ~ 10 Tg C underestimation of CO_2 uptake but there is
354 considerable uncertainty in the validity of such an extrapolation. Continuing loss of Arctic sea
355 ice is expected to increase CO_2 uptake in summer, and may further increase the uncertainty in
356 Arctic air-sea CO_2 flux estimates if near-surface stratification is not considered.

357 This is the first time to our knowledge that direct measurements by EC have been used to
358 quantify the potential bias in bulk flux estimates due to near-surface stratification in the Arctic
359 Ocean. A similar underestimation in CO_2 flux related to sea-ice melt may also occur in the
360 Southern Ocean. Detailed studies of upper ocean (0–10 m) gradients in $f\text{CO}_{2w}$, temperature,
361 salinity, DIC, TA and biological rates along with EC flux measurements, are required to
362 improve understanding of sea-ice melt impacts and near-surface stratification on air-sea
363 exchange.

364

365 *Data Availability Statement.* The raw EC data and hourly flux data can be accessed at:
366 <https://doi.org/10.5285/03C78C45-08B5-4D82-B09D-09C0B8A32C4D>. The CTD profile data
367 are stored at the British Oceanographic Data Centre (BODC):
368 https://www.bodc.ac.uk/data/bodc_database/nodb/cruise/17335/. AMSR-E data: [https://seaice.uni-](https://seaice.uni-bremen.de/data/amr2/asi_daygrid_swath/n3125/)
369 [bremen.de/data/amr2/asi_daygrid_swath/n3125/](https://seaice.uni-bremen.de/data/amr2/asi_daygrid_swath/n3125/). CCMP data:
370 <http://data.remss.com/ccmp/v02.1.NRT/>

371

372 *Acknowledgements:* The Natural Environment Research Council (NERC) supported the Arctic research
373 campaigns (DIAPOD, NE/P006280/2; ChAOS, NE/P006493/1 and PETRA, NE/R012830/1). CO_2 flux
374 measurements were made possible by funding from the NERC ORCHESTRA (NE/N018095/1) and
375 European Space Agency AMT4oceanSatFluxCCN (4000125730/18/NL/FF/gp) projects. DIC/TA data
376 were supported by Flagship program “Ocean Acidification and effects in northern waters” within the
377 FRAM-High North Research Centre for Climate and Environment, Tromsø, Norway. We thank
378 captains and crew of RRS *James Clark Ross* and all those who helped keep the CO_2 flux system running.
379 We thank Robyn Owen (BODC) for her kind help with the CTD profile data. The analysis of these data
380 is supported by the China Scholarship Council (CSC/201906330072).

381

382 **References**

- 383 Ahmed, M. M. M., Else, B. G. T., Capelle, D., Miller, L. A., & Papakyriakou, T. (2020).
384 Underestimation of surface $p\text{CO}_2$ and air-sea CO_2 fluxes due to freshwater stratification in an
385 Arctic shelf sea, Hudson Bay. *Elementa: Science of the Anthropocene*, 8(1): 084.
386 <https://doi.org/10.1525/elementa.084>
- 387 Anderson, L. G., Olsson, K., & Chierici, M. (1998). A carbon budget for the Arctic Ocean. *Global*
388 *Biogeochemical Cycles*, 12(3), 455–465. <https://doi.org/10.1029/98GB01372>
- 389 Arrigo, K. R., & van Dijken, G. L. (2015). Continued increases in Arctic Ocean primary production.
390 *Progress in Oceanography*, 136, 60–70. <https://doi.org/10.1016/j.pocean.2015.05.002>
- 391 Assmy, P., Fernández-Méndez, M., Duarte, P., Meyer, A., Randelhoff, A., Mundy, C. J., et al. (2017).
392 Leads in Arctic pack ice enable early phytoplankton blooms below snow-covered sea ice.
393 *Scientific Reports*, 7 (40850 2017), 1–9. <https://doi.org/10.1038/srep40850>
- 394 Atlas, R., Hoffman, R. N., Ardizzone, J., Leidner, S. M., Jusem, J. C., Smith, D. K., & Gombos, D.
395 (2011). A cross-calibrated, multiplatform ocean surface wind velocity product for
396 meteorological and oceanographic applications. *Bulletin of the American Meteorological*
397 *Society*, 92(2), 157–174. <https://doi.org/10.1175/2010BAMS2946.1>
- 398 Bates, N. R., & Mathis, J. T. (2009). The Arctic Ocean marine carbon cycle: evaluation of air-sea CO_2
399 exchanges, ocean acidification impacts and potential feedbacks. *Biogeosciences*, 6(11).
400 <https://doi.org/10.5194/bg-6-2433-2009>, 2009
- 401 Butterworth, B. J., & Miller, S. D. (2016). Air-sea exchange of carbon dioxide in the Southern Ocean
402 and Antarctic marginal ice zone. *Geophysical Research Letters*, 43(13), 7223–7230.
403 <https://doi.org/10.1002/2016GL069581>
- 404 Butterworth, B. J., & Else, B. G. T. (2018). Dried, closed-path eddy covariance method for measuring
405 carbon dioxide flux over sea ice. *Atmospheric Measurement Techniques*, 11(11), 6075–6090.
406 <https://doi.org/10.5194/amt-11-6075-2018>
- 407 Cai, W.-J., Chen, L., Chen, B., Gao, Z., Lee, S. H., Chen, J., et al. (2010). Decrease in the CO_2 uptake
408 capacity in an ice-free Arctic Ocean basin. *Science*, 329(5991), 556–559.
409 <https://doi.org/10.1126/science.1189338>
- 410 Calleja, Maria Ll, Duarte, C. M., Álvarez, M., Vaquer-Sunyer, R., Agustí, S., & Herndl, G. J. (2013).
411 Prevalence of strong vertical CO_2 and O_2 variability in the top meters of the ocean. *Global*
412 *Biogeochemical Cycles*, 27(3), 941–949. <https://doi.org/10.1002/gbc.20081>
- 413 Chierici, M., Vernet, M., Fransson, A., & Børsheim, K. Y. (2019). Net community production and

414 carbon exchange from winter to summer in the Atlantic water inflow to the Arctic Ocean.
415 *Frontiers in Marine Science*, 6(September), 1–24. <https://doi.org/10.3389/fmars.2019.00528>

416 Dong, Y., Yang, M., Bakker, D. C. E., Kitidis, V., & Bell, T. G. (2021). Uncertainties in eddy
417 covariance air-sea CO₂ flux measurements and implications for gas transfer velocity
418 parameterisations. *Atmospheric Chemistry and Physics*, 21(10), 8089–8110.
419 <https://doi.org/10.5194/acp-21-8089-2021>

420 Edson, J. B., Jampana, V., Weller, R. A., Bigorre, S. P., Plueddemann, A. J., Fairall, C. W., et al.
421 (2013). On the exchange of momentum over the open ocean. *Journal of Physical Oceanography*,
422 43(8), 1589–1610. <https://doi.org/10.1175/JPO-D-12-0173.1>

423 Else, Brent G T, Galley, R. J., Lansard, B., Barber, D. G., Brown, K., Miller, L. A., et al. (2013).
424 Further observations of a decreasing atmospheric CO₂ uptake capacity in the Canada Basin
425 (Arctic Ocean) due to sea ice loss. *Geophysical Research Letters*, 40(6), 1132–1137.
426 <https://doi.org/10.1002/grl.50268>

427 Fairall, C. W., Bradley, E. F., Godfrey, J. S., Wick, G. A., Edson, J. B., & Young, G. S. (1996). Cool-
428 skin and warm-layer effects on sea surface temperature. *Journal of Geophysical Research:*
429 *Oceans*, 101(C1), 1295–1308. <https://doi.org/10.1029/95JC03190>

430 Fischer, T., Kock, A., Arévalo-Martínez, D. L., Dengler, M., Brandt, P., & Bange, H. W. (2019). Gas
431 exchange estimates in the Peruvian upwelling regime biased by multi-day near-surface
432 stratification. *Biogeosciences*, 16(11), 2307–2328. <https://doi.org/10.5194/bg-16-2307-2019>

433 Fransson, A., Chierici, M., & Nojiri, Y. (2009). New insights into the spatial variability of the surface
434 water carbon dioxide in varying sea ice conditions in the Arctic Ocean. *Continental Shelf*
435 *Research*, 29(10), 1317–1328. <https://doi.org/10.1016/j.csr.2009.03.008>

436 Fransson, A., Chierici, M., Miller, L. A., Carnat, G., Shadwick, E., Thomas, H., et al. (2013). Impact
437 of sea-ice processes on the carbonate system and ocean acidification at the ice-water interface of
438 the Amundsen Gulf, Arctic Ocean. *Journal of Geophysical Research: Oceans*, 118(12), 7001–
439 7023. <https://doi.org/10.1002/2013JC009164>

440 Fransson, A., Chierici, M., Skjelvan, I., Olsen, A., Assmy, P., Peterson, A. K., et al. (2017). Effects of
441 sea-ice and biogeochemical processes and storms on under-ice water *f*CO₂ during the winter-
442 spring transition in the high Arctic Ocean: Implications for sea-air CO₂ fluxes. *Journal of*
443 *Geophysical Research: Oceans*, 122(7), 5566–5587.
444 <https://doi.org/https://doi.org/10.1002/2016JC012478>

445 Van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., & Wallace, D. W. R. (2011). MATLAB
446 program developed for CO₂ system calculations. *ORNL/CDIAC-105b*, 530.

- 447 Jähne, B. (2009). Air–sea gas exchange. in *Encyclopedia Ocean Sciences*, edited by J. H. Steele, K. K.
448 Turekian, and S. A. Thorpe, pp. 3434–3444, Elsevier, San Diego, Calif.
- 449 Landschützer, P., Gruber, N., Bakker, D. C. E., & Schuster, U. (2014). Recent variability of the global
450 ocean carbon sink. *Global Biogeochemical Cycles*, 28(9), 927–949.
451 <https://doi.org/10.1002/2014GB004853>
- 452 Landwehr, S., O’Sullivan, N., & Ward, B. (2015). Direct flux measurements from mobile platforms at
453 sea: Motion and airflow distortion corrections revisited. *Journal of Atmospheric and Oceanic*
454 *Technology*, 32(6), 1163–1178. <https://doi.org/10.1175/JTECH-D-14-00137.1>
- 455 Lewis, E. R., & Wallace, D. W. R. (1998). *Program developed for CO₂ system calculations*.
456 Environmental System Science Data Infrastructure for a Virtual Ecosystem.
457 <https://doi.org/10.15485/1464255>
- 458 Li, W. K. W., McLaughlin, F. A., Lovejoy, C., & Carmack, E. C. (2009). Smallest algae thrive as the
459 Arctic Ocean freshens. *Science*, 326(5952), 539. <https://doi.org/10.1126/science.1179798>
- 460 Liss, P. S., & Slater, P. G. (1974). Flux of gases across the air–sea interface. *Nature*, 247(5438), 181–
461 184. <https://doi.org/10.1038/247181a0>
- 462 Loose, B., Miller, L. A., Elliott, S., & Papakyriakou, T. (2011). Sea ice biogeochemistry and material
463 transport across the frozen interface. *Oceanography*, 24(3), 202–218.
464 <https://doi.org/10.5670/oceanog.2011.72>
- 465 McPhee, M. G., Proshutinsky, A., Morison, J. H., Steele, M., & Alkire, M. B. (2009). Rapid change in
466 freshwater content of the Arctic Ocean. *Geophysical Research Letters*, 36(10).
467 <https://doi.org/10.1029/2009GL037525>
- 468 Miller, L. A., Burgers, T. M., Burt, W. J., Granskog, M. A., & Papakyriakou, T. N. (2019). Air–sea
469 CO₂ flux estimates in stratified arctic coastal waters: how wrong can we be? *Geophysical*
470 *Research Letters*, 46(1), 235–243. <https://doi.org/10.1029/2018GL080099>
- 471 Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., et al. (2000). In
472 situ evaluation of air–sea gas exchange parameterizations using novel conservative and volatile
473 tracers. *Global Biogeochemical Cycles*, 14(1), 373–387. <https://doi.org/10.1029/1999GB900091>
- 474 Perovich, D. K., Light, B., Eicken, H., Jones, K. F., Runciman, K., & Nghiem, S. V. (2007).
475 Increasing solar heating of the Arctic Ocean and adjacent seas, 1979–2005: Attribution and role
476 in the ice–albedo feedback. *Geophysical Research Letters*, 34(19), L19505.
477 <https://doi.org/10.1029/2007GL031480>
- 478 Perovich, D., Meier, W., Tschudi, M., Hendricks, S., Petty, A. A., Divine, D., et al. (2020). Arctic

479 Report Card 2020: Sea Ice. (U. S. N. O. and A. A. O. of O. and A. R. P. M. E. L. (U.S.), T. S. of
480 Engineering, N. S. and I. D. C. (U.S.), U. of C. (Boulder campus), H. C. for P. and M. R. Alfred-
481 Wegener-Institut für Polar- und Meeresforschung / Alfred Wegener Institute, G. S. F. Center, et
482 al., Eds.). <https://doi.org/https://doi.org/10.25923/n170-9h57>

483 Prytherch, John, Brooks, I. M., Crill, P. M., Thornton, B. F., Salisbury, D. J., Tjernström, M., et al.
484 (2017). Direct determination of the air-sea CO₂ gas transfer velocity in Arctic sea ice regions.
485 *Geophysical Research Letters*, 44(8), 3770–3778. <https://doi.org/10.1002/2017GL073593>

486 Prytherch, J., & Yelland, M. J. (2021). Wind, convection and fetch dependence of gas transfer
487 velocity in an Arctic sea-ice lead determined from eddy covariance CO₂ flux measurements.
488 *Global Biogeochemical Cycles*, 35, e2020GB006633. <https://doi.org/10.1029/2020GB006633>

489 Romanovsky, V., Isaksen, K., D., D., Anisimov, O., A, I., Leibman, M., et al. (2017). Changing
490 permafrost and its impacts. In: Snow, Water, Ice and Permafrost in the Arctic (SWIPA) 2017
491 (pp. 65–102). <http://hdl.handle.net/11374/1931>

492 Rudels, B., Björk, G., Nilsson, J., Winsor, P., Lake, I., & Nohr, C. (2005). The interaction between
493 waters from the Arctic Ocean and the Nordic Seas north of Fram Strait and along the East
494 Greenland Current: Results from the Arctic Ocean-02 Oden expedition. *Journal of Marine*
495 *Systems*, 55(1–2), 1–30. <https://doi.org/10.1016/j.jmarsys.2004.06.008>

496 Rysgaard, S., Glud, R. N., Sejr, M. K., Bendtsen, J., & Christensen, P. B. (2007). Inorganic carbon
497 transport during sea ice growth and decay: A carbon pump in polar seas. *Journal of Geophysical*
498 *Research: Oceans*, 112(3), 1–8. <https://doi.org/10.1029/2006JC003572>

499 Spreen, G., Kaleschke, L., & Heygster, G. (2008). Sea ice remote sensing using AMSR-E 89-GHz
500 channels. *Journal of Geophysical Research: Oceans*, 113(C2).
501 <https://doi.org/10.1029/2005JC003384>

502 Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., & Sutherland, S. C. (1993). Seasonal
503 variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study. *Global*
504 *Biogeochemical Cycles*, 7(4), 843–878. <https://doi.org/10.1029/93GB02263>

505 Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., et al.
506 (2009). Climatological mean and decadal change in surface ocean pCO₂, and net sea-air CO₂
507 flux over the global oceans. *Deep Sea Research Part II: Topical Studies in Oceanography*,
508 56(8–10), 554–577. <https://doi.org/10.1016/J.DSR2.2008.12.009>

509 Wanninkhof, R., Asher, W. E., Ho, D. T., Sweeney, C., & McGillis, W. R. (2009). Advances in
510 quantifying air-sea gas exchange and environmental forcing. *Annual Review of Marine Science*,
511 1(1), 213–244. <https://doi.org/10.1146/annurev.marine.010908.163742>

- 512 Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine*
513 *Chemistry*, 2(3), 203–215. [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2)
- 514 Woolf, D. K., Land, P. E., Shutler, J. D., Goddijn-Murphy, L. M., & Donlon, C. J. (2016). On the
515 calculation of air-sea fluxes of CO₂ in the presence of temperature and salinity gradients.
516 *Journal of Geophysical Research: Oceans*, 121(2), 1229–1248.
517 <https://doi.org/10.1002/2015JC011427>
- 518 Yamamoto-Kawai, M., McLaughlin, F. A., Carmack, E. C., Nishino, S., & Shimada, K. (2009).
519 Aragonite undersaturation in the Arctic Ocean: effects of ocean acidification and sea ice melt.
520 *Science*, 326(5956), 1098–1100. <https://doi.org/10.1126/science.1174190>
- 521 Yang, M., Bell, T. G., Blomquist, B. W., Fairall, C. W., Brooks, I. M., & Nightingale, P. D. (2016).
522 Air-sea transfer of gas phase controlled compounds. In *IOP Conference Series: Earth and*
523 *Environmental Science* (Vol. 35, p. 12011). IOP Publishing. [https://doi.org/10.1088/1755-](https://doi.org/10.1088/1755-1315/35/1/012011)
524 [1315/35/1/012011](https://doi.org/10.1088/1755-1315/35/1/012011)
- 525 Yasunaka, S., Siswanto, E., Olsen, A., Hoppema, M., Watanabe, E., Fransson, A., et al. (2018). Arctic
526 Ocean CO₂ uptake: an improved multiyear estimate of the air–sea CO₂ flux incorporating
527 chlorophyll a concentrations. *Biogeosciences*, 15(6), 1643–1661. [https://doi.org/10.5194/bg-15-](https://doi.org/10.5194/bg-15-1643-2018)
528 [1643-2018](https://doi.org/10.5194/bg-15-1643-2018), 2018
- 529
- 530 **References From the Supporting Information**
- 531 Dong, Y., Yang, M., Bakker, D. C. E., Kitidis, V., & Bell, T. G. (2021). Uncertainties in eddy
532 covariance air–sea CO₂ flux measurements and implications for gas transfer velocity
533 parameterisations. *Atmospheric Chemistry and Physics*, 21(10), 8089–8110.
534 <https://doi.org/10.5194/acp-21-8089-2021>
- 535 Donlon, C. J., Minnett, P. J., Gentemann, C., Nightingale, T. J., Barton, I. J., Ward, B., & Murray, M.
536 J. (2002). Toward improved validation of satellite sea surface skin temperature measurements
537 for climate research. *Journal of Climate*, 15(4), 353–369. [https://doi.org/10.1175/1520-](https://doi.org/10.1175/1520-0442(2002)015<0353:TIVOSS>2.0.CO;2)
538 [0442\(2002\)015<0353:TIVOSS>2.0.CO;2](https://doi.org/10.1175/1520-0442(2002)015<0353:TIVOSS>2.0.CO;2)
- 539 Edson, J. B., Hinton, A. A., Prada, K. E., Hare, J. E., & Fairall, C. W. (1998). Direct covariance flux
540 estimates from mobile platforms at sea. *Journal of Atmospheric and Oceanic Technology*, 15(2),
541 547–562. [https://doi.org/10.1175/1520-0426\(1998\)015<0547:DCFEFM>2.0.CO;2](https://doi.org/10.1175/1520-0426(1998)015<0547:DCFEFM>2.0.CO;2)
- 542 Edson, J. B., Jampana, V., Weller, R. A., Bigorre, S. P., Plueddemann, A. J., Fairall, C. W., et al.
543 (2013). On the exchange of momentum over the open ocean. *Journal of Physical Oceanography*,

544 43(8), 1589–1610. <https://doi.org/10.1175/JPO-D-12-0173.1>

545 Fairall, C. W., Bradley, E. F., Godfrey, J. S., Wick, G. A., Edson, J. B., & Young, G. S. (1996). Cool-
546 skin and warm-layer effects on sea surface temperature. *Journal of Geophysical Research:*
547 *Oceans*, 101(C1), 1295–1308. <https://doi.org/10.1029/95JC03190>

548 Kitidis, V., Brown, I., Hardman-Mountford, N., & Lefèvre, N. (2017). Surface ocean carbon dioxide
549 during the Atlantic Meridional Transect (1995–2013); evidence of ocean acidification. *Progress*
550 *in Oceanography*, 158, 65–75. <https://doi.org/10.1016/j.pocean.2016.08.005>

551 Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., et al. (2000). In
552 situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile
553 tracers. *Global Biogeochemical Cycles*, 14(1), 373–387. <https://doi.org/10.1029/1999GB900091>

554 Spreen, G., Kaleschke, L., & Heygster, G. (2008). Sea ice remote sensing using AMSR-E 89-GHz
555 channels. *Journal of Geophysical Research: Oceans*, 113(C2).
556 <https://doi.org/10.1029/2005JC003384>

557 Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., & Sutherland, S. C. (1993). Seasonal
558 variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study. *Global*
559 *Biogeochemical Cycles*, 7(4), 843–878. <https://doi.org/10.1029/93GB02263>

560 Yang, M., Bell, T. G., Blomquist, B. W., Fairall, C. W., Brooks, I. M., & Nightingale, P. D. (2016).
561 Air-sea transfer of gas phase controlled compounds. In *IOP Conference Series: Earth and*
562 *Environmental Science* (Vol. 35, p. 12011). IOP Publishing. [https://doi.org/10.1088/1755-](https://doi.org/10.1088/1755-1315/35/1/012011)
563 [1315/35/1/012011](https://doi.org/10.1088/1755-1315/35/1/012011)

564

565