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1 **Sensitivity of the global ocean carbon sink to the ocean skin in a climate model**

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14

15 **Key points:**

16 - Considering the ocean skin increases the global ocean CO₂ sink by +0.26 to +0.37 PgC yr⁻¹

17 (~15% for 2000-2014) in an Earth System Model

18 - Enabling the ocean skin adjustment to feedback on ocean carbon concentrations dampens

19 this increase to +0.13 PgC yr⁻¹ (~5% for 2000-2014)

20 - This global adjustment depends on the CO₂ flux formulation and ultimately on the model

21 capacity to transfer CO₂ into the ocean interior.

22

23

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26

27 **Abstract**

28 The ocean skin is composed of thin interfacial microlayers of temperature and mass of less
29 than 1 mm where heat and chemical exchanges are controlled by molecular diffusion. It is
30 characterized by a cooling of $\sim -0.2\text{K}$ and an increase in salinity of $\sim 0.1\text{ g/kg}$ (absolute salinity)
31 relative to the water below. A surface observation-based air-sea CO_2 flux estimate considering
32 the variation of the CO_2 concentration in these microlayers has been shown to lead to an
33 increase in the global ocean sink of the anthropogenic CO_2 by $+0.4\text{ PgC yr}^{-1}$ (15% of the global
34 sink). This study analyzes this effect in more details using a 15-year (2000-2014) simulation
35 from an Earth System Model (ESM) that incorporates a physical representation of the ocean
36 surface layers (diurnal warm layer and rain lenses) and microlayers. Results show that
37 considering the microlayers increases the simulated global ocean carbon sink by $+0.26$ to
38 $+0.37\text{ PgC yr}^{-1}$ depending on assumptions on the chemical equilibrium. This is indeed about
39 15% of the global sink (2.04 PgC yr^{-1}) simulated by the ESM. However, enabling the ocean skin
40 adjustment to feedback on ocean carbon concentrations reduces this increase to only $+0.13$
41 (± 0.09) PgC yr^{-1} . Coupled models underestimate the ocean carbon sink by $\sim 5\%$ if the ocean skin
42 effect is not included.

43

44 **Plain Language Summary**

45 The ocean skin is a thin layer of less than a millimeter that is in contact with the atmosphere,
46 where the heat and chemical exchanges are controlled by molecular diffusion. It typically
47 corresponds to a temperature at the ocean interface that is cooler by -0.2K than the water at
48 a depth of a millimeter. It also corresponds to a salinity that is slightly higher at the interface.
49 Taking into account these temperature and salinity changes in this thin layer can change
50 calculations of the global ocean carbon sink substantially. We use a global Earth System Model

51 including a representation of the ocean skin to study this impact. We found an increase of 15%
52 in the simulated global ocean carbon sink. This is consistent with past studies. Enabling the
53 flux to feedback on the ocean carbon concentration significantly reduces its impact. We
54 conclude by discussing the uncertainties in the global ocean carbon sink associated with the
55 formulation of the carbon flux and the representation of the ocean skin.

56

57 **1. Introduction**

58 The global ocean represents a major sink of anthropogenic carbon emissions, averaging
59 $2.8 \pm 0.4 \text{ PgC yr}^{-1}$ during the decade 2011–2020 (26 % of total CO₂ emissions, Friedlingstein et
60 al. 2022). This estimate is obtained by using independent approaches: (i) An ensemble of
61 global ocean biogeochemical models forced by atmospheric reanalysis and atmospheric CO₂
62 concentration and (ii) an ensemble of observation-based data products using the Surface
63 Ocean CO₂ Atlas (SOCAT, Bakker et al. 2016). These data are based on interpolations of oceanic
64 CO₂ fugacity measurements, and then corrected for the preindustrial natural carbon
65 outgassing (Regnier et al. 2022). These model- and data-based estimates, cumulated in time,
66 are compared to estimates of changes in ocean carbon inventories based on hydrographic
67 campaign (Gruber et al. 2019). Both approaches (i) and (ii) have inherent uncertainties due to,
68 for example, sparse coverage of oceanic CO₂ measurements (e.g. Walker Brown et al. 2015,
69 Olivier et al. 2022) or the representation of unresolved processes in the numerical models.
70 However, even a perfect agreement between these complementary approaches would hide
71 uncertainties due to the consideration of oceanic variables (e.g. temperature, salinity,
72 dissolved carbon concentrations) at a depth of one to several meters and not at the ocean
73 interface. In situ CO₂ fugacity (or effective partial pressure) measurements are from ships and
74 to a lesser extent from moorings, both of which typically measure water characteristics at 1-

75 5 m depth. In models, temperature (T), salinity (S) and the CO_2 partial pressure computed from
76 alkalinity (Alk) and dissolved inorganic carbon (DIC) are mean values from the model's upper
77 level that is typically 1-2 m but can be of 10 m in some Earth System Model (ESM)
78 configurations. Yet, there can be substantial changes in T , S , Alk and DIC within the first tens
79 of centimeters (e.g. Ho and Schanze 2020).

80 Under the stabilizing effect of solar radiation or rain, a thin stratification of a few tenths
81 of meters to a few meters can form at the ocean interface. Diurnal warm layers correspond
82 to a temperature increase near the ocean surface during daylight when the wind is weak and
83 sky is clear (e.g., Stommel et al. 1969, Soloviev and Lukas 2014). They are particularly frequent
84 in the tropics but can also be strong and frequent in high latitudes during the summer (Stuart-
85 Menteth et al 2003, Kawai and Wada 2007, Bellenger and Duvel 2009). On the other hand,
86 freshening by rain can lead to the formation of stable fresh and often colder lenses (e.g.
87 Katsaros and Buettner 1969, Reverdin et al. 2012, Moulin et al. 2021) that can correspond to
88 a decrease down to -9 g/kg and -1.5K (Reverdin et al. 2020). Rain lenses are frequent in the
89 tropics where the precipitation rate is high and the wind speed is low (e.g. Drushka et al. 2016,
90 Moulin et al. 2021) but they can also occur at higher latitudes (Ten Doeschate et al. 2019,
91 Supply et al. 2020). In addition, vertical gradients in temperature and salinity exist in the
92 viscous boundary microlayer that typically extends within the first millimeter of the ocean and
93 constitutes the Temperature Boundary Layer (TBL) and the Mass Boundary Layer (MBL), which
94 are the diffusive microlayers for temperature and salinity respectively (Fig.1). Saunders (1967)
95 first described the physics of these layers in which the temperature and salinity gradients are
96 controlled by sensible and latent heat fluxes and infrared radiation at the interface and by
97 molecular and turbulent diffusion in the ocean. Most of the time, this leads to a cool skin of
98 around -0.2K to -0.3K (Fairall et al. 1996) and to an increase in salinity of about 0.1 g/kg (Zhang

99 and Cai 2007, Yu 2010, Zhang and Zhang 2012), but the ocean skin can lead to cooler and
100 fresher microlayers under rain conditions (Schlüssel et al 1997, Soloviev and Lukas 2014).

101 It has been suggested that thermohaline stratification in the first meters of the ocean
102 impacts CO₂ exchange at the ocean interface. Diurnal warming tends to increase ocean
103 outgassing (Ward et al. 2004). On the contrary, rain has been shown to have multiple effects
104 such as increasing the gas transfer velocity either in or out of the ocean by enhancing near-
105 surface turbulence and bubbles (Ho et al. 1997), increasing the carbon sink through dilution
106 in the first meter of the ocean (Turk et al. 2010, Ho and Schanze 2020). Note that freshening
107 by sea-ice melt and river runoff in coastal regions can also impact near surface stratification
108 and thus CO₂ fluxes by lowering the water-side CO₂ concentration (e.g., Miller et al. 2019,
109 Dong et al. 2021), but these processes will not be examined in this study.

110 Air-sea CO₂ exchange occurs in the ubiquitous microlayer described above (e.g., Liss and
111 Slater 1974), and the temperature change across it has been suggested to be important.
112 Robertson and Watson (1992) first suggested that the cool skin increases the global ocean
113 carbon sink by +0.6 PgC yr⁻¹ (positive flux downward) at atmospheric pCO₂ of 350 µatm. This
114 estimate was then revised to +0.4 PgC yr⁻¹ by taking into account sub-monthly wind variability
115 (Van Scoy et al. 1995). Woods et al. (2014) showed that this estimate is dependent on the
116 simplified formula used to diagnose the temperature difference across the microlayer and
117 suggested that the previous estimates are overestimated. There has been some debate about
118 whether one should consider the gross cool skin effect in the computation of the CO₂ fluxes
119 as is the case in the above-cited studies. Indeed, as discussed in Bolin (1960), diffusion across
120 the ocean Mass Boundary Layer (MBL) is the process that limits the rate at which CO₂ is
121 exchanged between the atmosphere and the ocean. Due to the higher water molecular
122 diffusion rate for heat than for mass (e.g. Saunders 1967), the MBL is only a fraction of the

123 TBL. From this, McGillis and Wanninkhof (2006) argued that the cool skin adjustment on CO₂
124 flux depends on the temperature difference across the MBL. Because this difference is a
125 fraction of the total cool skin, they predict a weak CO₂ flux adjustment assuming a linear
126 temperature profile in the TBL. Based on these considerations, Zhang and Cai (2007)
127 estimated that the cool skin effect on CO₂ flux is about +0.05 PgC yr⁻¹ and largely compensated
128 by the increase in salinity in the MBL. However, they only consider the change in solubility
129 associated with changes in temperature and salinity and not on the interfacial CO₂
130 concentration (see the discussion in Woolf et al. 2016). Using a uniform -0.14K temperature
131 and a +0.1 g/kg salinity difference between the sub-skin and the interface, Woolf et al. (2016)
132 estimate an increase of global ocean sink to be roughly +0.34 Pg C yr⁻¹. Using SOCAT-based
133 product, and taking constant temperature and salinity differences in the ocean skin of -0.17K
134 and 0.1 g/kg, Watson et al. (2020) found a mean increase of ocean sink of +0.4 Pg C yr⁻¹ for
135 1992-2018. Using monthly mean surface meteorology from ERA5 to compute the cool skin
136 effect from Fairall et al. (1996), Dong et al. (2022) also found a comparable increase due to
137 the cool skin effect of about 0.39 Pg C yr⁻¹ for 1982-2020 without taking into account the
138 competing MBL salinity gradient effect.

139 Note that, according to Watson et al. (2020), another correction has to be made to the
140 SOCAT data because the measured CO₂ concentrations correspond to a depth of 1 meter or
141 more. They used satellite sub-skin temperature estimates (Banzon et al. 2016) to determine
142 the waterside CO₂ concentration and found an additional increase in the flux of +0.4 PgC yr⁻¹
143 for 1992-2018. Note that the Watson et al. (2020) estimate in the latest global carbon budget
144 (Friedlingstein et al. 2022) used a new version of the SST satellite product (OISSTv2.1,
145 Merchant et al. 2019) that corrected a cool bias present in the former version of this SST
146 product (OISSTv2.0), but it remains an outlier among the other estimates. Using buoy SST as

147 reference, Dong et al. (2022) found a warm bias in SOCAT SST which impact is $+0.19 \text{ PgC yr}^{-1}$
148 on the average for 1982-2020. Acknowledging the remaining substantial uncertainty around
149 the river flux adjustment, the CO_2 sink increases due to the taking into account of the cool skin
150 and warm bias correction appears to be able to reconcile the SOCAT-based estimates with the
151 independent Gruber et al. (2019) 1994-2007 ocean sink estimate (Watson et al. 2020, Dong
152 et al. 2022).

153 Previous evaluations of the impact of the diffusive microlayer on carbon exchanges were
154 off-line diagnostics based on observations with limitations in terms of spatiotemporal
155 coverage (Robertson and Watson 1992, Van Scoy et al. 1995, Zhang and Cai 2007, Woods et
156 al. 2014, Woolf et al. 2016, Ashton 2016, Watson et al. 2020, Shutler et al. 2020, Dong et al.
157 2022). Furthermore, some of the studies used monthly-averaged of surface winds or idealized
158 wind distributions to compute the CO_2 transfer velocity and most assumed constant and
159 homogeneous temperature and salinity differences across the diffusive layers. To overcome
160 the issue of diverse and limited data in time and space to compute global air-sea CO_2 fluxes,
161 we use the coherent, although imperfect, set of variables from a coupled climate model (IPSL-
162 CM6, Boucher et al. 2020). Further, to assess the necessity of taking into account the near-
163 surface vertical gradients in ocean temperature and salinity, the Bellenger et al. (2017)
164 parameterization that represents the near ocean surface temperature and salinity profiles (in
165 the microlayer and below) that are not resolved by the ocean model is included in IPSL-CM6.
166 Air-sea CO_2 fluxes are then diagnosed using a range of expressions from past literature to
167 illustrate the necessity of a physically based and interactive diagnostic of the ocean surface
168 layers in computing these fluxes.

169 The next section presents the design of the sensitivity experiments and the analysis
170 tool used in this study, section 3 contains the main results, and Section 4 discusses the
171 uncertainties.

172

173 **2. Approach and Methods**

174

175 2.1 Earth System Model

176 The Institut Pierre-Simon Laplace Coupled Model Version 6.1, Low Resolution (IPSL-CM6A-
177 LR) was used in this study, and details of the model and its evaluation can be found in Boucher
178 et al. (2020). IPSL-CM6A-LR will be referred to as IPSL-CM6 in the following. Here, we only
179 describe the model components and parameterizations that are important for our study. The
180 atmospheric (LMDZ, Hourdin et al. 2019) and oceanic (NEMO, Madec et al., 2017) components
181 exchange energy, water and carbon and are coupled every 90 minutes. The atmospheric
182 model configuration has a horizontal resolution of $2.5^{\circ} \times 1.5^{\circ}$ and the ocean resolution is $1^{\circ} \times 1^{\circ}$.
183 The ocean model configuration has a non-uniform vertical resolution that increases from 1 m
184 at the surface to 10 m at 100 m depth and 200 m at the bottom. The ocean model includes
185 the biogeochemical model NEMO-PISCES (Aumont et al. 2015), representing, in particular, the
186 ocean carbon cycle and including both its inorganic and organic parts and their respective
187 influences on the seawater concentrations of dissolved inorganic carbon (DIC) and alkalinity
188 (Alk). The model salinity is absolute salinity in g/kg and so are the results presented here.

189

190 2.2 The ocean skin parameterization

191

192 Figure 1a schematically represents the vertical temperature and salinity profiles that occur
193 within the ocean model first layer and that are parameterized following Bellenger et al. (2017)
194 that is available online (see data availability section). Figure 1a also provides the notations for
195 the different depths that will be considered in this study, namely at the interface (*int* subscript)
196 at the base of the MBL and TBL (*MBL* and *TBL* subscripts), and at the middle of the ocean
197 model first level ($h/2$ subscript, with h the depth of the ocean model first level).

198 The ocean skin parameterization from Bellenger et al. (2017) used here is based on
199 Saunders (1967). It computes differences in temperature and salinity between the interface
200 and the bases of the TBL and MBL (Fig. 1a). The parameterization assumes that the TBL and
201 MBL depth are proportional to each other and proportional to the kinematic viscosity divided
202 by the water-side friction velocity. This friction velocity is a function of surface fluxes of heat,
203 radiation and momentum. The dependence of the Saunders proportional parameter on the
204 turbulence regime is taken into account following Fairall et al. (1996). In addition, the
205 stabilizing (freshening) and increased turbulence due to rain are also taken into account as
206 detailed in Schlüssel et al. (1997). From this, the differences in temperature and salinity across
207 the TBL and MBL ($T_{Int} - T_{TBL}$ and $S_{Int} - S_{MBL}$) and the TBL and MBL depths (z_{TBL} and z_{MBL})
208 are computed at each time step (see implementation details below). Note that because
209 thermal diffusivity is larger than the diffusivity of salt, z_{TBL} is larger than z_{MBL} . The temperature
210 at the base of the MBL is deduced assuming a linear temperature profile within the TBL from
211 z_{MBL} and z_{TBL} .

212 The Bellenger et al. (2017) parameterization further diagnoses the differences in
213 temperature and salinity between the base of the TBL/MBL and the ocean model first level at
214 $h/2$ depth (Fig. 1a). This part of the parameterization is an extension of Zeng and Beljaars
215 (2005) that was originally limited to represent temperature increase with diurnal warming.

216 Bellenger et al. (2017) extended it to salinity variations to allow negative temperature
 217 anomalies associated with rain. The one-dimensional heat and salinity budgets are integrated
 218 between a given depth d and the base of the microlayer assuming a temperature profile of
 219 the form:

$$220 \quad T_{TBL} - T(z) = \left[\frac{(z+z_{TBL})}{-d+z_{TBL}} \right]^\nu (T_{TBL} - T_d) \quad (1)$$

221 With z being the depth (negative), T_d is the mixed layer temperature corresponding to a $d =$
 222 3m depth, and ν is a shape parameter equal to 0.3 in Zeng and Beljaars (2005). A similar
 223 profile is used for salinity. This provides a time evolution of temperature and salinity
 224 difference below the microlayer depending on surface fluxes (heat and radiative fluxes,
 225 momentum flux and rainfall) and vertical mixing that is parameterized in the framework of
 226 the Monin-Obukhov similarity theory (Large et al. 1994) and is a function of the same surface
 227 fluxes. Note that changes in salinity and temperature due to sea-ice melt are not included in
 228 the Bellenger et al. (2017) parameterization.

229 Inputs of the Bellenger et al. (2017) ocean skin parameterization are therefore surface
 230 fluxes (heat, radiation, rain and momentum) that are computed by the atmospheric
 231 component of IPSL-CM6 at each physical time-step. Therefore, the ocean skin
 232 parameterization is implemented in the atmospheric component and $T_{Int} - T_{TBL}$ and $S_{Int} -$
 233 S_{MBL} and $T_{TBL} - T_{h/2}$ and $S_{MBL} - S_{h/2}$ are computed online at each atmospheric physical
 234 time-step (15 minutes). Note that the interface temperature is used to compute the turbulent
 235 heat fluxes and the upward longwave radiation from the ocean surface of the next timestep.

236 To validate the ocean surface temperature and salinity gradients produced by IPSL-CM6
 237 with the Bellenger et al. (2017) parameterization, we compared the distributions of 90
 238 minutes outputs of our model with outputs of the Bellenger et al. (2017) parameterization
 239 forced by hourly ERA5 fluxes (Hersbach et al., 2020). The results are presented in Section 3.1.

240

241 2.3 Air-sea CO₂ flux formulations

242 The air-sea CO₂ flux (F , in mol m⁻² s⁻¹, positive downward) can be written as (McGillis and
243 Wanninkhof 2006):

$$\begin{aligned} 244 \quad F &= k_w \sqrt{660/Sc(T)} [[CO_{2aq}]_i(T, S) - [CO_{2aq}]_w(T, S, DIC, Alk)] \\ 245 \quad &= k_w \sqrt{660/Sc(T)} [K_0(T, S) pCO_2^{atm}(T, S) - [CO_{2aq}]_w(T, S, DIC, Alk)] \quad (2) \end{aligned}$$

246 Where k_w is the gas transfer velocity (in m s⁻¹) depending on the surface wind following Ho
247 et al. (2006) and Wanninkhof (2014), Sc is the Schmidt number, $[CO_{2aq}]_i$ and $[CO_{2aq}]_w$ are the
248 interfacial and waterside aqueous CO₂ concentrations (in mol m⁻³). The interfacial CO₂
249 concentration can be written as the product of K_0 , the CO₂ aqueous-phase solubility
250 coefficient (a function of temperature and salinity in mol m⁻³ atm⁻¹, Weiss 1974), and pCO_2^{atm}
251 the CO₂ partial pressure (in atm) at the atmosphere interface, which only depends on the
252 water vapor saturation pressure that is a function of the interface temperature and salinity
253 (McGillis and Wanninkhof 2006). The aqueous carbon concentration $[CO_{2aq}]_w$ is computed by
254 NEMO-PISCES (Aumont et al. 2015) from the MOCSY carbonate chemistry set of equations
255 (Orr and Epitalon 2015) and is a function of the T , S , Alk and DIC . One question is to determine
256 the depths at which T , S , Alk and DIC should be evaluated in the terms of (2). In the standard
257 version of the IPSL-CM6, the air-sea carbon flux is estimated by (2) using T , S , Alk and DIC at
258 $h/2$. This classical bulk flux calculation is simply noted F (black arrow in Fig. 1b).

259 Figure 1b, illustrates how $[CO_{2aq}]_w$ and $[CO_{2aq}]_i$ vary with T and S taken at different depths
260 for the situation depicted in Fig. 1a. $[CO_{2aq}]_w$ is an increasing function first of S and then of T
261 (see Annex and Woolf et al. 2016). Below the interface, $[CO_{2aq}]_w$ decreases with increasing
262 depth due to the salinity increase in the MBL (Fig. a). Below the MBL base and in the absence
263 of rain, the changes in S are weak and changes in T control the changes in $[CO_{2aq}]_w$. Thus,

264 $[\text{CO}_{2\text{aq}}]_w$ increases with depth and thus with temperature in the TBL; then, it decreases down
265 to $h/2$ -depth in relation to the diurnal warm layer (Fig. 1a). On the other hand, $[\text{CO}_{2\text{aq}}]_i$ is a
266 decreasing function first of temperature and then salinity (see Annex) and will depend on the
267 depth at which temperature and salinity are evaluated. In the situation represented in Fig. 1a,
268 with $T_{h/2} > T_{int}$, this lead to $[\text{CO}_{2\text{aq}}]_i(T_{int}, S_{int}) > [\text{CO}_{2\text{aq}}]_i(T_{h/2}, S_{h/2})$ (Fig. 1b).

269 The limiting step in CO_2 exchanges between the ocean and the atmosphere is the diffusion
270 of CO_2 molecules in the MBL, which is the diffusive layer for salt (Bolin 1960, McGillis and
271 Wanninkhof 2006). According to McGillis and Wanninkhof (2006), the flux should then be
272 computed from the difference in CO_2 concentrations at the top (the interface) for $[\text{CO}_{2\text{aq}}]_i$ and
273 at the bottom of this layer for $[\text{CO}_{2\text{aq}}]_w$. This flux is noted F_{MBL} (red arrow in Fig.1b).

274 As underlined by Woolf et al. (2016), this formulation implicitly hypothesizes a linear
275 temperature profile and that the chemical equilibrium is reached in the MBL. They name this
276 hypothesis the “equilibrium model”. However, the residence time of a water parcel in the TBL
277 is generally shorter than the timescale for chemical repartitioning of the carbonate species
278 induced by changes in temperature and salinity, which is on the order of 10s (Dong et al. 2022,
279 Woolf et al. 2016). Therefore, in what they name the “rapid model”, Woolf et al. (2016) argue
280 that the TBL base temperature and salinity (Fig. 1a) account for the MBL chemical
281 repartitioning better and should be used to compute $[\text{CO}_{2\text{aq}}]_w$. The flux computed accordingly
282 to this “rapid model” is noted F_{TBL} (blue arrow in Fig. 1b). As the TBL base temperature is
283 warmer than the MBL base temperature (Fig 1a), the rapid model leads to a larger waterside
284 CO_2 concentration than the equilibrium model (see Annex). Therefore, F_{TBL} leads to a weaker
285 increase in CO_2 sink than F_{MBL} (Fig 1b).

286 To assess the impact of considering a uniform ocean skin (Watson et al. 2020), we
287 introduce another diagnostic F_{Wat} (light blue arrow in Fig. 1b) for which $[\text{CO}_{2\text{aq}}]_w$ is computed

288 at $h/2$ -depth and $[\text{CO}_{2\text{aq}}]_i$ is computed using empirically-based constant differences of -0.17K
 289 and $+0.1\text{ g/kg}$ across the TBL and the MBL respectively (see Fig. 1a and b).

290 Table 1 synthesizes the different CO_2 fluxes that are computed and details the
 291 corresponding temperature and salinity that are considered. Additional diagnostics F_{skinM} and
 292 F_{skinT} are computed as F_{MBL} and F_{TBL} but neglecting T and S changes below the ocean skin.
 293 Comparing F_{skinM} and F_{skinT} results to F_{MBL} and F_{TBL} quantifies the impact of diurnal warm layers
 294 and rain lenses stratification within the first model layer of 1 m depth. A last diagnostic F_{NoS} is
 295 comparable to F_{MBL} but does not take into account the limiting effect of the salty skin.

296 All the CO_2 fluxes are computed online by the IPSL-CM6 model every 45 min., which
 297 corresponds to the ocean model timestep that considers the temperature and salinity
 298 corrections computed by Bellenger et al. (2017) during the latest coupling timestep (every 90
 299 min.). To evaluate Alk and DIC at a given depth for the computation of $[\text{CO}_{2\text{aq}}]_w$ in (2), we
 300 assume that, near the surface, Alk and DIC differ from their value at $h/2$ -depth only because
 301 of concentration changes caused by rain and evaporation. We thus assume that they have the

302 same ratio of dilution as salinity and so we can write $\frac{S_{\text{MBL}} - S_{h/2}}{S_{h/2}} = \frac{\text{Alk}_{\text{MBL}} - \text{Alk}_{h/2}}{\text{Alk}_{h/2}} =$
 303 $\frac{\text{DIC}_{\text{MBL}} - \text{DIC}_{h/2}}{\text{DIC}_{h/2}}$.

304 Considering the other terms in (2): We assume that the bulk transfer parameterization for
 305 k_w derived from the global ^{14}C budget (Wanninkhof 2014), which is usually applied to
 306 atmospheric and oceanic parameters, corresponding typically to 10 m height and 5 m depth,
 307 can be used to evaluate the ocean skin effect on the carbon fluxes. The implications of this
 308 hypothesis will be further discussed in detail in the discussion section. Note that we do not
 309 include the rain effect on the transfer velocity (Ho et al. 1997). The Schmidt number is a
 310 function of temperature and salinity and should be evaluated below the ocean skin (Yang et

311 al. 2022). However, evaluating it at the interface, at the MBL base or at the ocean model first
312 level leads to very small differences (not shown). Therefore, in the following, it will always be
313 evaluated at the ocean model first level ($T_{h/2}$ and $S_{h/2}$).

314

315 2.4 Simulations

316 Two 15-year IPSL-CM6 simulations with imposed global-mean atmospheric CO₂
317 concentration corresponding to present-day conditions (years 2000 to 2014) were performed.
318 We repeated the last 15 years of the CMIP6 historical simulations with IPSL-CM6A-LR (scenario
319 starts from 2015), using the r1i1p1f1 member available on ESGF as initial conditions for
320 January 2000 (Boucher et al. 2020, link in the data availability section). Both simulations use
321 the IPSL-CM6 model (CMIP6 version) with the Bellenger et al. (2017) parameterization
322 included. In contrast with the CMIP6 version of the model, the Bellenger et al. (2017)
323 parameterization was used to compute the sensible and latent heat and the infrared fluxes.
324 In the diagnostic (DIAG) simulation, the prognostic CO₂ flux used to compute the evolution of
325 the oceanic carbon was from the classical bulk formulation F and the CO₂ fluxes deduced from
326 other formulations were calculated only as diagnostics (Table 1). In the coupled (CPL)
327 simulation, the F_{MBL} carbon flux was used to compute the evolution of oceanic carbon so that
328 the new parameterization affected the simulated ocean carbon cycle. Because the equilibrium
329 model (F_{MBL}) leads to a larger adjustment than the rapid model (F_{TBL}), this will provide an upper
330 limit of the impact of the ocean skin on CO₂ flux in a coupled framework. We indicate the
331 considered simulation using a superscript on the CO₂ flux notation (for example, F^{DIAG}).

332

333 **3. Results**

334

335 3.1 Air-Sea CO₂ fluxes

336 Figure 2 compares CO₂ fluxes from the DIAG simulation to the SeaFlux data product of
337 Fay et al. (2021). The mean CO₂ flux F^{DIAG} over 2000-2014 (Fig.2a) shows a latitudinal pattern
338 consistent with SeaFlux (Fig. 2b). Main outgassing regions are found in tropical and sub-
339 tropical oceans with fluxes down to -30 g C m⁻² yr⁻¹ in the eastern Equatorial Pacific. The ocean
340 acts mainly as a sink for subtropical and mid-latitude regions with maxima reaching +40 g C
341 m⁻² yr⁻¹ locally in the Southern Ocean and in the storm track regions. There are some large
342 local biases such as in the northern Pacific Ocean where the sink is overestimated by the
343 model by up to +20 g C m⁻² yr⁻¹ and in the equatorial ocean where the outgassing is
344 underestimated in a comparable manner (Fig. 2c). Overall, the global oceanic CO₂ sink
345 simulated by our model in the DIAG simulation (Fig. 2d black thin line) is underestimated
346 compared to the Global Carbon Budget (GCB) estimate that includes both models and data
347 products or only the latter (*resp.* bold dashed black and green lines, Friedlingstein et al. 2022).
348 The CPL simulation only slightly reduces the underestimation of the global sink by the model
349 (Fig. 2d black thin dashed line). In addition, neither DIAG nor CPL actually reproduce the
350 increasing tendency in the global oceanic sink (less than +0.01 PgC yr⁻¹ vs +0.06 PgC yr⁻¹ for
351 GCB during 2000-2014).

352

353 3.2 Near-surface T and S vertical gradients

354 Figure 3 shows the distributions of temperature differences across the TBL, and salinity
355 differences across the MBL and between the base of these layers and the oceanic mixed
356 layer taken at 3 m. The values were obtained using the Bellenger et al. (2017)
357 parameterization in IPSL-CM6 (solid lines) and the same parameterization forced by ERA5
358 (dashed lines). Note that, in our model, the temperature difference across the MBL is

359 about 1/5th of the difference across the TBL. First, the distributions produced by IPSL-CM6
360 and diagnosed from ERA5 are in good agreement, except for slightly more frequent
361 temperature differences below -0.4K across the TBL in IPSL-CM6 (Fig. 3a). The global mean
362 differences in salinity and temperature across MBL and TBL are 0.06 g/kg and -0.23K for
363 IPSL-CM6 and 0.07 g/kg and -0.17K for ERA5. These values are comparable with the values
364 of 0.1 g/kg and -0.17K chosen by Watson et al. (2020) based on in situ measurements by
365 Donlon et al. (2002). Below the ocean skin, the change in temperature and salinity due to
366 warm layers and rain lenses are generally an order of magnitude lower than changes in
367 the ocean skin, with mean differences on the order of 10⁻² K for temperature and 10⁻³ g/kg
368 for salinity. Therefore, and as it will be shown in the next section and consistently with
369 Woolf et al. (2016), the difference in the global ocean CO₂ sink due to near-surface *T* and
370 *S* vertical gradients from Bellenger et al. (2017) is mainly due to the ocean skin.

371 Figure 4 shows the maps of mean temperature and salinity differences across their
372 respective diffusive boundary layers (TBL and MBL) in IPSL-CM6 and ERA5. Spatial
373 distributions of the cooling and increase in salinity in the TBL and MBL by IPSL-CM6 and
374 ERA5 are in close agreement except for the high latitudes where the model is producing
375 too strong a cooling (Fig. 4a and b). There is no such overestimation in salinity increase
376 across the MBL at high latitudes (Fig. 4c and d). In fact, at high latitudes in the model,
377 strong cooling of the sea surface by infrared radiation and sensible heat flux gives a
378 stronger cool skin (around -0.4K) that is not associated with a clear increase in salinity
379 across the MBL. The difference in temperature across the TBL is stronger than the -0.17K
380 chosen by Watson et al. (2020) almost everywhere in the tropics and subtropics. A similar
381 feature is visible for the change in salinity across the MBL (Fig. 4c and d), which is
382 frequently stronger than the 0.1 g/kg threshold in the tropical and subtropical regions

383 except for the Intertropical Convergence Zone (ITCZ) region. In the ITCZ, frequent rain and
384 light winds lead to a fresh ocean skin with $S_{Int} - S_{MBL} \sim -0.1$ g/kg and a cool skin of -0.3K. In
385 the subtropics, large evaporation and stronger wind speed may lead to large positive $S_{Int} -$
386 $S_{MBL} \sim +0.3$ g/kg and a cool skin of -0.4K. Finally, in the mid-latitudes, high wind speeds
387 induce strong mixing that largely reduces the TBL and MBL effects.

388

389 3.3 Impacts on air-sea CO₂ fluxes - diagnostics

390 The annual mean global ocean carbon sinks, estimated from the DIAG simulation for
391 the standard flux (F^{DIAG}), for the different diagnostics (F_{MBL}^{DIAG} , F_{TBL}^{DIAG} , F_{Wat}^{DIAG} , F_{SkinM}^{DIAG} ,
392 F_{SkinT}^{DIAG} and F_{NoS}^{DIAG}) and the corresponding differences with F^{DIAG} are reported in Table 1.
393 The increase in the global ocean carbon sink from the diagnosed fluxes ranges from +0.26
394 to +0.39 PgC yr⁻¹, which is 13-19% of the standard sink of 2.04 PgC yr⁻¹.

395 In the following, we will focus on F_{MBL}^{DIAG} , F_{TBL}^{DIAG} and F_{Wat}^{DIAG} , which are reported in
396 Figure 5. First, the global sink computed from F_{MBL}^{DIAG} (+0.37 PgC yr⁻¹) increases more than
397 the one computed from F_{TBL}^{CT} (+0.26 PgC yr⁻¹). This is because the former includes the
398 effect of a large part of the cool skin on $[CO_{2aq}]_w$, which is an increasing function of T
399 (Annex). The equilibrium model gives a sink strengthening 40% larger than with the rapid
400 model. Using the rapid model but uniform ocean skin F_{Wat}^{DIAG} leads to stronger sink (+0.33
401 PgC yr⁻¹) than with the interactive ocean skin F_{TBL}^{DIAG} (+0.26 PgC yr⁻¹). The difference in the
402 adjustments using F_{MBL}^{DIAG} , F_{TBL}^{DIAG} and F_{Wat}^{DIAG} are statistically significant (to the 99.9%
403 level, see the standard deviations in the last column of Table 1). The three flux estimates
404 induce an additional sink that increases with time at a rate of $+1.5 \times 10^{-3}$ PgC yr⁻² (Fig. 5b),
405 which is comparable to the $+2.5 \times 10^{-3}$ PgC yr⁻² obtained by Dong et al. (2022). Figure 5c
406 shows the seasonal variations of hemispherical CO₂ sink with maxima during the

407 corresponding hemisphere's winter. F_{Wat}^{DIAG} shows weaker seasonal variations than
408 F_{MBL}^{DIAG} and F_{TBL}^{DIAG} in both hemispheres. In addition, the overestimation of the global sink
409 when using a uniform ocean skin (F_{Wat}^{DIAG} vs F_{TBL}^{DIAG}) is mainly due to an overestimation of
410 the sink in the southern hemisphere. The hemispherical sinks variations largely
411 compensate to result in a weak seasonal variation of the global sink.

412 Figure 6 compares F^{DIAG} to the three alternative estimates F_{MBL}^{DIAG} , F_{TBL}^{DIAG} and F_{Wat}^{DIAG} .
413 These estimates increase the ocean CO₂ sink everywhere with some specific patterns.
414 F_{MBL}^{DIAG} increases CO₂ sink especially in the tropical and subtropical oceans (Fig. 6b). This
415 increase is particularly marked in the trade winds regions of the western Pacific and
416 Atlantic Oceans and, for the mid-latitudes, in the Gulf Stream, the Kuroshio, and the
417 Agulhas Current regions. Because the cool skin temperature difference is not a function of
418 wind alone, there is no simple relationship between the flux adjustment in Fig. 6b neither
419 with the mean cool skin shown in Fig. 4a nor with the wind speed as it is discussed in
420 section 4.3. However, regions of very large cool skin, like the warm pool and polar regions,
421 correspond to weak flux adjustment because the strong cool skin are associated with very
422 low wind speed. Although weaker, the adjustment using F_{TBL}^{DIAG} shows a comparable
423 pattern (Fig. 6c). In contrast, applying F_{Wat}^{DIAG} would increase CO₂ sink in the mid-to-high
424 latitudes (40N-70N and 40S-70S, Fig. 6d), especially in the Southern Ocean where F_{Wat}^{DIAG}
425 would lead to an increase in air-sea carbon fluxes that exceed 10% of the mean annual
426 carbon flux (Fig. 6a). Mid-to-high latitudes regions are characterized by relatively high
427 winds and intense near-surface turbulence that largely erodes the temperature gradient
428 within the TBL to cooling weaker than -0.1K (Fig. 4a) and thus weaker than -0.17K. Strong
429 winds also increase the CO₂ flux by increasing the gas transfer velocity k_w in (2). Therefore,
430 in IPSL-CM6 and using the rapid model assumption, using a constant difference of -0.17K

431 following Watson et al. (2020) would result in an overestimate of the impact of the cool
432 skin on CO₂ fluxes in mid-to-high latitudes (+1 to +2 g C m⁻² yr⁻¹ in the Southern Ocean, Fig.
433 6b and c), as well as on the global CO₂ sink (Table 1, +0.33 Pg C yr⁻¹ for F_{Wat} vs +0.26 Pg C
434 yr⁻¹ for F_{TBL}).

435 The spatial distribution of F^{DIAG} carbon flux shows a clear seasonality with a large
436 carbon sink in the mid-to-high latitudes of the winter hemisphere where stronger winds
437 blow (Fig. 7a and b). Furthermore, Figure 7 c-f show the spatial pattern behind the
438 hemispherical variation of the CO₂ sink of Fig. 5c. F_{MBL}^{DIAG} and F_{TBL}^{DIAG} increase the CO₂ sink
439 mainly in the winter hemisphere, with maxima in the subtropical Gulf Stream and Kuroshio
440 regions in boreal winter (Fig. 7c and e), with weak increase is observed in the tropical and
441 subtropical regions of the summer hemisphere (Fig. 7d and f). In contrast, F_{Wat}^{DIAG} shows
442 seasonal variability that is stronger higher latitudes in the northern Atlantic and Pacific
443 oceans in DJF and in the Southern Ocean in JJA (+2 to +3 g C m⁻² yr⁻¹) (Fig. 7g and h). The
444 increase in CO₂ sink in the tropics does not show comparable equatorial asymmetry and
445 the Southern Ocean adjustment remains a non-negligible part of the average carbon flux
446 in DJF (+1 to +2 g C m⁻² yr⁻¹) explaining the weaker seasonal variations in Figure 5c.

447 When comparing the increase in the carbon sink with (i.e., F_{MBL}^{DIAG} for the equilibrium
448 model and F_{TBL}^{DIAG} for the rapid model) and without (i.e., F_{SkinM}^{DIAG} for the equilibrium
449 model and F_{SkinT}^{DIAG} for the rapid model) taking into account the sub-skin temperature and
450 salinity variations above $h/2$ -depth shows that, as expected from Fig. 3, the effect of
451 unresolved warm layers and rain lenses is minimal for an ocean model with 1 m resolution
452 at the surface, resulting in a reduction of the sink by only -0.02 PgC yr⁻¹. This difference is
453 mainly due to warm layer formation in the equatorial oceans (not shown). In addition,
454 comparing the F_{MBL}^{DIAG} and F_{NoS}^{DIAG} sinks shows that the compensating effect of the saline

455 skin on the global CO₂ sink is also weak (-0.02 PgC yr⁻¹) and mainly located in tropical
456 regions where $S_{int}-S_{MBL}$ is large (Fig. 4c).

457 3.4 Impacts on air-sea CO₂ fluxes - prognostic

458 In the previous section, we showed the impact of the ocean skin on air-sea CO₂ fluxes
459 diagnostics that do not impact the ocean carbon budget. In this section, we compare air-
460 sea carbon fluxes from F^{DIAG} to those from a coupled (CPL) simulation in which F_{MBL}^{CPL} is
461 used to compute the evolution of DIC in the ocean model. Because the associated
462 feedback is clearly negative, an attenuated effect is to be expected. Figure 8a shows the
463 2000-2014 global ocean carbon sink in DIAG and CPL simulations using the respective
464 prognostic fluxes F^{DIAG} and F_{MBL}^{CPL} as well as their difference (also in Table 1). In CPL, the
465 ocean carbon sink is increased by about +0.13 (± 0.09) Pg C yr⁻¹ compared to DIAG (Figure
466 8a). This is only about 35% of the ocean sink augmentation diagnosed for F_{MBL}^{DIAG} (+0.37
467 $\pm 7 \cdot 10^{-3}$ Pg C yr⁻¹). In addition, one can note that the year-to-year standard deviation of the
468 $F_{MBL}^{CPL} - F_{blk}^{DIAG}$ resulting global ocean sink is large and about +0.09 Pg C yr⁻¹. This is
469 comparable to the standard deviations of the global ocean sink diagnosed from either
470 DIAG or CPL and larger than the year-to-year standard deviations of the adjustment
471 diagnosed in DIAG. This is because using F_{MBL} instead of F as a prognostic carbon flux
472 modifies the simulated marine biogeochemistry that feedbacks on the ocean heat budget
473 through a biophysical coupling (Lengaigne et al. 2009) and on the simulated climate so
474 that the DIAG and CPL simulations diverge. This divergence manifests itself through
475 difference in patterns and timing of atmospheric dynamical synoptic perturbations in
476 particular at mid-to-high latitudes. This results in larger differences in CO₂ flux variability
477 in these regions (Fig. 8b, the black curve and its standard deviation). Because of this
478 divergence of the two simulations, we only show zonal mean profiles of the CO₂ flux and

479 ocean model first level pCO₂ differences in Figure 8b (shadings represent their year-to-
480 year variability). The use of F_{MBL}^{CPL} tends to increase the ocean carbon sink at almost all
481 latitudes. This increase in CO₂ flux is only significant to the 95% confidence level. However,
482 the increase in the first level of pCO₂ is significant in the tropics (Fig.8b, the red curve).
483 There is an accumulation of carbon at the ocean surface in the CPL simulation. This can
484 explain the limitation of the increase in the carbon sink when using F_{MBL} rather than F as
485 prognostic flux. Therefore, taking into account all interaction loops and depending on the
486 ability of the ocean model to transfer the carbon into the ocean interior, the use of F_{MBL}
487 leads to a significantly weaker adjustment in a coupled framework than what could be
488 inferred from a simple offline diagnostic.

489

490 **4 Discussion**

491

492 4.1 Uncertainties due to the ocean skin representation

493 A first source of uncertainty is the representation of the ocean skin. Assuming a linear
494 dependency of the CO₂ sink adjustment to the temperature difference in the TBL and using
495 the mean difference of 0.06K between IPSL-CM6 and ERA5 estimates lead to an
496 uncertainty of ± 0.07 PgC yr⁻¹. Taking into account this uncertainty, the adjustment using a
497 uniform ocean skin with the diagnostic flux F_{Wat}^{DIAG} (+0.33 PgC yr⁻¹) although weaker is not
498 significantly different than the adjustment found by Watson et al. (2020, $+0.4 \pm 0.04$ PgC
499 yr⁻¹) and Dong et al. (2022, $+0.39 \pm 0.08$ PgC yr⁻¹). The adjustment found with an interactive
500 ocean skin and the rapid model with the diagnostic flux F_{TBL}^{DIAG} (+0.26 PgC yr⁻¹) is also on
501 the same order of magnitude because part of this difference is due to unresolved warm
502 layers (-0.02 PgC yr⁻¹) and salinity skin (-0.02 PgC yr⁻¹) effects that are not taken into

503 account by previous studies. Surprisingly, whereas we find a significant sensitivity of the
504 adjustment to considering an interactive ocean skin or not (F_{TBL}^{DIAG} vs F_{Wat}^{DIAG}), Dong et al.
505 (2022) and Watson et al. (2020) adjustments are very close to each other. This is partly
506 explained by the fact that Dong et al. (2022) do not consider warm layer and salty skin
507 corrections that would tend to reduce the adjustment. This may also arise from the use of
508 monthly mean parameter in computing the adjustment.

509 4.2 Uncertainties due to the chemical equilibrium

510 A second uncertainty comes from the chemical equilibrium assumption at the base of
511 the MBL. The difference between the equilibrium model F_{MBL}^{DIAG} and the rapid model
512 F_{TBL}^{DIAG} (+0.11 PgC yr⁻¹) is a measure of this uncertainty. As discussed by Dong et al. (2022)
513 and Woolf et al. (2016), the residence time of a water parcel in the TBL is generally on the
514 order of 1 s. This is shorter than the 10 s timescale of the chemical repartitioning of the
515 carbonate species that is induced by changes in temperature and salinity. This is the
516 reason why they recommend the rapid model that takes the temperature at the base of
517 the TBL to represent the actual chemical repartitioning at the base of the MBL and
518 compute $[CO_{2aq}]_w$ in (2). However, they also note that the residence time of a water parcel
519 can be longer under weak wind conditions: It can reach about 6 s for a 2 ms⁻¹ wind speed
520 (Garbe et al. 2004) and might even be longer due to the stabilizing effect of sunlight. These
521 conditions are frequent in the tropics which may make the equilibrium hypothesis more
522 suitable there. It is also where the difference between F_{MBL}^{DIAG} and F_{TBL}^{DIAG} adjustments is
523 the largest (Fig. 6b and c). The actual flux adjustment due to ocean skin is therefore
524 certainly in between the results obtained for F_{MBL}^{DIAG} and F_{TBL}^{DIAG} . Refining the ocean skin
525 parameterization to take into account the residence time of water parcel and the

526 kinematics of the chemical repartitioning of the carbonate system could help reduce this
527 uncertainty.

528 4.3 Cool skin as a function of wind speed only

529 Because the cool skin mainly depends on the wind speed (Donlon et al. 2002), the use
530 of a wind-only parameterization may appear sufficient to represent the cool skin effect in
531 models. Figure 9a shows the mean temperature difference across the TBL computed by
532 Bellenger et al. (2017) as a function of the model wind speed at 10 m. The large standard
533 deviation in Fig. 9 shows that the modeled cool skin does not only depend on wind speed
534 but also on other factors such as air-sea gradients in temperature and humidity (e.g. Luo
535 and Minnett 2020). Figure 9b shows the mean annual difference between the cool skin
536 temperature computed either by the Bellenger et al. (2017) parameterization or from the
537 mean wind-only relationship shown in Figure 9a. A striking result is that large regions of
538 negative and positive anomalies appear on this annual mean map (Fig. 9b). Negative
539 anomalies mean that the average cool skin is stronger than the one deduced from the
540 wind-only relationship, and vice versa. In absolute value, these mean anomalies can be of
541 the order of magnitude as the cool skin effect ($\sim 0.1\text{K}$, Fig. 9b, Fig. 4a and b). If a mean wind
542 dependency of the cool skin (Fig 9a) such as Donlon et al. (2002) is used to represent the
543 cool skin effect in a model, it would lead to such regional biases in temperature at the
544 interface and thus to regional errors in CO_2 fluxes of the order of magnitude discussed
545 previously (Fig. 6b and c).

546 4.4 Uncertainties due to the CO_2 transfer velocity

547 This study is based on the assumption that the widely used bulk flux formulation of the
548 transfer velocity k_w in (2) that is derived from measurements in the bulk of water and air
549 (see Wanninkhof et al. 2009 for a review) do not implicitly take into account the cool skin

550 effect and can therefore be applied to study the impact of the ocean skin on the CO₂ flux.
551 Dong et al. (2022) argued that global k_w based on ¹⁴C inventory is not sensitive to the ocean
552 skin correction due to the large air-sea ¹⁴C difference. The same argument stands for in
553 situ measurements based on ³He/SF₆ dual-tracers (e.g., Ho et al. 2006, Y. Dong personal
554 communication). Therefore, the usual k_w formulation appears to be suitable to study the
555 ocean skin effect as it has been implicitly hypothesized in previous studies (Robertson and
556 Watson 1992, McGillis and Wanninkhof 2006, Woolf et al. 2016, and Watson et al. 2020).

557 However, the bulk k_w accounts for a variety of processes such as exchanges mediated
558 by bubbles, sea sprays and whitecaps associated with wave breaking. These processes
559 become important for moderate winds (Fairall et al. 2000, Hare et al. 2004, Woolf et al.
560 2019). Because, these processes do not depend on the molecular microlayers, the use of
561 a bulk transfer coefficient may lead to an overestimation of the associated CO₂ flux
562 adjustment. In order to apply the ocean skin correction only to the part of the exchange
563 mediated by the molecular sublayer, it seems suitable to treat separately the different CO₂
564 transfer processes.

565

566 5 Conclusions

567 This study explored the impact of thermal and saline gradients in the ocean skin on
568 global atmosphere-ocean CO₂ fluxes. To achieve this, a global model with interactive
569 temperature and salinity changes in the thermal and mass boundary layers (TBL and MBL)
570 and the first layer of the ocean model (Bellenger et al. 2017) was used. These changes
571 observed were dominated by temperature and salinity variations in their respective
572 diffusive boundary layers, with an average increase in salinity of +0.06 g/kg and a decrease

573 in temperature of -0.23K. These results were consistent with those obtained by using ERA5
574 to force the parameterization of the ocean skin.

575 Using a bulk formulation of the CO₂ flux (McGillis and Wanninkhof 2006, Woolf et al.
576 2016), several flux diagnostics are computed using temperature and salinity at different
577 depths with or without (i) assuming the chemical equilibrium at the base of the MBL, (ii)
578 considering an interactive ocean skin, (iii) taking into account unresolved gradients below
579 the microlayer in the ocean model's first level and (iv) taking into account the salinity skin
580 (Table 1). These diagnostics are consistent with previous studies (Woolf et al. 2016 and
581 2019, Watson et al. 2020, Shutler et al. 2020, Dong et al. 2022). It was however possible
582 to reveal the sensitivity of the adjustment to these different assumptions: Depending on
583 the assumption of whether the chemical equilibrium is reached at the base of the MBL
584 (F_{MBL}) or not (F_{TBL}) leads to diagnostic global CO₂ sink adjustment of +0.37 and +0.26 Pg yr⁻¹,
585 respectively. With a 1-m surface resolution ocean model, the unresolved warm layers
586 and rain lenses only account for a reduction of the adjustment of -0.02 PgC yr⁻¹,
587 comparable to the impact of the salty skin. Uniform ocean skin (F_{Wat}) lead to regional
588 biases in the modeled CO₂ fluxes (+1 to +2 Pg C yr⁻¹ in the Southern Ocean, Fig. 6) and in
589 the global sink (+0.33 against +0.26 Pg C yr⁻¹). This could impact the simulated carbon cycle
590 and the representation of pathways of anthropogenic carbon, in particular, in the
591 Southern Ocean where the vertical mixing induces large carbon subduction (e.g., Bopp et
592 al. 2015). More importantly, ocean skin adjustment in a coupled model is weaker than
593 diagnostic estimates. Indeed, we show that taking into account retroaction loops by
594 enabling the ocean skin to feedback on ocean carbon concentrations dampens the
595 magnitude of this adjustment to +0.13 (±0.09) PgC yr⁻¹. Although significantly weaker than
596 previous diagnostics, and although this adjustment obtained assuming the equilibrium

597 model constitutes an upper limit, this remains a non-negligible impact on the global ocean
598 carbon sink (on the order of 5%) with regional signature and it is linked to a change of the
599 modeled mean surface pCO₂. The magnitude of these changes ultimately depends on the
600 capacity of the ocean model to transfer CO₂ in its interior.

601 Future modeling efforts should thus take into account the ocean skin impact on CO₂
602 flux. An interactive parameterization of the ocean skin appears to be necessary to prevent
603 regional errors in CO₂ flux. As a next step, a detailed flux parameterization (e.g., Fairall et
604 al. 2000) should be tested in climate models because the ocean skin adjustment would be
605 only applied to the exchanges mediated by the molecular microlayer. This should further
606 reduce the impact of the ocean skin on the modeled CO₂ sink. Note that this effort to
607 separate the different process, that are not all sensitive to the ocean skin, seems also
608 important for observation assessments of global CO₂ sink. This may as well reduce the
609 diagnosed impact of ocean skin on the global sink compared to previous estimates
610 (Watson et al. 2020, Dong et al. 2022). On the other hand, taking into account the
611 kinematics of chemical repartitioning of the carbonate species with temperature and
612 salinity (Woolf et al. 2016) could increase the ocean skin effect in the tropics and thus the
613 adjustment of the global sink.

614

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626

627 **Annex - Sensitivity of CO₂ flux to ocean near-surface temperature and salinity changes.**

628 We derive an approximate formula for the change in carbon flux due to perturbations
 629 in temperature and salinity near the ocean surface. This will provide a synthesis of the
 630 different sensitivities of the main terms of equation (2) to T and S discussed in Woolf et al.
 631 (2016) and their order of magnitudes. In the following, we assume that the aqueous carbonate
 632 system is in chemical equilibrium for a given environment (that is for given T , S , DIC and Alk).

633 Neglecting the sensitivity of the Schmidt number on temperature for changes of at
 634 most a few degrees that are considered here, and supposing no change in the wind, the total
 635 derivative of the flux reads:

$$636 \quad dF = k_w \sqrt{660/Sc(T)} [d[CO_{2aq}]_i(T, S) - d[CO_{2aq}]_w(T, S, DIC, Alk)] \quad (A1)$$

637 The total derivative of $[CO_{2aq}]_i$ can be directly derived using formula from Weiss (1974) and
 638 provided by McGillis and Wanninkhof (2006). The total derivative for $[CO_{2aq}]_w$, which reflects
 639 a change in aqueous CO₂ due to chemical processes, reads:

$$640 \quad d[CO_{2aq}]_w = dT \frac{\partial [CO_{2aq}]_w}{\partial T} + dS \frac{\partial [CO_{2aq}]_w}{\partial S} + dAlk \frac{\partial [CO_{2aq}]_w}{\partial Alk} + dDIC \frac{\partial [CO_{2aq}]_w}{\partial DIC} \quad (A2)$$

641 We make the hypothesis that near the surface, Alk and DIC only change by dilution:

$$642 \quad dAlk \frac{\partial [CO_{2aq}]_w}{\partial Alk} = Alk \frac{dS}{S} \frac{\partial [CO_{2aq}]_w}{\partial Alk} \quad (A3)$$

643 Noting that the solubility K_0 is not a function of Alk and DIC and introducing γ_{Alk} and γ_{DIC} the
 644 sensitivity of pCO_{2w} to Alk and DIC , the two last terms in (A2) can be written:

$$645 \quad dAlk \frac{\partial [CO_{2aq}]_w}{\partial Alk} + dDIC \frac{\partial [CO_{2aq}]_w}{\partial DIC} = dS (K_0 \frac{pCO_{2w}}{S} \gamma_{Alk} + K_0 \frac{pCO_{2w}}{S} \gamma_{DIC}) \quad (A4)$$

646 Using approximations in Sarmiento and Gruber (2006), it comes that $\gamma_{Alk} + \gamma_{DIC} = 1$ and thus
 647 substituting (A4) in (A2) leads to:

$$648 \quad d[CO_{2aq}]_w = dT \frac{\partial [CO_{2aq}]_w}{\partial T} + \left(\frac{\partial [CO_{2aq}]_w}{\partial S} + K_0 \cdot \frac{pCO_{2w}}{S} \right) dS \quad (A5)$$

649 Using the relationship of pCO_{2w} mean sensitivity to temperature and salinity given by
 650 Takahashi et al. (2009) leads to:

$$651 \quad d[CO_{2aq}]_w = \left(\frac{\partial K_0}{\partial T} + \gamma_T K_0 \right) pCO_{2w} dT + \left(\frac{\partial K_0}{\partial S} + \frac{2K_0}{S} \right) pCO_{2w} dS \quad (A6)$$

652 This last equation enables to make a simple estimate of the sensitivities of $[CO_{2aq}]_w$ to changes
 653 in temperature (dT) and salinity (dS) for given values of T , S and pCO_{2w} .

654 In order to illustrate the validity of our approximation to represent changes in the
 655 water-side CO_2 concentration near the surface, we show on Figure A1 a scatterplot of the
 656 $d[CO_{2aq}]_w$ approximated from (A6) and computed using $dT=T_{int}-T_{h/2}$ and $dS=S_{int}-S_{h/2}$ as a
 657 function of $d[CO_{2aq}]_w = [CO_{2aq}]_w(T_{int}, S_{int}, DIC_{int}, Alk_{int}) -$
 658 $[CO_{2aq}]_w(T_{h/2}, S_{h/2}, DIC_{h/2}, Alk_{h/2})$ computed by the IPSL-CM6 model following MOCSY set
 659 of equations (Orr and Epitalon 2015). Note that we compute the difference to a hypothetical
 660 interfacial $[CO_{2aq}]_w$ in order to have larger differences in T and S (see Fig 3). Although slightly
 661 overestimating the change in $[CO_{2aq}]_w$, (A6) is a good approximation where the sea
 662 temperature is above $0^\circ C$ (and even better in relatively warm waters).

663 Figure A2 shows the sensitivity of $[CO_{2aq}]_i$ and $[CO_{2aq}]_w$ to Temperature and Salinity
 664 (respectively divided by the atmospheric CO_2 mole fraction and pCO_{2w}) and their ratio. The
 665 interface concentration $[CO_{2aq}]_i$ is a decreasing function of both temperature and salinity (Fig.
 666 A2a and c). Its temperature sensitivity is 4-6 times larger than to salinity (Fig. A2e). This means
 667 that an increase of 0.6 g/kg in S_{int} is needed to offset a decrease of -0.1K in T_{int} . This is rarely
 668 the case, so usually the dominating effect is an increase of $[CO_{2aq}]_i$ due to the cool skin. On the
 669 other hand, $[CO_{2aq}]_w$ is an increasing function of temperature and salinity (Fig. A2b and d). Its
 670 sensitivity to salinity is 3 to 10 times larger than its sensitivity to temperature (Fig. A2f). This
 671 ratio increases up to 17 with decreasing temperature to $0^\circ C$, but our approximation does not

672 hold in cold Polar regions (Fig. A1). If $[CO_{2aq}]_w$ is evaluated at the base of the MBL (in F_{MBL}), the
673 variations in T and S that can influence it are changes below the TBL and MBL ($T_{TBL}-T_d$ and $S_{MBL}-$
674 S_d) and changes in the cool skin below the MBL ($T_{TBL}-T_{MBL}$). The former is due to diurnal warm
675 layer formation or rain-induced freshening and cooling. Because these differences are usually
676 weak in our simulations (Fig. 3) they only affect $[CO_{2aq}]_w$ locally. The latter corresponds in our
677 simulations to 4/5th of $T_{int}-T_{TBL}$, the entire cool skin effect, and induces a decrease in $[CO_{2aq}]_w$.
678 Finally, an increase in $[CO_{2aq}]_i$ and a decrease in $[CO_{2aq}]_w$ together induce the obtained increase
679 in the global carbon sink (Figure 5a, the red bar). For F_{TBL} , the main impact (except for warm
680 layers and rain lenses) is the increase in $[CO_{2aq}]_i$ with decreasing T .

681 Note that, considering only the impact of temperature on CO_2 flux (A1) leads to :

$$682 \quad F_{MBL} - F = k_w \sqrt{660/Sc(T)} [(T_{Int} - T_{h/2}) \frac{\partial [CO_{2aq}]_i}{\partial T} - (T_{MBL} - T_{h/2}) \frac{\partial [CO_{2aq}]_w}{\partial T}] \quad (A7)$$

683 That can be rearranged to

$$684 \quad F_{MBL} - F = k_w \sqrt{660/Sc(T)} [(T_{Int} - T_{h/2}) \left(\frac{\partial [CO_{2aq}]_i}{\partial T} - \frac{\partial [CO_{2aq}]_w}{\partial T} \right) + (T_{Int} - T_{MBL}) \frac{\partial [CO_{2aq}]_w}{\partial T}]$$

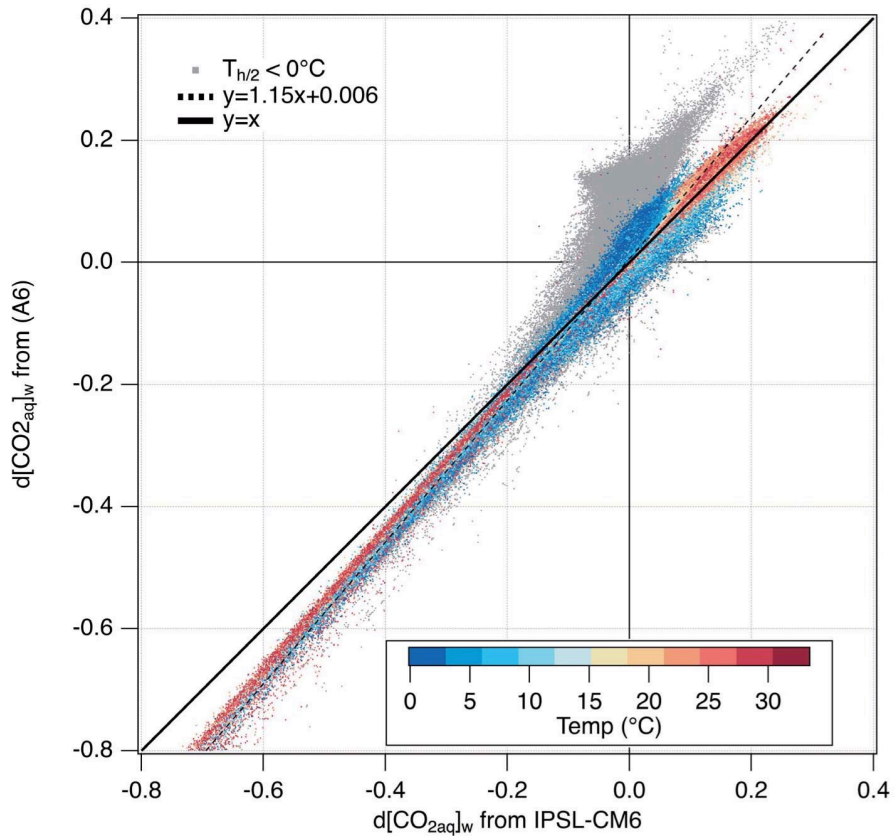
685 (A8)

686 The first term in the parenthesis is positive, the second is negative. Therefore, the flux
687 adjustment due to F_{MBL} increase when T_{MBL} tends to T_{int} (or if the MBL becomes thinner).
688 Therefore, unlike discussed in McGillis and Wanninkhof (2006) and as discussed by Woolf et
689 al. (2016), a thinner MBL would lead to a stronger F_{MBL} flux adjustment with a maximum value
690 given by the total temperature difference in the ocean skin ($T_{int} - T_{h/2}$) that is reached for T_{MBL}
691 $= T_{int}$.

692

693 **Data availability statement**

694 The ocean skin parameterization (Bellenger et al. 2017) is open-access and can be downloaded
695 at <https://gitlab.in2p3.fr/ipsl/lmd/dpao/ocean-skin>. The CMIP6 historical simulations with
696 IPSL-CM6A-LR (and in particular the r1i1p1f1 member) are available on ESGF: [https://esgf-
698 node.ipsl.upmc.fr/search/cmip6-ipsl/](https://esgf-
697 node.ipsl.upmc.fr/search/cmip6-ipsl/). Surface ERA5 hourly data can be accessed from
699 [https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-
701 levels?tab=overview](https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-
700 levels?tab=overview). Daily CO₂ fluxes from DIAG ad CPL simulations and temperature and
702 salinity changes in the ocean skin from DIAG can be found
703 <https://zenodo.org/record/7731926>

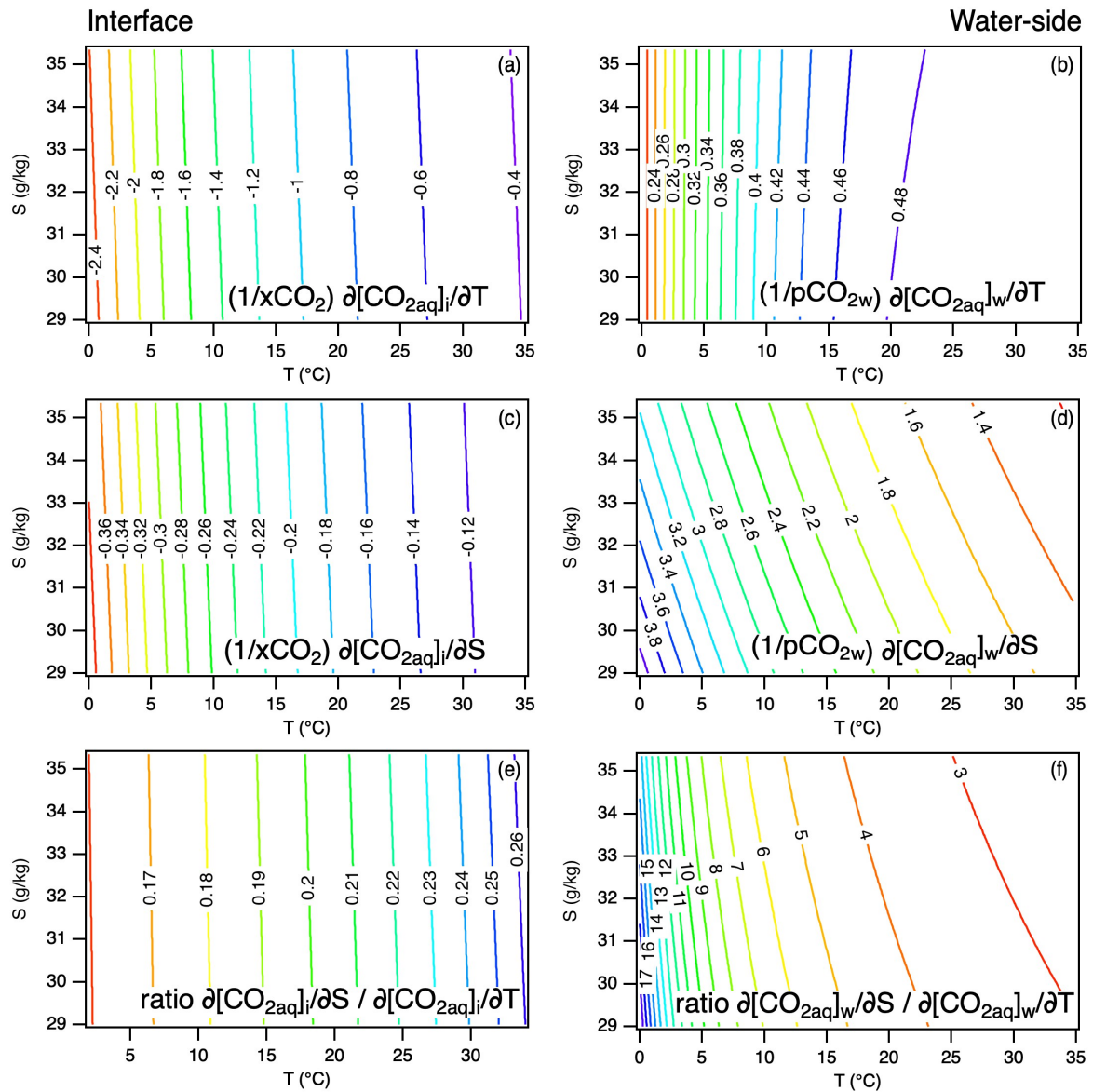


704

705 **Figure A1.** Differences in the aqueous carbon concentration $[\text{CO}_{2\text{aq}}]_{\text{w}}$ in mmol m^{-3} between
 706 the interface and $h/2$ approximated from (A6) using $dT=T_{\text{int}}-T_{h/2}$ and $dS=S_{\text{int}}-S_{h/2}$ and IPSL-CM6
 707 outputs ($d[\text{CO}_{2\text{aq}}]_{\text{w}}$ approx.) and directly calculated by IPSL-CM6 ($d[\text{CO}_{2\text{aq}}]_{\text{w}}$ IPSL-CM6). Color is
 708 the ocean model first level temperature (grey dots for temperatures below 0°C). The linear fit
 709 is also plotted.

710

711



712

713 **Figure A2.** Sensitivity of the interfacial carbon concentration $[CO_{2aq}]_i$ divided by the
 714 atmospheric concentration of CO_2 (xCO_2 , a and c) and the aqueous carbon concentration
 715 $[CO_{2aq}]_w$ divided by the CO_2 partial pressure in water (pCO_{2w} , b and d) to temperature (a and
 716 b) and Salinity (c and d) and the ratio of these sensitivities for (e) $[CO_{2aq}]_i$ and (f) $[CO_{2aq}]_w$ as a
 717 function of temperature and salinity. The sensitivities of $[CO_{2aq}]_i$ and $[CO_{2aq}]_w$ to T and S are
 718 respectively in $mol\ m^{-3}\ atm^{-1}\ K^{-1}$ and $mol\ m^{-3}\ atm^{-1}\ (g/kg)^{-1}$, pCO_{2w} in atm and xCO_2 the
 719 atmospheric CO_2 mole fraction in mol/mol. The sensitivities of $[CO_{2aq}]_i$ are from Weiss
 720 formulation and the sensitivities of $[CO_{2aq}]_w$ are computed from (A6).

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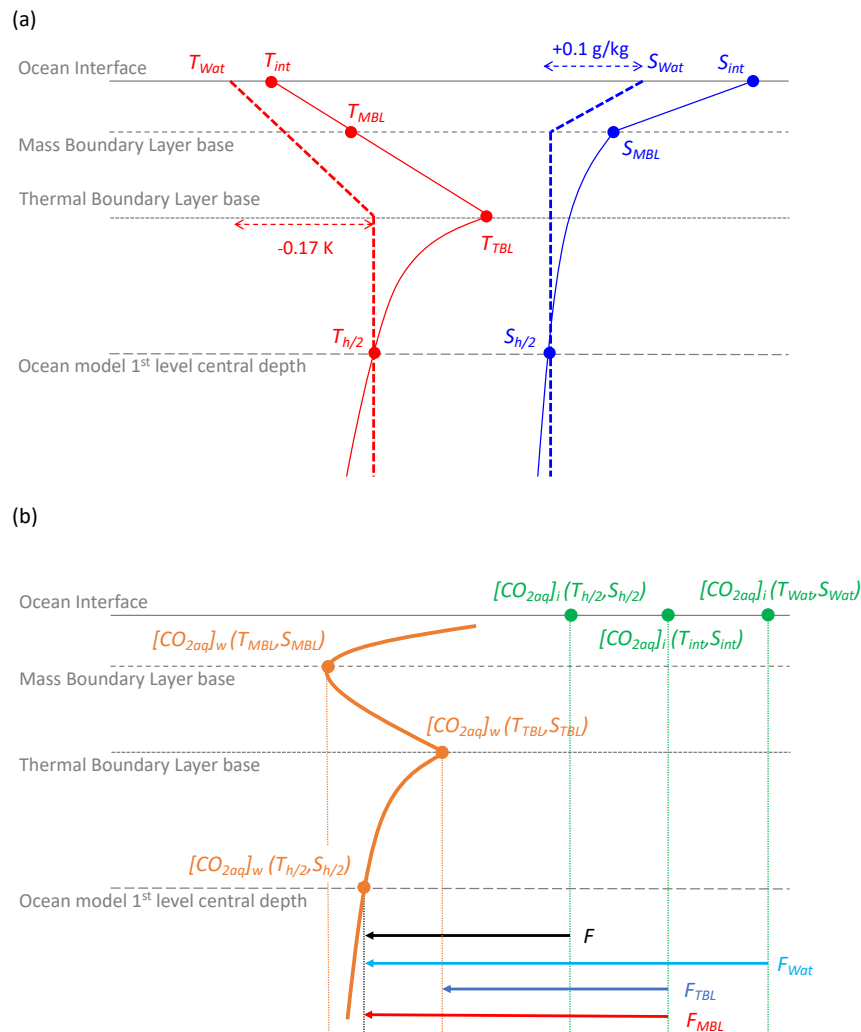
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909 **Table 1.** This table gathers information on the two simulations (DIAG and CPL) that are
910 presented in this study and the details of the different CO₂ prognostic fluxes used interactively
911 to compute the carbon cycle in the model. The other fluxes are only diagnostic. Temperature
912 and salinity that are used to compute the different terms of the CO₂ fluxes are reported. The
913 subscripts correspond to the level at which the temperature and salinity are considered (see
914 figure 1a). The table also provides the mean 2000-2014 annual global carbon sink (PgC yr⁻¹)
915 for the different fluxes and the difference compared to the basic flux *F*. Corresponding year-
916 to-year standard deviations are provided in parenthesis (no detrending applied). *The last two*
917 *lines recalls the recent observation-based estimates of the skin effect by Watson et al. (2020)*
918 *and Dong et al. (2022).*
919

Simulation	CO ₂ fluxes	Rapid (Rap.) or Equilibrium (Eq.) Model	$[\text{CO}_{2\text{aq}}]_i = K_{0p} \text{CO}_2^{\text{atm}}$	$[\text{CO}_{2\text{aq}}]_w$	Global CO ₂ sink (PgC yr ⁻¹)	CO ₂ sink increase (PgC yr ⁻¹)
DIAG	<i>F</i> (prognostic)	-	$T_{h/2}, S_{h/2}$	$T_{h/2}, S_{h/2}$	+2.04 (0.09)	-
	<i>F</i> _{MBL} (diagnostic)	Eq. Model	T_{int}, S_{int}	T_{MBL}, S_{MBL}	+2.42 (0.09)	+0.37 (7.10 ⁻³)
	<i>F</i> _{TBL} (diagnostic)	Rap. Model	T_{int}, S_{int}	$T_{TBL}, S_{TBL} = S_{MBL}$	+2.31 (0.09)	+0.26 (5.10 ⁻³)
	<i>F</i> _{Wat} (diagnostic)	Rap. Model	$T_{h/2}-0.17, S_{h/2}+0.1$	$T_{h/2}, S_{h/2}$	+2.38 (0.1)	+0.33 (8.10 ⁻³)
	<i>F</i> _{skinM} (diagnostic)	Eq. Model	$T_{h/2} + T_{int} - T_{TBL}, S_{h/2} + S_{int} - S_{MBL}$	$T_{h/2} + T_{MBL} - T_{TBL}, S_{h/2}$	+2.44 (0.09)	+0.39 (8.10 ⁻³)
	<i>F</i> _{skinT} (diagnostic)	Rap. Model	$T_{h/2} + T_{int} - T_{TBL}, S_{h/2} + S_{int} - S_{MBL}$	$T_{h/2}, S_{h/2}$	+2.33 (0.09)	+0.28 (5.10 ⁻³)
	<i>F</i> _{noS} (diagnostic)	Eq. Model	T_{int}, S_{MBL}	T_{MBL}, S_{MBL}	+2.44 (0.09)	+0.39 (8.10 ⁻³)
CPL	<i>F</i> _{MBL} (prognostic)	Rap. Model	T_{int}, S_{int}	T_{MBL}, S_{MBL}	+2.18 (0.1)	+0.13 (0.09)
Observation-based estimate <i>Watson et al. (2020)</i> for 1992-2018						+0.4 (0.04)
Observation-based estimate <i>Dong et al. (2022)</i> for 1982-2020						+0.39 (0.08)

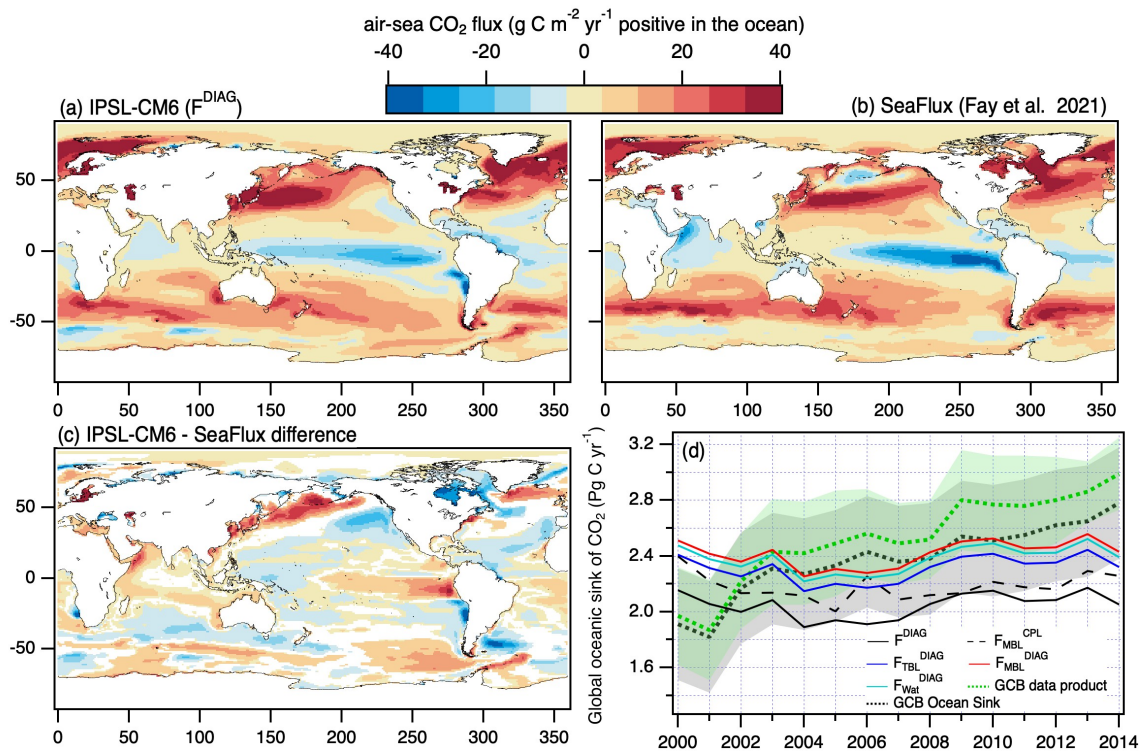
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923 **Figure 1.** Schematic of (a) temperature (red) and salinity (blue) profiles below the ocean-
 924 atmosphere interface and within the first level of the ocean model of depth $h=1\text{m}$ (central
 925 depth $h/2=0.5\text{m}$) for a typical daylight situation and (b) water CO_2 concentration profile
 926 ($[CO_{2aq}]_w$, orange) and interfacial CO_2 concentrations ($[CO_{2aq}]_i$, green) corresponding to T and
 927 S taken at different depth from (a). Starting from the ocean interface, there is an increase in
 928 temperature with increasing depth down to the base of the Thermal Boundary Layer (TBL).
 929 This is the ocean's "cool skin". Then the temperature decreases with depth within the first
 930 meter due to a warm layer formation (in this case, the diurnal warming is less than the cool

931 skin effect). There is a decrease with increasing depth for salinity, mostly within the Mass
932 Boundary Layer (MBL) due to surface evaporation at the interface. The characteristics of the
933 TBL and the MBL reflect the characteristics of molecular diffusion. Because species or mass
934 diffusion is weaker than heat diffusion, the TBL is thicker than the MBL. The TBL is typically
935 0.5-1 mm thick and the MBL is typically $1/10^{\text{th}}$ of the TBL ($1/5^{\text{th}}$ in our simulation). A linear
936 profile in temperature is assumed in the TBL to deduce T_{MBL} (see text for details). Dashed
937 profiles represent the constant corrections that are applied to $T_{h/2}$ and $S_{h/2}$ to obtain T_{Wat} and
938 S_{Wat} following Watson et al. (2020). Color arrows in (b) represent a subset of CO_2 fluxes from
939 table 1 corresponding to T and S profiles from (a). $[\text{CO}_{2aq}]_i$ is mainly a decreasing function of T
940 whereas $[\text{CO}_{2aq}]_w$ is an increasing function of T and S (see Annex). The black arrow represents
941 the classical bulk flux (F), the red arrow represents the flux computed using the “equilibrium
942 model” assumption (F_{MBL}), the blue arrows represent the flux using the “rapid model”
943 assumption with an interactive ocean skin (F_{TBL} , blue) or a uniform one (F_{Wat} , light blue).
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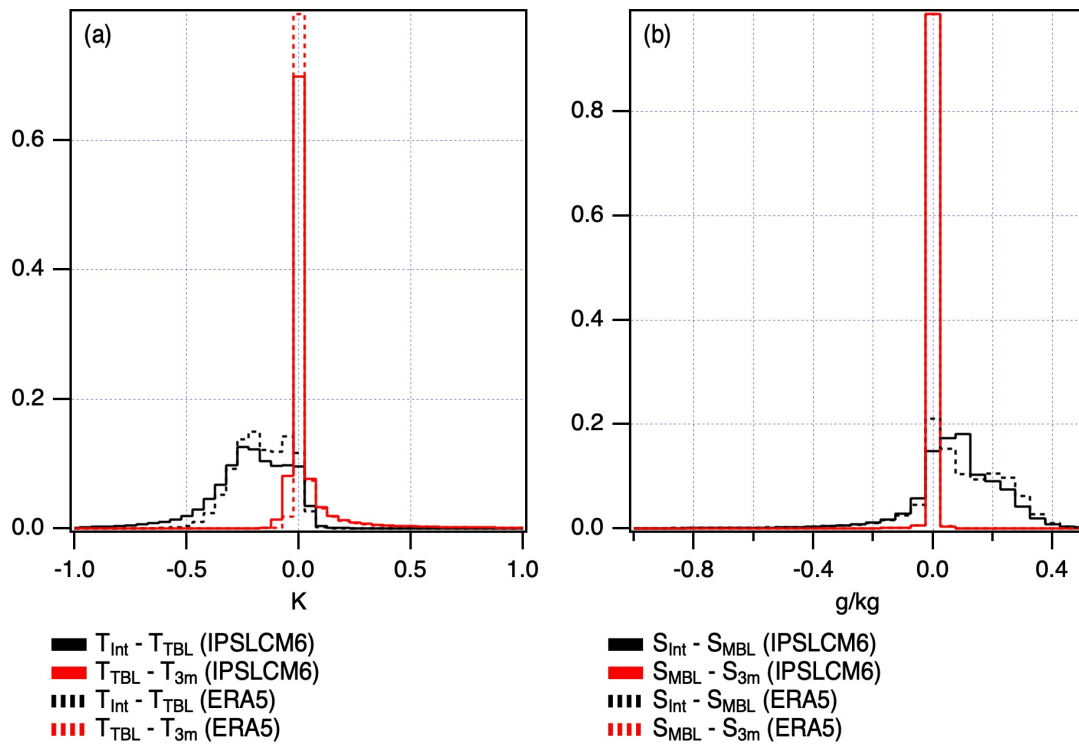


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 946 **Figure 2.** Maps of mean air-sea CO₂ fluxes between 2000-2014 (positive into the ocean, colors)
 947 from (a) the F^{DIAG} flux from the DIAG simulation with IPSL-CM6 and (b) SeaFlux data product
 948 average for the 6 interpolation methods for the pCO₂ maps and 5 wind products presented in
 949 Fay et al. (2021) and (c) the difference between IPSL-CM6 and SeaFlux product (only difference
 950 significant to the 99% level are plotted). (d) Time series of the global annual CO₂ sink (PgC yr⁻¹)
 951 from the Global Carbon Budget (Friedlingstein et al. 2022) based on data products (dashed
 952 green, standard deviation shaded), models and data products (dashed black, standard
 953 deviation shaded) and computed from F^{DIAG} (thin black), F_{MBL}^{DIAG} (thin red), F_{TBL}^{DIAG} (thin blue)
 954 and F_{Wat}^{DIAG} (thin light blue) IPSL-CM6 reference simulation (DIAG) and F_{MBL}^{CPL} (thin dashed
 955 black) from the coupled (CPL) simulation.

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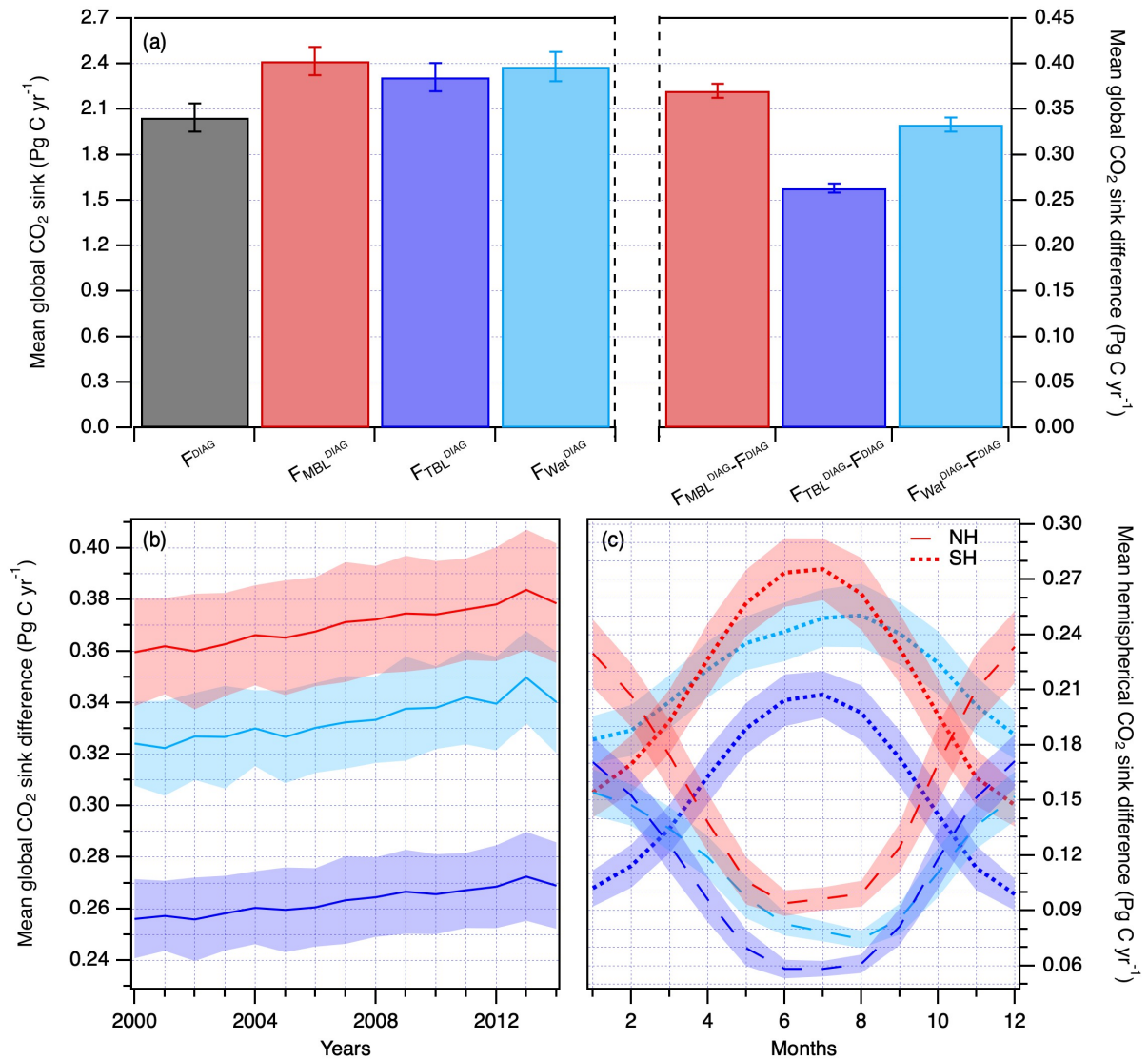
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961 **Figure 3.** Probability distributions of (a) the temperature differences between the interface962 and the base of the Thermal Boundary Layer $T_{Int} - T_{TBL}$ (TBL, black) and the base of the TBL and963 $d=3m$ depth $T_{TBL} - T_{3m}$ (red) and (b) likewise for salinity $S_{Int} - S_{MBL}$ (black) and $S_{MBL} - S_{3m}$ (red).

964 Solid lines are from the 15 years DIAG simulation with IPSL-CM6 and dashed lines are from

965 Bellenger et al. (2017) forced by 18 years of 1-hour ERA5 data.

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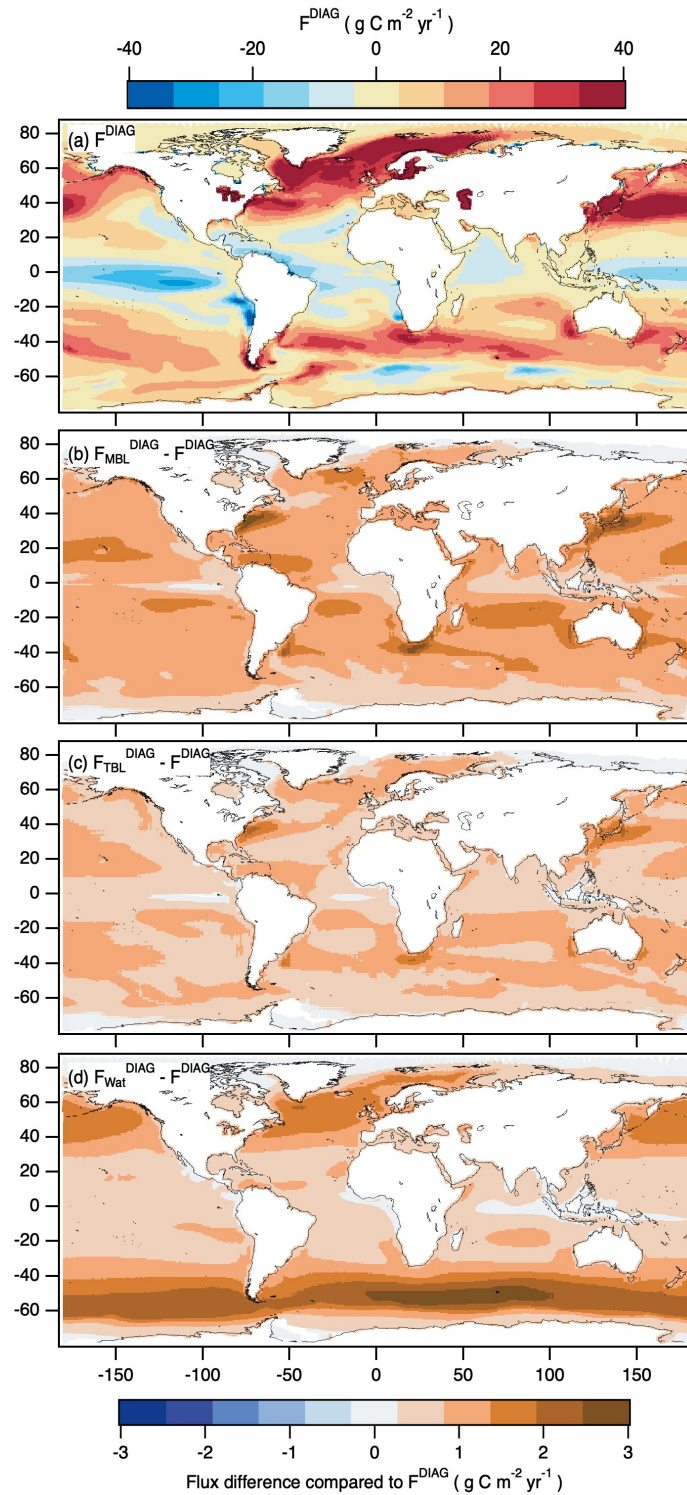
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977 **Figure 5.** (a) Mean 2000-2014 global ocean carbon sink (PgC yr⁻¹, left axis) from DIAG
 978 simulation computed with F^{DIAG} (black bar), F_{MBL}^{DIAG} (red bar), F_{TBL}^{DIAG} (blue bar) and F_{Wat}^{DIAG}
 979 (light blue bar) and corresponding mean differences in global carbon sink with the one
 980 computed with F^{DIAG} (PgC yr⁻¹, right axis). Whiskers represent the year-to-year standard
 981 deviations (no detrending applied). (b) Time series of the annual global ocean CO₂ sink
 982 differences between F_{MBL}^{DIAG} (red), F_{TBL}^{DIAG} (blue) and F_{Wat}^{DIAG} (light blue) and F^{DIAG} from DIAG
 983 simulation (Pg yr⁻¹, shading are the intra-annual standard deviation of the corresponding
 984 differences) and (c) monthly mean seasonal cycle of the northern (dashed) and southern

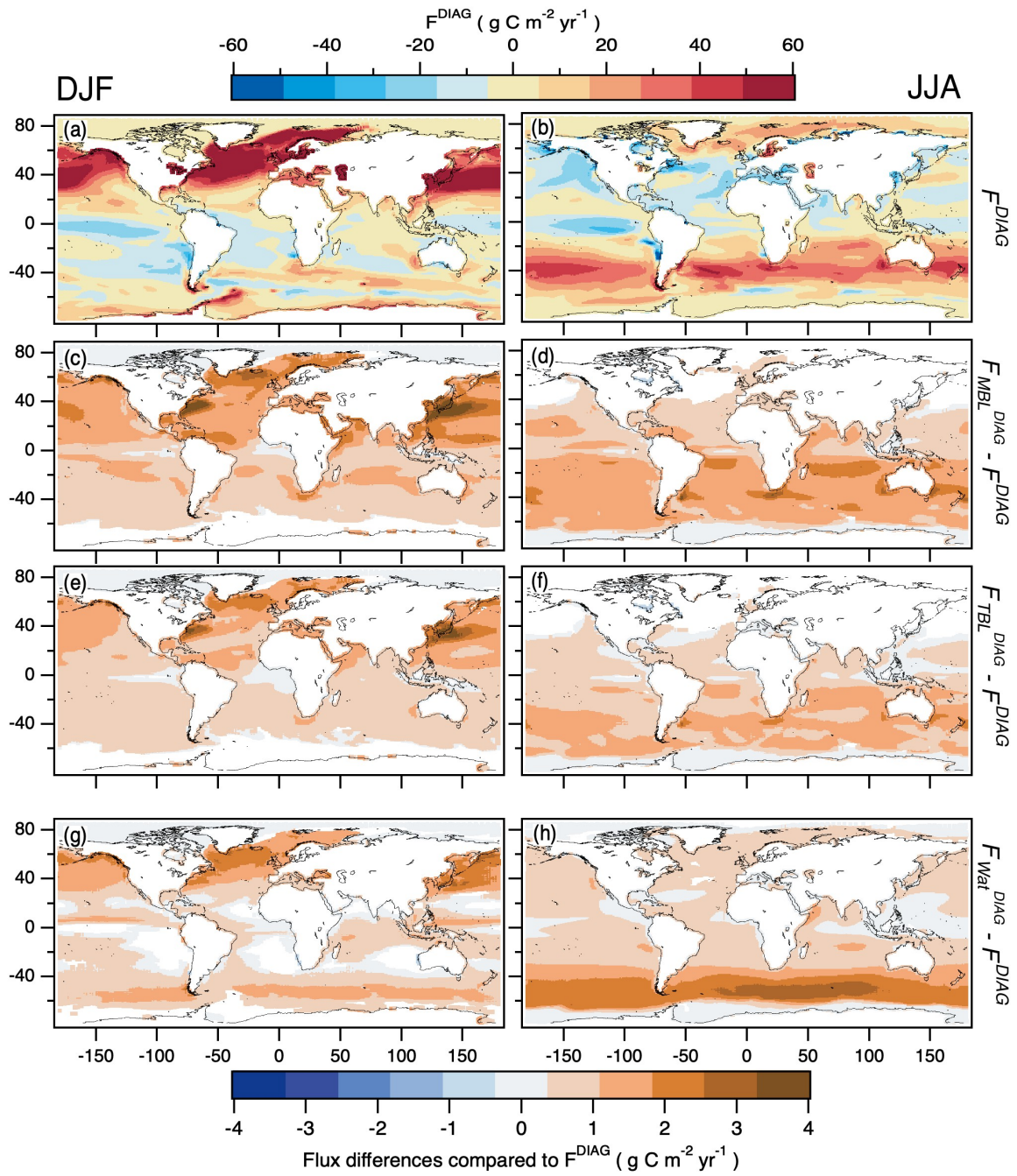
985 (dotted) hemisphere CO₂ sink differences (Pg yr⁻¹, colors are as in (b), shading represents the
986 day-to-day standard deviation for each month).

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 990 **Figure 6.** Mean maps for 15 years of DIAG simulation of (a) F^{DIAG} ($\text{g C m}^{-2} \text{ yr}^{-1}$) and (b) the
 991 $F_{MBL}^{DIAG} - F^{DIAG}$ difference ($\text{g C m}^{-2} \text{ yr}^{-1}$), (c) the $F_{TBL}^{DIAG} - F^{DIAG}$ difference ($\text{g C m}^{-2} \text{ yr}^{-1}$) and (d)
 992 the $F_{Wat}^{DIAG} - F_{blk}^{DIAG}$ difference ($\text{g C m}^{-2} \text{ yr}^{-1}$). Only differences significant to the 99% level
 993 with the student t-test are plotted.

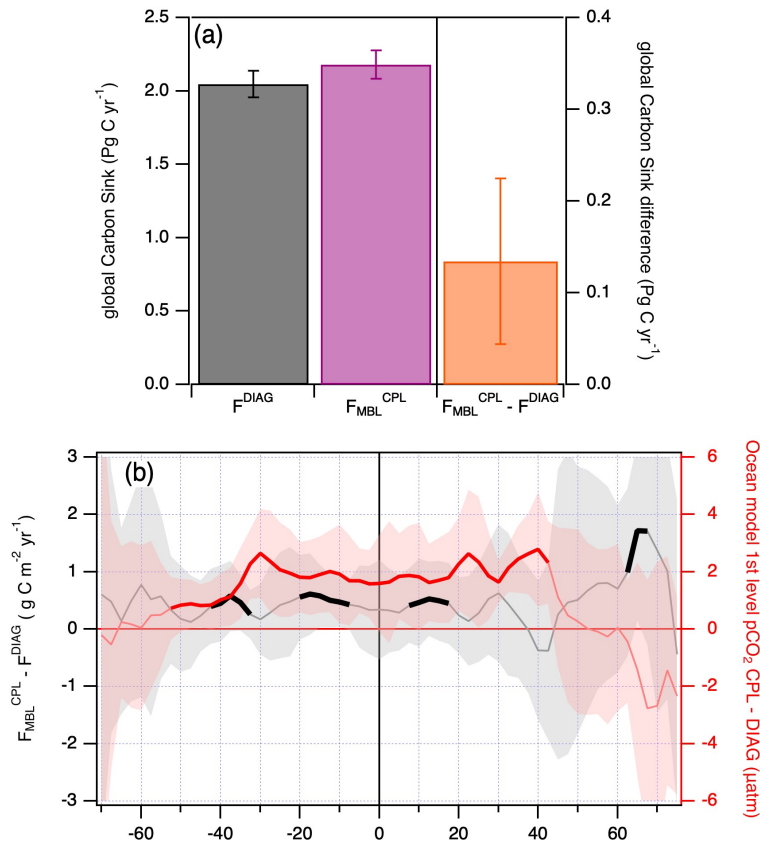


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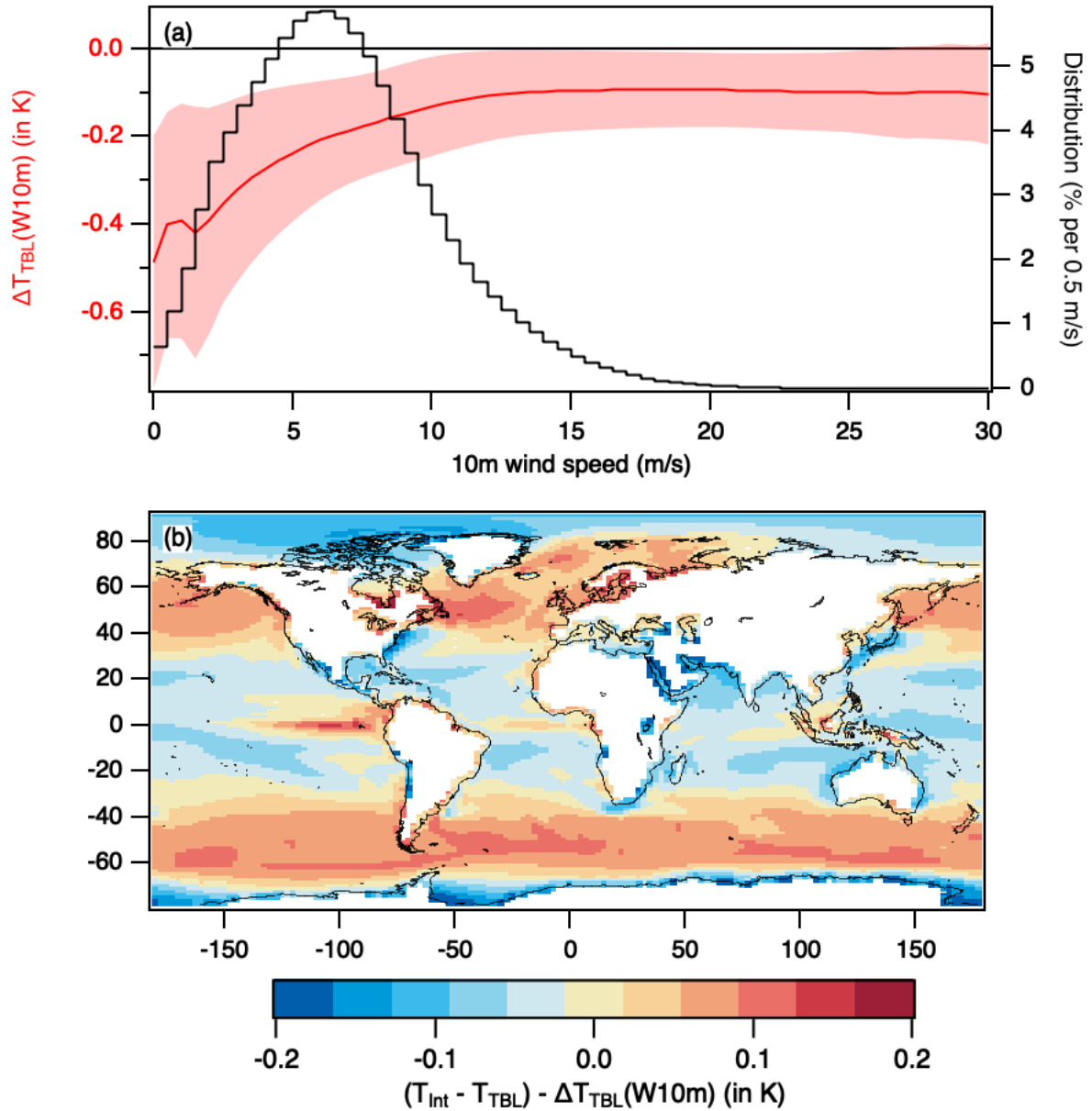
995 **Figure 7.** As Figure 5 but for December-January-February (a, c, e and g) and June-July-August

996 (b, d, f and h). Only differences significant to the 99% level with the student t-test are plotted.

997



998
 999 **Figure 8.** (a) Mean global carbon sink (PgC yr⁻¹) from DIAG and CPL simulations computed with
 1000 F^{DIAG} (black bar, left axis) and F_{MBL}^{CPL} (purple bar, left axis), respectively; the difference is
 1001 plotted in orange (right axis). Whiskers represent the year-to-year standard deviation. F_{MBL}^{CPL}
 1002 $- F^{DIAG}$ is significantly different from zero at the 99% level. (b) The zonal and 15-year mean
 1003 difference between F_{MBL}^{CPL} and F^{DIAG} (g C m⁻² yr⁻¹, left axis) and the difference between the
 1004 ocean model's first level pCO₂ between CPL and DIAG simulations (µatm, red, right axis).
 1005 Shadings represent the year-to-year variability. Lines are bold where the difference is
 1006 significantly different from zero at the 99% level.
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1008

1009 **Figure 9.** (a) Mean cool skin effect as a function of 10m wind speed ($T_{\text{int}} - T_{\text{TBL}} = \Delta T_{\text{TBL}}(W10m)$,
 1010 red solid line) from IPSL-CM6 and associated standard deviation (red shading) and 10m wind
 1011 speed distribution per 0.1 m/s bin (black line). (b) 15-year mean difference (colors in K)
 1012 between the cool skin effect from IPSL-CM6 and the cool skin effect computed from the mean
 1013 relationship plotted in (a). The difference between the cool skins is computed using 90 min-
 1014 model outputs and averaged over time.