

Abstract

The presence of vertical temperature and salinity gradients in the upper ocean and the occurrence of variations in temperature and salinity on time scales from hours to many years complicate the calculation of the flux of carbon dioxide (CO₂) across the sea surface. Temperature and salinity affect the interfacial concentration of aqueous CO₂ primarily through their effect on solubility with lesser effects related to saturated vapour pressure and the relationship between fugacity and partial pressure. The effects of temperature and salinity profiles and changes in the aqueous concentration act primarily through the partitioning of the carbonate system. Contrary to some recent analysis, it is shown that the effect on CO₂ fluxes of a cool skin on the sea surface is large and ubiquitous. An opposing effect on calculated fluxes is related to the occurrence of warm layers near the surface; this effect can be locally large but will usually coincide with periods of low exchange. A salty skin and salinity anomalies in the upper ocean also affect CO₂ flux calculations, though the haline effects are generally weaker than the thermal effects.

1 Introduction

Over the last two decades there has been considerable debate over the importance of temperature values used in the calculation of global and regional CO₂ fluxes. The significance of precise temperatures can be readily understood from two facts. Firstly, atmospheric and upper ocean CO₂ concentrations are almost in balance globally, with a net influx into the contemporary ocean of only approximately 2% of the diffusive exchange. Secondly, the efflux and influx depend on the fugacity or partial pressure in the upper ocean and atmosphere respectively and the sensitivity of fugacity in seawater is estimated at more than 4% per degree Kelvin temperature change (Takahashi et al., 2009). Thus there appears to be a serious risk that mishandling temperature even

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slightly (i.e. biases of 0.1 K and less) can lead to substantial errors in calculated net flux.

Much of the discussion has surrounded the thermal skin effect, the phenomenon that the top millimetre or so of the upper ocean (the “thermal skin”) is generally slightly cooler than the water below (the “mixed layer”). In the simpler cases, there will be a profile of temperatures in the upper millimetre, with temperatures increasing asymptotically to a “foundation temperature”. There have been several estimates of an underestimate of calculated net global CO₂ uptake due to neglecting the thermal skin e.g. (Robertson and Watson, 1992; Van Scoy et al., 1995) of up to one third of the uncorrected uptake (e.g. a correction of $\approx 0.6 \text{ Pg C yr}^{-1}$ according to Robertson and Watson; $\approx 0.4 \text{ Pg C yr}^{-1}$ according to Van Scoy et al., 1995).

McGillis and Wanninkhof (2006) have pointed out that the air-sea CO₂ flux is determined by a concentration difference across a very thin layer (much less than one millimetre) at the top of the ocean. As part of their analysis they consider the thermal skin effect and note that only a fraction (perhaps only one tenth) of the temperature drop across the “thermal molecular boundary layer” or “thermal skin” will occur over the thickness of the “mass molecular boundary layer” that governs gas exchange. They infer that the significance of the thermal skin effect had been exaggerated by previous studies. Zhang and Cai (2007) followed the analysis of McGillis and Wanninkhof (2006) and calculated a reduced thermal correction of $\approx 0.05 \text{ Pg C yr}^{-1}$ that would be almost exactly cancelled by an opposing haline effect associated with the salty skin of the ocean.

Here we review and adopt much of the framework provided by McGillis and Wanninkhof (2006). We note three distinct mechanisms that link near-surface CO₂ concentrations and temperature (Sect. 2). The significance of each mechanism to different layers of the ocean is estimated, borrowing quantitative values from the illustrative example provided by McGillis and Wanninkhof. Thus, we concentrate upon the thermal profile of the upper ocean (Sect. 3) and upon diffusive transfer in molecular sub-layers immediately below the sea surface (Sect. 4). We consider the effects of

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temperature trends and variation on fluxes calculated from limited data collected over a few decades. A clarification to the correct inclusion of the “thermal skin effect” in gas flux calculations is summarized in Sect. 5. Here we have revisited the significance of the thermal skin effect by considering particularly the error incurred if a sea surface temperature at any chosen depth in the upper metres of the ocean (variously defined and named as “Bulk SST” or “SSTdepth” in the literature) is used for all temperature and solubility calculations. A larger opposing effect is associated with ignoring the formation of a shallow warm layer (Sect. 6), but this effect will occur infrequently.

We consider additional effects related to salinity (Sect. 7). Generally, the analogous haline effects are smaller than the thermal effects, but worth including in a thorough calculation. The importance of climatological variation or secular trends in salinity and the sensitivity to the underlying cause is discussed (this section draws on the specific experience of analysing Arctic seas, reported in detail by Land et al., 2012).

We have deliberately omitted another connection between temperature and gas fluxes: the coupling of heat and gas fluxes through irreversible thermodynamics. In principle that coupling also affects CO₂ fluxes, but we consider that Doney (1995) has adequately demonstrated that the effect is negligible for all practical purposes. We also assume that the gas at the interface will be in perfect equilibrium with the concentration in the lower atmosphere. That assumption requires neglect of vertical gradients in the marine atmospheric boundary layer and the “kinetic layer” immediately above the sea surface (see section 3 of Doney, 1995). Some effects of carbon chemistry are included, but we have assumed that hydration and dehydration rates are too low to significantly alter the transfer velocity of CO₂ (Bolin, 1960).

The intention is to provide a coherent account of the issues surrounding temperature and salinity handling, particularly as they relate to the calculation of air-sea CO₂ fluxes, regionally or globally. Studies applying this account and the resulting recommendations will be published elsewhere.

2 Temperature and CO₂; vapour pressure, solubility and isochemical repartitioning

The top of the ocean is depicted schematically in Fig. 1. Here we define an absolute interface (I) directly in contact with the atmosphere. Below that interface we define two boundary layers: Mass Boundary Layer or Molecular Boundary Layer (MBL) appropriate to the transfer of gases and salt (slightly different thicknesses may be assigned to each solute, but we simplify this to a single definition) such that gradients of mass concentration associated with an air-sea disequilibrium are confined to this layer. Similarly a thermal skin is defined such that temperature gradients associated with an interfacial heat flux are confined to this skin layer. The thermal skin is characteristically a factor of ten thicker than the MBL. A number of additional depths and temperatures are shown schematically in Fig. 1 and will be explained further below.

The net air-sea flux of a gas depends on the concentration difference of the volatile across the MBL; in the case of CO₂ we are concerned with the aqueous concentration of CO₂. A correct calculation of the concentration difference depends on using appropriate temperatures (and salinities) and applying one procedure for calculation at the interface and a very different procedure for calculations at the base of the MBL and below.

The concentration at the top of the MBL, the interface (I) is done on the basis that it will be in perfect equilibrium with the atmosphere above. In other words, Henry's Law describes the relationship between the dissolved concentration in the interfacial water and the atmospheric concentration immediately above. Here we adopt the method described by McGillis and Wanninkhof (2006) to calculate atmospheric concentration. We start with an estimate of the dry molecular fraction of CO₂ in the atmosphere, X_{CO_2} . We need also an atmospheric pressure, P , and a saturation water vapour pressure $p_{\text{H}_2\text{O}}$ in order to calculate the partial pressure of CO₂, at sea level, p_{CO_2} , thus,

$$p_{\text{CO}_2} = (P - p_{\text{H}_2\text{O}})X_{\text{CO}_2} \quad (1)$$

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The saturation water vapour pressure is dependent on temperature and salinity and should be calculated using the interfacial water temperature, T_1 , and interfacial salinity, S_1 . Here we share the practice of McGillis and Wanninkhof and use a formula from Weiss and Price (1980); see equation A1 of McGillis and Wanninkhof (2006).

The sensitivity to vapour pressure is the first (and the smallest) of three effects of temperature on the calculated concentration gradient. The magnitude of the effect is temperature dependent and should be calculated from the various equations described above and below, but for illustration we can use the example provided by McGillis and Wanninkhof (2006; see especially figure 1 and table therein) that implies an sensitivity of $-0.2\% \text{ K}^{-1}$ of the interfacial concentration to an error in the applied temperature by this mechanism alone (i.e. if the actual interfacial temperature was 15°C , but it was assumed to be 16°C , the surface concentration would be underestimated by 0.2% as a result of overestimating vapour pressure and thus underestimating the partial pressure of CO_2).

Having calculated a partial pressure, it is thorough to apply the distinction between fugacity and partial pressure. Again, we follow the recommendation of McGillis and Wanninkhof and apply a fugacity correction given by Weiss (1974); see equation A5 in McGillis and Wanninkhof (2006). This equation again includes temperature and strictly speaking is an additional mechanism of temperature sensitivity, but it is very small and we group it with the vapour pressure effect to give a combined effect on interfacial fugacity that is still rounded to $-0.2\% \text{ K}^{-1}$.

The aqueous concentration of CO_2 in the interface, C_1 , must then be calculated from the solubility, K_o , and the interfacial fugacity, f_1 , thus:

$$C_1 = K_o f_1 \quad (2)$$

The solubility, K_o , is temperature and salinity dependent and must be precisely calculated. Unfortunately, the formulae available for calculating solubility are quite imprecise. For example, McGillis and Wanninkhof (2006; see especially figure 5) show that the solubilities predicted by Weiss (1974) and by Li and Tsui (1971) typically differ by 2%

in warm seawater. This uncertainty introduces an inevitable ambiguity in the estimate of surface fluxes. A substantial error may occur by not consistently using the same formula at both the interface and within the water column and therefore this should certainly be avoided.

5 Since solubility depends on temperature and salinity, the calculation of interfacial concentration using solubility introduces another bias resulting from mishandling the temperature or salinity in the solubility formula. It is essential to use the correct interfacial temperature and salinity in the calculation. The sensitivity to solubility is the second and largest of three effects of temperature on the calculated concentration gradient. As
10 a first illustration, we can use again the example provided by McGillis and Wanninkhof that implies a sensitivity of $-2.5\% \text{ K}^{-1}$ of the interfacial concentration to an error in the applied temperature by this mechanism alone, or $-2.7\% \text{ K}^{-1}$ as a combined effect on the calculated interfacial concentration with the “effect on fugacity” described above. A more precise calculation should be based on taking the derivative of the solubility with respect to temperature, where we chose the formula for solubility given by Weiss
15 (1974). The result for a fixed salinity of 35 is shown in Fig. 2. The value of $-2.5\% \text{ K}^{-1}$ is typical for fairly warm water (coinciding with the more exact value for a temperature between 25 and 26 °C) but the sensitivity rises to almost $-4\% \text{ K}^{-1}$ at 0 °C.

That concludes the procedure to calculate the correct interfacial concentration. We
20 consider next the procedure of estimating the aqueous concentration of CO_2 at the base of the MBL, C_M . We assume that data will be generally available in the form of a measured fugacity corrected as necessary to give the true fugacity at the measurement site. Each measurement is effectively of the “bulk water” metres below the interface and can be designated as measured fugacity, $f_{B, \text{local}}$ (it is worth noting that “bulk” is appropriately vague for water drawn from outside the ship’s hull on a moving ship). We shall
25 assume that a local temperature and salinity can be assigned and therefore, the correct local concentration in the bulk, $C_{B, \text{local}}$, can be calculated. We shall discuss some further subtleties in the following sections, but for now we shall assume that we wish to estimate the concentration at the base of the MBL, C_M and we have available estimates

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for the temperature and salinity at that location. We shall also assume for now (and justify in the next section) that it is reasonable to assume that while the temperature and salinity may differ from “B, local” to “M”, the total dissolved inorganic carbon (DIC) and the alkalinity are unchanged. Thus, we need to consider an “isochemical” change in the carbonate system between the two locations, where isochemical is here defined such that total DIC (T_{CO_2}) and alkalinity (T_{Alk}) are unchanged but pH and aqueous CO₂ concentration may vary. This situation has been considered among others by McGillis and Wanninkhof (2006) and Takahashi et al. (2009). The partitioning of the carbonate system (the distribution of total DIC among bicarbonate, carbonate, carbonic acid and aqueous CO₂) is temperature and salinity dependent. Thus, while total DIC and alkalinity are conserved in a temperature change in isochemical conditions, the concentration of CO₂ will change. Generally warming leads to a slightly higher fraction of the total DIC being partitioned into CO₂. Thus warming a parcel of water leads to higher dissolved CO₂ concentration by “isochemical repartitioning”. The sensitivity of partitioning to temperature is the third major sensitivity of the calculated concentration gradient to temperature. Isochemical Repartitioning within the upper ocean is related to both temporal variations and the vertical and horizontal distribution. We will discuss the appropriate equations below, but for illustration we can use again the example provided by McGillis and Wanninkhof that implies a sensitivity of $+1.5\% \text{ K}^{-1}$ of the concentration below the MBL to an error in the assumed temperature.

A general equation for isochemical correction is required. This same equation can be applied to two slightly different tasks. Almost universally, it is necessary to correct ship-based measurements using an equilibrator for the effect of the slight warming before measurement, which can be calculated from the difference between the temperature in the equilibrator and the in situ temperature. Secondly, where the sea temperature at the measurement site is not representative of the temperature of interest (for example, a “climatological” temperature at the base of the MBL), but an isochemical transformation between the two temperatures is a reasonable assumption, then the same equation

can be applied. We will discuss the type of transformation that is applicable to common situations in the next sections.

It is notable that if we are interested in calculating a climatology, then it is simpler to apply the isochemical equation only once, direct from the equilibrator to the climatological conditions. The estimated in situ temperature may be useful to filter out data where the contrast between the measured in situ temperature and the expected climatological data is suspiciously high, but importantly any error in the in situ data is otherwise irrelevant to the calculation. A slight sensitivity to the in situ temperature is incurred if the calculation is in two parts via the in situ temperature and inconsistent formulae are used for the two parts of the calculation, otherwise errors in estimated in situ temperature (which can be rather substantial, due to the difficulty of estimating the warming between the intake and the equilibrator) are eliminated from the error budget of the final outputs.

The clearest calculation of the isochemical effect is to calculate the effect on concentration directly. However, it is also valid to calculate an isochemical effect on fugacity – which will consist of contributions from the repartitioning and from the change in solubility – and then calculate the corrected concentration. Thus for a δT increase in water temperature, an increase of 4% δT in fugacity is first calculated, from which the 2.5% δT change due to solubility is subtracted in calculating concentration to arrive at the 1.5% δT increase in concentration due to repartitioning. This effect was noted by Hare et al. (2004) and included in their equation 12, but they incorrectly reversed the sign of the temperature difference.

A widely applied correction is based on a measurement of fugacity change of North Atlantic seawater in isochemical conditions by Takahashi et al. (1993). The correction can be expressed either in a more exact temperature dependent form, or a simpler form:

$$\partial \ln p_{\text{CO}_2} / \partial T (^{\circ}\text{C}) = 0.0433 - 8.7 \times 10^{-5} T (^{\circ}\text{C}) \quad (3)$$

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$$\partial \ln p_{\text{CO}_2} / \partial T (\text{K}) = 0.0423 \quad (4)$$

The sensitivity does vary with temperature and Takahashi et al. (2009) chose to use the former, more precise expression for corrections between the equilibrator and in situ, but used the simpler form for an estimate of the “error due to undersampling” (which is related to the issue of the in situ temperatures being unrepresentative of climatology). The second version (Eq. 4) has been more commonly used historically and is still in common use, for example for corrections from equilibrator temperature and in situ in the construction of the SOCAT database (Pfeil et al., 2012). Equation (3) is likely to be more accurate. Takahashi et al. (2009) state that since the typical temperature changes in an underway system are small the error in using Eq. (4) is negligible. We note that it is nonetheless an identifiable systematic bias that should be avoided where practical. In principle, it is possible for most data records to “retrieve” the original equilibrator values and then apply Eq. (3) throughout.

McGillis and Wanninkhof (2006) recommend that the correction is made directly to concentrations and that the full equations of the carbonate system are used (Mehrbach et al., 1973; Lewis and Wallace, 1998; Dickson and Millero, 1987). That is undoubtedly a more thorough method but it does require additional information on total DIC and alkalinity. McGillis and Wanninkhof (2006) point out methods that ignore the varying chemistry of seawater (note the report of Takahashi et al., 1993) is based only on a North Atlantic surface water sample) will neglect the true variability in the isochemical changes. They credit Copin-Montegut (1988) and Goyet et al. (1993) with showing that “the temperature dependence is a function of temperature, salinity and $T_{\text{CO}_2} / T_{\text{Alk}}$ ratio”. McGillis and Wanninkhof (2006; see figure 3 and associated text) report the sensitivity of fugacity to temperature may vary from 5.3 % at 0 °C to 3.7 % at 30 °C (in part a response to the associated latitudinal gradient in total DIC, T_{CO_2}). The temperature-dependent version of the formula based on Takahashi et al. (1993) trends in the same direction but the trend is very much weaker.

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It may be appropriate to use available measurements of total DIC, T_{CO_2} , and alkalinity, T_{Alk} , and complete chemical calculations, however we are limited by data availability and there are some remaining uncertainties due to substantial differences in subsidiary equations (McGillis and Wanninkhof, 2006; Mehrbach et al., 1973; Dickson and Millero, 1987; Goyet et al., 1993). Therefore, we propose that Eq. (3) is the pragmatic choice.

3 Profiles, distribution and variation

Temperature, salinity and parameters of the CO_2 system all vary in the ocean. As a prerequisite for inferring general values of properties from local and sparsely sampled measurements of CO_2 and other properties, we need to understand these distributions and how variations of carbonate parameters are related to variations of other oceanic properties and to the atmospheric build up of CO_2 . For example, it is essential to understand when an assumption of “isochemical re-partitioning” is reasonable.

Temperature varies in the vertical; a fairly common example is described schematically in Fig. 3. The water at the sea surface is typically cooler than below, increasing with depth over the first millimetre. The water in at least a few metres below (and more often over tens of metres) is usually actively mixed by the action of the wind and thus temperature, salinity, carbonate parameters and most other properties are almost constant in the vertical. In Fig. 3, we show a common but minority situation where there is a relatively shallow, actively-mixed warm layer that has separated from deeper water due to surface warming (a diurnal layer; generally associated with strong daytime insolation combined with light winds). This layer will also usually be slightly more saline than the deeper water due to evaporation, but this may be counteracted by rainfall. A rarer phenomenon is a freshwater “pool” at the surface associated with high rainfall and gentle winds (Soloviev and Lukas, 1996). Diurnal warm layers are fairly common where insolation is high and the wind is fairly weak, but will breakdown each night to form a more typical deeper mixed layer. Figure 3 depicts a “relic mixed layer” below the

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diurnal warm layer and extending to either a seasonal or permanent thermocline. More often this layer will extend to the sea surface (excepting the cool skin). Importantly the entire layer from the base of the surface skin to the top of the seasonal thermocline will be mixed at least daily. When mixed, the entire water column is returned to a “foundation temperature”. Generally any nighttime measurement within the water column measures foundation temperature. During the daytime, a measurement will only retrieve foundation temperature if it is below any daytime warming. Therefore, some sea surface temperature climatologies use only nighttime data to calculate a foundation temperature. Since changes in total DIC and alkalinity within one day are usually miniscule it is usually reasonable to assume that these properties are uniform within this layer. Similarly, with some caution we might approximate that within any reasonable geographical area and time period, mixed layer total DIC, T_{CO_2} , and alkalinity, T_{Alk} , are invariant and the variations in the fugacity and concentration of CO_2 are primarily isochemical (strong variations in salinity may be an exception as discussed in Sect. 7). Thus, we can make a limited justification for taking numerous samples of measured CO_2 in a single calendar month and geographical area (say, a $1^\circ \times 1^\circ$ grid square) and correcting each to the climatological temperature of that area and time. The sample mean of the corrected concentrations can be assumed to be an unbiased estimator of the true mean, while the sample standard deviation and standard error will reflect a number of phenomena including some chemical variation.

Below the seasonal mixed layer, the water is necessarily denser, which may be due to salinity rather than temperature. In Fig. 3 we depict cooler water below the seasonal mixed layer, but in many cases the water is warmer but more saline. This water is physically and chemically distinct. The total DIC, T_{CO_2} , and especially the alkalinity, T_{Alk} , are almost invariably higher in the deeper water. The concentration of aqueous CO_2 will also depend on temperature and salinity. Figure 3 depicts an example where the net effect is higher concentration in the deep water, but the important thing is that the deeper water is chemically distinct. Where there is an exchange with this deeper water (e.g. entrainment of thermocline water by a deepening mixed layer) the change

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in mixed layer properties will not be isochemical in nature and no such assumption is tenable. For example, both the seasonal and inter-annual variations in upper ocean properties will normally involve such exchange and an “isochemical transformation” cannot be supported. Similarly, exchange between atmosphere and ocean is considerable on seasonal time scales and this exchange also represents changes in the upper ocean that are not isochemical. It may be pragmatic to neglect departures from constant chemistry within a single month (or at least, to treat each sample within a given month transformed by an isochemical calculation to the climatological temperature of that month as equally representative). Applying isochemical transformations over more than one month cannot be justified.

Another interesting case is the relatively slow secular variations over many years in upper ocean properties. In all likelihood many mechanisms are significant. However, it is reasonable to argue that the complexities of changing ocean chemistry can to a first approximation be ignored and that on long time scales the fugacity of the upper ocean will simply “track” the upward trend of atmospheric partial pressure. The actual variation in various oceanic basins has been reviewed by Takahashi et al. (2009). The results show some variation between basins but these may be influenced by inter-annual and inter-decadal variations in sources and sinks (e.g. Watson et al., 2009). For the purposes of calculating “climatological values” of CO₂ flux for a “reference year”, it seems reasonable to take the simple approach of correcting oceanic fugacities for the long-term trend in atmospheric partial pressure. It is sensible to filter out “ocean anomalies” e.g. data heavily affected by El Nino. There are also some ambiguities in defining the appropriate atmospheric trend, but the simplest approach is to use a mean value of trend for recent decades.

4 The thermal and mass “skins”

McGillis and Wanninkhof (2006) have noted that there is an important distinction between the transfer of mass and heat in the upper millimetres of the ocean due to their

is attributed to a gradual “hand over” across the molecular boundary layers between purely molecular diffusion at the interface and dominant turbulent transport. Various models of this process are current, but they generally imply a stochastic process and inhomogeneous concentration or temperature at any depth within the skin. Nevertheless, it is possible to consider an average temperature and concentration profile, which will be curved as the hand over to turbulent transport progresses further as the interface recedes. The average profiles for CO₂ and temperature are shown schematically in Fig. 4. Though we expect a ratio in thickness of approximately 10, the figure is not drawn to scale, rather the mass boundary layer is enlarged sufficiently to describe it clearly.

Key depths are depicted in Fig. 4. “M” signifies the base of the mass boundary layer and “T” the base of the thermal boundary layer. “I” determines the precise interface between air and sea. Interfacial concentration and temperature is a useful mathematical concept, but quite difficult to define physically and impractical to measure. A more practical value of sea surface temperature is the radiometric temperature, T_{Rad} . Since infrared radiation is absorbed by a thin layer of seawater, the infrared radiation from the sea surface into the atmosphere is emitted by a very thin layer, $\sim 20 \mu\text{m}$ thick. Usually T_{Rad} (or SST_{skin}, as it is sometimes named) is considered to be an adequate practical alternative to the abstract concept of interfacial temperature, T_i (or SST_{int}). Since the radiometric thickness is not much less than the equivalent stagnant layer thickness for mass, T_{Rad} may also be a pragmatic substitute for T_M . T_{Rad} is not a substitute for the temperature at the base of the thermal skin, which should instead be similar to the bulk temperature, T_B , in the rest of the surface mixed layer. However, it must also be noted that some radiometric temperature datasets, while detecting the temperature variation at the skin are actually calibrated to temperature at depth. Therefore it is important to use T_{Rad} that are calibrated (or corrected back to) skin temperatures.

There is some ambiguity in the precise form of the averaged concentration gradient (full and dashed red curves in Fig. 4). An air-sea flux is driven by a concentration difference across the mass boundary layer and in both versions of the concentration

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profile, we depict the main concentration difference between “I” and “M” (in this case decreasing from the surface down, consistent with a net flux into the sea). A significant gradient in total DIC is not expected below “M”, since this water should be “well mixed”. However, there is expected to be a temperature gradient between “M” and “T” and thus “isochemical repartitioning” implies that at equilibrium there should be a constant concentration of CO₂ below the base of the thermal boundary layer but a progressively lower concentration in the cooler water above; i.e. $C_B = C_T$, but $C_T > C_M$. That situation is depicted by the dashed red curve in Fig. 4. Note however that we specified “at equilibrium”. The isochemical repartitioning depends on the kinetics of the carbonate system however, and thus the hydration/dehydration kinetics are important. The time scale for molecular diffusion of CO₂ across the equivalent stagnant layer thickness for heat (~ 300 μm) should be similar to typical hydration times (i.e. of the order of 100 s). Given the similar time scales and the crudity of the representation of the boundary layers, it is genuinely ambiguous whether equilibrium will be achieved. Note however that below the base of the mass boundary layer, turbulence will be substantial and therefore transport faster than by molecular diffusion alone, therefore the diffusion time scale may be significantly shorter than the reaction time scale and there may be insignificant repartitioning of the carbonate species between “M” and “T”. The logic of “rapid” diffusion and thus a minimal concentration gradient is shown by the full red curve in Fig. 4. On balance the “rapid model” is likely to be a better approximation than the “equilibrium model”, but there is genuine ambiguity since the models described here are quite crude and the kinetic rates vary. For example, since the time scale of hydration is much less than 100 s in warm seawater, it is possible that the equilibrium model is the better approximation at low latitudes.

5 Temperature mishandling and the skin effects

A new analysis of the effect of neglecting the thermal skin effect culminates from the discussions above. Note that “neglecting the thermal skin” generally means using a

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or more approximately taking $C_1 \approx C_M$

$$dC \approx (4.2\% - 1.5\%x) \Delta T C_1 \quad (7)$$

Contrary to the analysis of McGillis and Wanninkhof (2006), the fact that the “mass transfer skin” is thinner than the thermal skin can only enhance the importance of the thermal skin by up to an additional 50% (the maximum is calculated assuming the typical sensitivities of -2.5% and $+1.5\%$ described above, $C_1 \approx C_M$, full equilibration and $x \approx 0.1$). However, we think that this is almost certainly an overestimate and given the uncertainties in the calculation of the repartitioning effect it is probably better to focus on the interfacial effect and build the uncertainty into a generous estimate of the uncertainty of ΔT .

Since gas transfer velocities are low in low wind speeds, it is more important to have a reasonably accurate estimate of the thermal skin effect in moderate and high wind speeds. Donlon et al. (1999) reported a mean cool skin $\Delta T = 0.14 (\pm 0.1)$ K for wind speeds in excess of 6 m s^{-1} . Applying the central value of temperature 0.14 K and confidence limits of ± 0.1 K globally with the “rapid model” formula should give a reasonable estimate of the global effect. Thus, a total correction, dC , of the air-sea concentration difference, ΔC , is simply equal to the correction to C_1 , given by approximately

$$dC \approx 2.7\% \Delta T C_1 \quad (8)$$

$$dC \approx 0.38 (\pm 0.27)\% C_1 \quad (9)$$

This formula implies an additional uptake to the oceans of between 0.1 Pg C yr^{-1} and 0.6 Pg C yr^{-1} on an exchange of $\approx 90 \text{ Pg C yr}^{-1}$ and an estimate of the contemporary net uptake of $1.6 (\pm 0.9) \text{ Pg C yr}^{-1}$ (Takahashi et al., 2009). (Note that this calculation assumes all of the exchange is across the sea surface. The correction should only be applied to transfer directly across the surface but not to bubble-mediated transfer; Woolf, 1993; Hare et al., 2004.)

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A more careful calculation using the complete equations for the thermal effects is required, but this simple calculation shows that the thermal skin effect is substantial.

A small additional effect on flux calculations is in the calculation of transfer velocities. Transfer velocities depend on Schmidt number or molecular diffusion coefficient of the dissolved gas, which are temperature dependent. A radiative temperature, T_{Rad} , is appropriate to this calculation for transfer directly across the sea surface but only a small error will be incurred by using a deeper water temperature.

6 Warm layers

We have considered the effect of a cool skin and the result of misassigning the relatively warm temperature of underlying water to the top of the skin (the interface, “I” in Fig. 1) and within the thermal skin (the base of the molecular boundary layer, “M” in Fig. 1). There is another opposing case where a relatively cool temperature is wrongly assigned to “M” and “I”. This will occur where a nighttime temperature or temperature from a considerable depth is assigned to near the surface during daytime on an occasion where the surface water is significantly warmed forming a layer distinct from the relic mixed layer below (see Fig. 3). The formation of warm layers occurs quite commonly during the daytime in low winds and high insolation, commonly referred to as diurnal warming. Where there is some stirring of the surface water, we expect an actively mixing warm layer to form a daytime mixed layer separated by a diurnal thermocline from the relic mixed layer below. For greater insolation and lower winds, the warm layer is relatively intense and shallow. On most days (lower insolation and higher winds) a distinct warm layer will not form though the entire mixed layer may warm very slightly during daytime. Warm layers have been observed and modelled for decades (Price et al., 1986; Fairall et al., 1996). The improvement of Earth Observation capabilities enabled a more global perspective (Gentemann et al., 2003; Stuart-Menteth et al., 2003). McNeil and Merlivat (1996) pointed out the substantial impact of warm layers on

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CO₂ fluxes. This subject has been returned to since and here we provide only a brief review.

Similarly to Sect. 5 for the thermal skin, we will consider the effect of a misassignment of a temperature at depth or nighttime to shallower water. In the case of a warm layer, we will define this warm layer to be ΔT_W warmer than the water in the relic mixed layer and we calculate the effect on CO₂ calculations where the relic or nighttime temperature is incorrectly assigned to the surface water. A thermal skin will be superposed on the warm layer, therefore we assume the interface to be warmer than the relic water by $\Delta T_W - \Delta T$. It is simpler to treat the warm layer effect as a simple additive effect, therefore the specific correction for warm layers will be described below and this should be added to the thermal skin and haline effects.

The effect of misassigning relic temperature to the interfacial temperature is similar in principle to ignoring the thermal skin effect at the interface and therefore we can adapt Eq. (5) to the warm layer case. Thus, the necessary correction to the interfacial concentration if a relic temperature was used initially is given by

$$dC_{IW} \approx -2.7 \% \Delta T_W C_I \quad (10)$$

Similarly, too low a temperature may be assigned to the base of the MBL and this also needs to be corrected. The correction is again similar to that applied for a thermal skin except that for a warm layer there is no ambiguity that equilibrium repartitioning is appropriate. A warm layer increases the temperature at the base of the molecular boundary, forcing some additional part into aqueous CO₂. The increase in the concentration at the base of the MBL is then given by

$$dC_{MW} \approx 1.5 \% \Delta T_W C_M \quad (11)$$

The effect of a warm layer is to decrease the concentration at the interface and increase the concentration at the base of the MBL, in both cases subtracting from the net air-to-sea flux. The total correction, dC_W , of the air-sea concentration difference, ΔC , is given

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by approximately

$$dC_W \approx -1.5 \% \Delta T_W C_M - 2.7 \% \Delta T_W C_I \quad (12)$$

or more approximately taking $C_I \approx C_M$

$$dC_W \approx -4.2 \% \Delta T_W C_M \approx -4.2 \% \Delta T_W C_I \quad (13)$$

5 This is an important effect and will oppose that identified for the thermal skin effect. The effect is stronger for a given temperature difference than that associated with the thermal skin effect and the warm layer effect can commonly exceed 2°C (Gentemann et al., 2003) and exceptionally can be much higher (Merchant et al., 2008), thus an order of magnitude greater than the skin effect. On the other hand, warm layers will
10 occur infrequently, breakdown at night and predominantly occur in light winds when gas transfer velocities will be low. A detailed and global calculation is beyond the scope of this study, but some indication of the importance of the warm layer is practical by reviewing some previous studies.

15 McNeil and Merlivat estimated the warm layer effect on the basis of measurements from free floating buoys in the eastern equatorial Pacific and the Mediterranean Sea. For the eastern equatorial Pacific they estimate a daily averaged warming of 0.13°C , almost exactly opposing the typical cool skin effect (0.14°C ; Donlon et al., 1999). As noted above, the effect of cool skins and warm layers is not equivalent, but this observation does suggest the warm layer effect is of similar importance to the cool skin
20 effect at least in some regions. Much more recently, Kettle et al. (2009) have estimated the impact of warm layers in the central Atlantic and Mediterranean Sea using data from the SEVIRI geostationary satellite. The effect is temporally and spatially variable, but Kettle et al. (2009) conclude that the effect increases the net flux out of the central Atlantic three-fold, though this dramatic result stems from a close balance of influx and outflux in this region. In these publications, the effect on CO_2 flux is calculated
25 by applying a sensitivity of $4.23 \% \text{ }^\circ\text{C}^{-1}$ to either the water side (McNeil and Merlivat, 1996 or the air side (Kettle et al., 2009); neither of these calculations is strictly correct,

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but it can be seen from Eq. (13) that they will be fairly accurate if $C_1 \approx C_M$. Taking a broader view of the prevalence and strength of diurnal warming (e.g. Stuart-Menteth et al., 2003), it is apparent that the importance of warm layers will vary enormously from region-to-region. The effect may often be very large (perhaps sufficient to counteract the cool skin effect) in many low latitude regions. The effect will be relatively unimportant in high-latitude regions, but even in the Arctic, diurnal warming events do occur (Eastwood et al., 2011). The effect on CO₂ fluxes globally will be challenging to quantify accurately, but its importance demands action.

A detailed calculation of warm layer effects requires good input data and a satisfactory model of warm layers. Where concentration is raised by warm layer formation, an outgoing flux is forced, implying a leakage that diminishes the averaged effect (McNeil and Merlivat, 1996). This effect is significant for most gases, but negligible for CO₂ due to the effect of the carbonate system. By a similar argument, it is reasonable to ignore diurnal fluctuations in total CO₂, but it is not satisfactory to ignore the effect of diurnal temperature on the partitioning of the carbonate system. The characteristics of the warm layer and the CO₂ flux depend on detailed meteorological conditions, including cloud coverage and wind speed (Jeffery et al., 2008). The co-dependence of warm layer characteristics and gas transfer velocity on wind speed implies that a simple calculation based for example on the diurnal amplitude of the surface temperature and a daily wind speed could be inaccurate, but some simplification will be needed given the limited observational data. Kettle et al. (2009) concluded that ignoring the daily structure was acceptable and therefore reasonably accurate calculations were accessible. A more detailed calculation may require the use of one-dimensional models (e.g. Jeffery et al., 2008).

7 Haline effects

Almost identical considerations to the analysis in Sects. 2–6 can be applied to haline effects. Effects analogous to those described for temperature (i.e. solubility, vapour

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pressure and fugacity effects at the interface, repartitioning effects within the water column) apply to salinity, but the sensitivity of saturated vapour pressure, the fugacity-pressure relationship, solubility and carbonate speciation each have distinct values for temperature and salinity, all of which follow from the same equations. It is sensible to calculate corrections for salinity at the same time as for temperature since almost identical methods apply and the salinity corrections may also be substantial. Generally the interface is expected to be more saline than below (thus a “salty skin”) due to continual evaporation at the interface. The solubility of aqueous CO₂ reduces with salinity implying that a salty skin reduces interfacial concentration, an opposite effect to a cool skin. The sensitivity of solubility to salinity according to Weiss (1974) is shown in Fig. 6, showing a sensitivity of -0.6 % at low sea temperatures diminishing to -0.5 % at high sea temperatures.

Zhang and Cai (2007) quote Schmidt numbers, Sc (where Schmidt number = molecular diffusivity / kinematic viscosity) of 7.5, 600 and 780 for heat, CO₂ and NaCl respectively in water at 20 °C. To a useful approximation, transfer velocities will scale as $k_w \sim Sc^{-1/2}$ and the equivalent stagnant layer thickness will scale as $L \sim Sc^{-1/2}$. Therefore, in respect of skin effects, the situation for the salty skin is simpler than for the cool skin since the skin layers for gas and salt will be similar in thickness, while the thickness of the thermal boundary layer will be an order of magnitude greater. This implies that there will not be a significant salinity gradient from depth to the base of the MBL and thus no repartitioning effect.

The sea surface will be slightly more saline than deeper water due to continual evaporation. Zhang and Cai (2007) derived a theoretical expression for the salty skin that implies that the salinity difference across the salty skin in practical salinity units is approximately 70 % of the negative thermal skin effect in °C. Applying the sensitivities of solubility to salinity and temperature, Zhang and Cai report that the haline and thermal skin effects on CO₂ flux are of very similar magnitude but opposing (each about 0.05 Pg C yr⁻¹). The calculation depends on the magnitude of the salinity anomaly and that is fairly uncertain since the most recent estimates of this anomaly (Zhang and

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should increase to 1.6 at low latitudes and 1.7 at high latitudes (Sarmiento and Gruber, 2006). $\gamma_S = 1.7$ may also be appropriate for ice melt (Land et al., 2012).

It is clear that calculations of haline effects are worth including but will necessarily be quite uncertain.

8 Conclusions

McGillis and Wanninkhof (2006) have identified a few important mechanisms by which temperature influences the calculated aqueous concentration gradient of CO_2 . We show that careful handling of temperatures is necessary. In particular, we show that neglecting the thermal skin effect and substituting a bulk sea surface temperature in all calculations produces very large errors in air-sea CO_2 fluxes (in contradiction to McGillis and Wanninkhof (2006) but broadly supporting Robertson and Watson (1992) and other earlier studies). The greater part of the effect results from solubility, vapour pressure and fugacity calculations at the interface. The solubility and vapour pressure effects are relevant to other poorly soluble gases. In contradiction to the conclusion of McGillis and Wanninkhof, the difference in characteristic skin thickness between heat and gases can only enhance the importance of skin effects to CO_2 flux calculations. The additional effect arises from repartitioning of the carbonate system during diffusion between the base of the thermal skin and the base of the mass boundary layer (MBL). This effect is ambiguous due to the similar time scales of the diffusion and hydration-dehydration reaction, and is likely to be greatly diminished. Opposing effects at the interface and the base of the MBL are associated with warm layers; in this case, there is no ambiguity in the effect of repartitioning, which will have a strong effect. The repartitioning effect has been recognised by Hare et al. (2004), but is clarified here.

A cool and salty skin is usual on the sea surface. The salty skin will coincide with the mass boundary layer (MBL) controlling gas transfer, but the thermal skin is an order of magnitude thicker. The largest error is associated with substituting Bulk SST (T_B) for the interfacial temperature (T_I). That effect is primarily related to the solubility

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calculation but an additional effect related to saturated vapour pressure should not be neglected. That substitution results in underestimates of the interfacial concentration and downward flux. Corrections add a contribution to downward flux. If a bulk salinity is substituted for interfacial salinity, an opposing but smaller error is incurred.

5 The distinction between Bulk SST and the temperature at the base of the mass molecular boundary layer (T_M) is more ambiguous in effect. If the carbonate system repartitions CO_2 as a result of temperature changes from the base of the thermal skin to the base of the mass molecular boundary layer, then a significant additional error is incurred by substituting T_B for T_M . By the substitution, the concentration and upward flux
10 are over estimated; a correction subtracts from the upward flux. This effect potentially increases the total thermal skin effect on CO_2 fluxes by up to 50 %, but it is unlikely the effect is that large since repartitioning will be incomplete at most.

A radiometric sea surface temperature T_{Rad} (calibrated to the skin temperature) is not identical to either T_I or T_M , but is a pragmatic and widely available substitute for
15 either or both that will greatly reduce the errors incurred by using T_B indiscriminately.

Similar but opposing effects are related to warm layer phenomena. Where a deep or nighttime temperature is applied when a warm layer is in place, the interfacial concentration will be overestimated and the concentration at the base of the MBL will be underestimated leading to an anomalous downward flux. Correcting for warm layers
20 adds an upward flux.

The inclusion of repartitioning effects is certainly important when handling in situ fugacity measurements, both to correct for warming prior to measurement and to correct for sampling anomalies in temperature and salinity. Some ambiguities are inevitable since the effect on aqueous concentration depends on the circumstances underlying
25 the change in salinity or temperature. An assumption of “constant chemistry”, that is an isochemical change in aqueous concentration resulting from repartitioning of the carbonate system, may be necessary, but is rather unsatisfactory. Notably, the correction will be very inaccurate where salinity is reduced by rainfall or ice melt. Transformations between different seasons should be avoided since seasonal changes are unlikely to

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be isochemical in nature. However, for correcting oceanic CO₂ measurements to a reference year in order to construct a climatology, applying a secular trend in atmospheric and oceanic partial pressures after an isochemical transformation to the climatological temperature and salinity of the measurement month and location appears to be the most secure approach.

It is necessary to consider both thermal and haline effects in any thorough analysis of air-sea gas fluxes.

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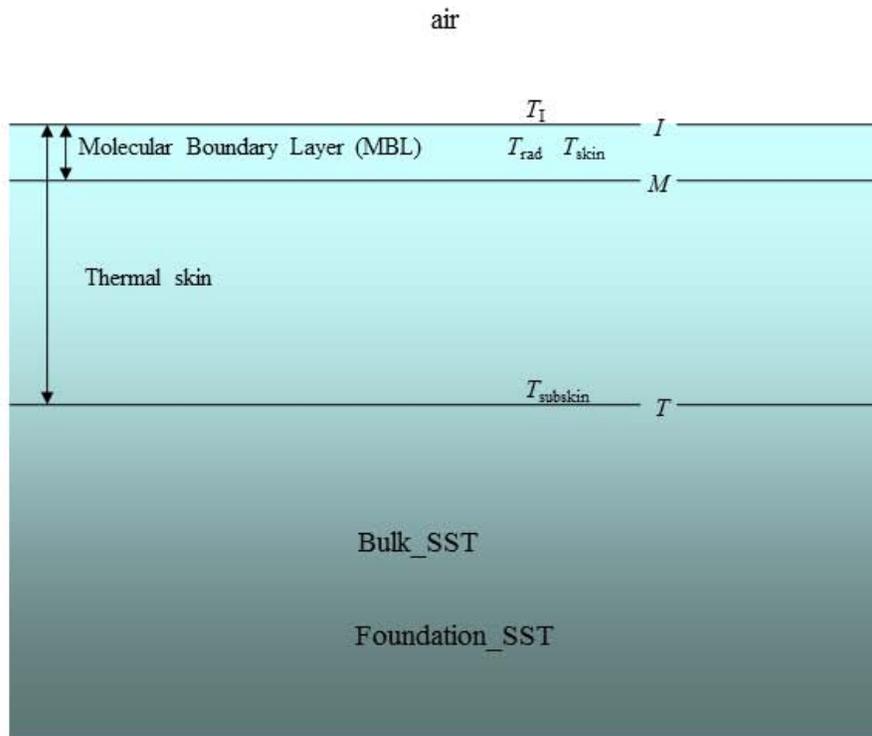


Fig. 1. A schematic of the surface ocean, depicting the definition of the molecular boundary layer (MBL), thermal skin and various temperatures and depths.

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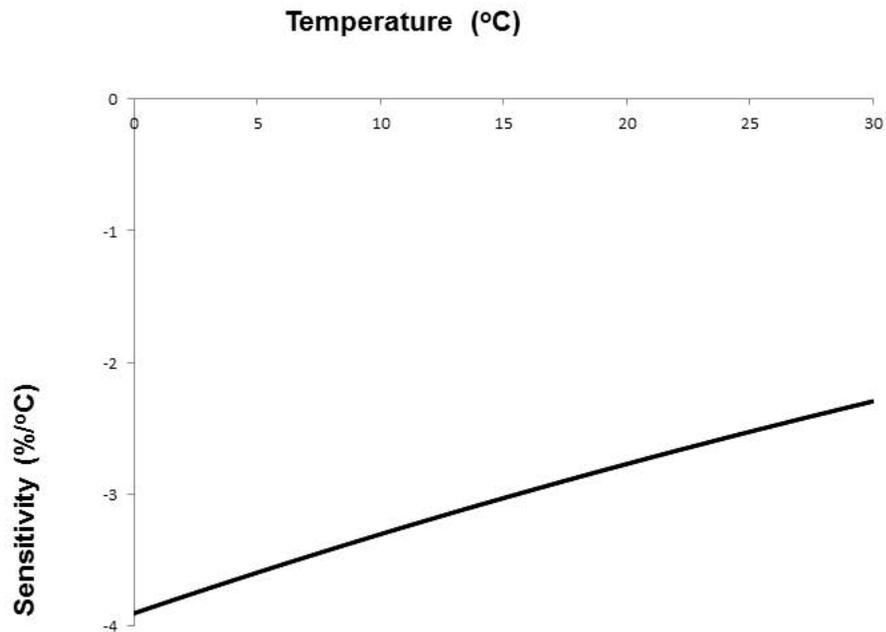


Fig. 2. Sensitivity of the solubility of carbon dioxide to temperature at $S = 35$ as a function of temperature. Sensitivity is defined as $100 \times \partial \ln K_0 / \partial T$ and calculated according to the relationship of Weiss (1974).

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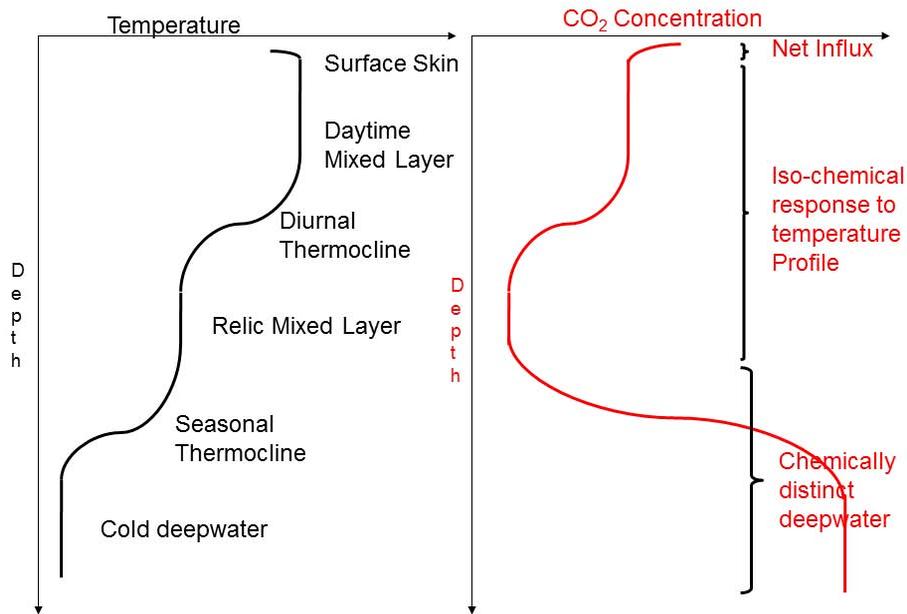


Fig. 3. Schematics of the vertical profiles of temperature and CO₂ concentration. Temperature profile in black, CO₂ in red.

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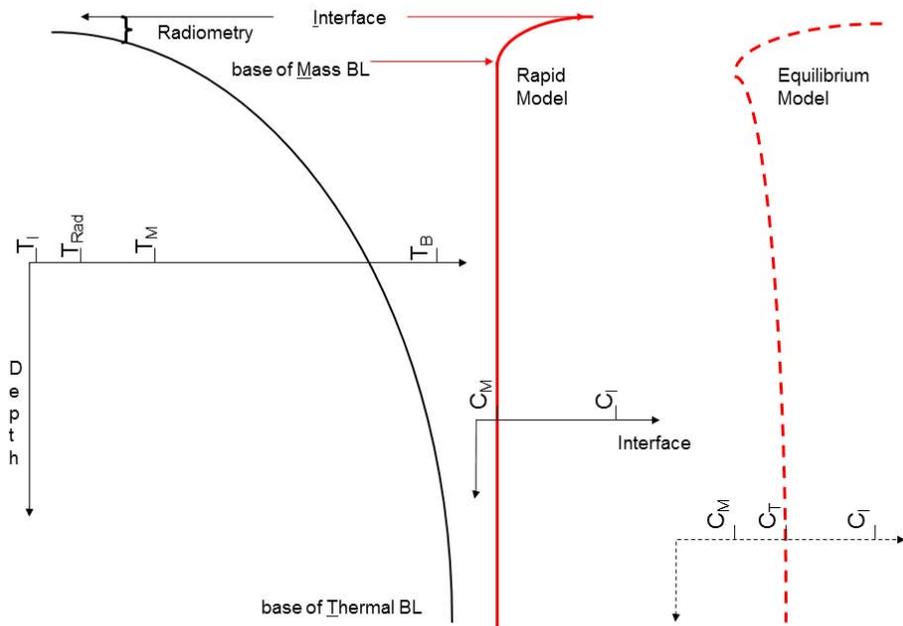


Fig. 4. Schematics of vertical profiles within the surface microlayer. Temperature profile in black, CO₂ in red. Two CO₂ profiles are shown on offset concentration scales, each appropriate to one of two limiting cases described in the text. The full red curve describes the profile for a “rapid model” while the dashed red curve describes the profile for an “equilibrium model”.

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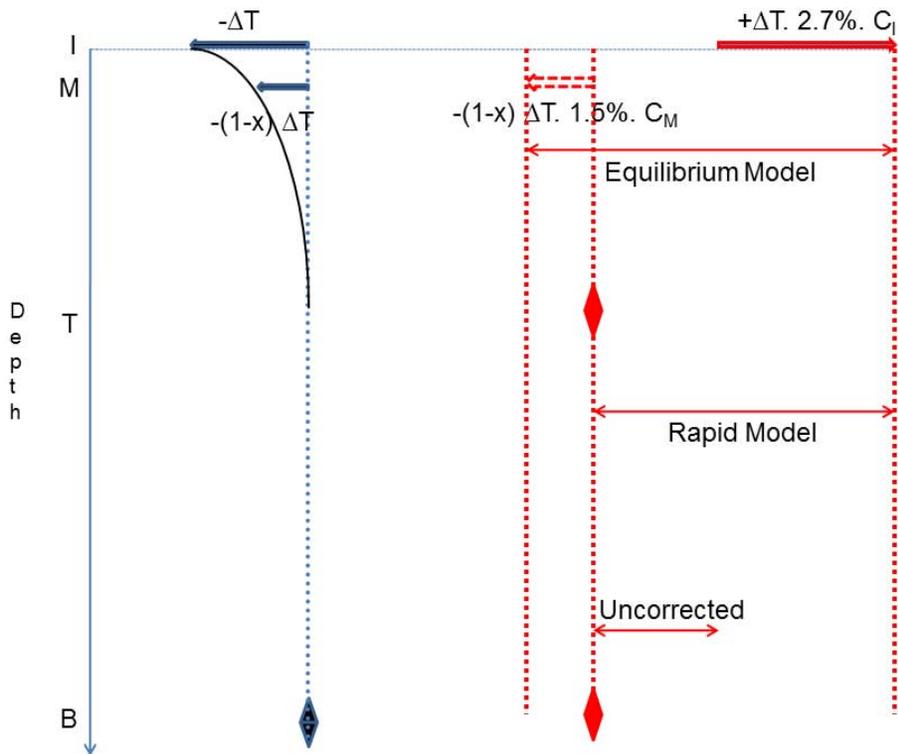


Fig. 5. A schematic explaining corrections to temperature for the cool skin effect. An “uncorrected” concentration difference is calculated using a bulk SST and then corrected using the appropriate temperatures. The main correction is at the interface. In the rapid model this is the only correction, but in the equilibrium model an additional correction is applied at the base of the molecular mass boundary layer. Both corrections increase the net downward flux (as shown), or will decrease, or reverse a net upward flux.

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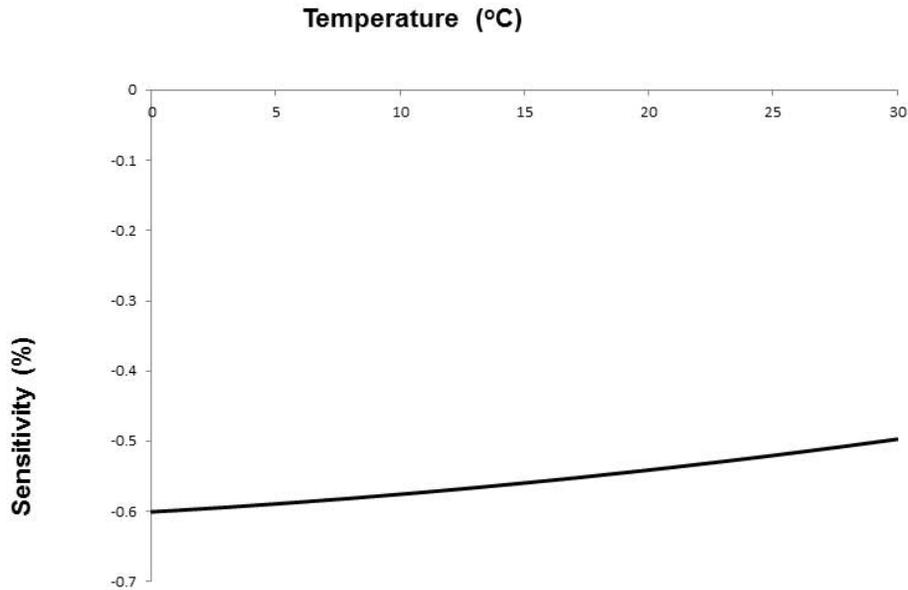


Fig. 6. Sensitivity of the solubility of carbon dioxide to salinity as a function of temperature. Sensitivity is defined as $100 \times \partial \ln K_0 / \partial S$ and calculated according to the relationship of Weiss (1974).

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