

The warm oceanic surface layer: Implications for CO₂ fluxes and surface gas measurements

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Abstract. The ocean and air-sea interface are important for the exchange of heat, momentum, water vapour and carbon-dioxide. The details of the exchange mechanisms, which are often coupled and complex, have to be understood in order to assess the future role of the global oceans in climate change. Recently, much attention has focused on the 'thermal skin effect', cooling or warming of the uppermost millimeters of the sea surface, and its global implications for enhancing CO₂ uptake [Robertson and Watson, 1992; Van Scoy et al., 1995]. Routinely, air-sea flux estimates derived from oceanic pCO₂ measurements are corrected for the usually cooler thermal skin by applying a correction factor [Sarmiento and Sundquist, 1992; Wong et al., 1995]. Here we describe how near surface warming of the upper few meters of the ocean by solar radiation, routinely observed but not fully appreciated in this context, can significantly affect the net daily exchange of CO₂ over and above the skin effect, and can even lead to a reversal of the direction of the air-sea flux calculated from pCO₂ measurements and wind speed alone. The warming and cooling cycle produces a net asymmetry between CO₂ invasion and evasion, having the effect of decreasing CO₂ invasion and increasing CO₂ evasion.

Introduction

The uppermost 2 m of the ocean surface typically absorbs ~50 % of the total solar radiation heat reaching the Earth's surface; about 5 % is deposited into the uppermost millimeters as infrared radiation is quickly absorbed. This diurnal solar heat input, which is non-uniformly distributed in both depth and time of day, combined with heating and cooling due to latent, sensible and net radiative surface heat fluxes, can develop two significant thermal gradients within the upper ocean. First, a 'thermal skin' of typically a few millimeters thick can develop at the sea surface. Secondly, during the day time, when net solar heating is sufficiently large to counteract the mixing effect of the wind, a warm oceanic surface layer of typically a few meters deep can develop [Bond and McPhaden, 1995; Fairall et al., 1996; McNeil and Farmer, 1995; Price et al., 1986]. The sea surface temperature (T_s), which determines CO₂ solubility and hence CO₂ flux to the atmosphere, can then be defined [Fairall et al., 1996] in terms of the bulk water column temperature below the warm surface layer (T_m) and temperature corrections associated with the warm layer (ΔT_w) and the usually cooler thermal skin (ΔT_c) by

$$T_s = T_m + \Delta T_w - \Delta T_c. \quad (1)$$

Typically, thermal skin corrections for the global oceans give [Schluessel et al., 1990; Van Scoy et al., 1995] $\Delta T_c = 0.3 \pm 0.4$ °C, but depend on the wind speed and net radiative heat loss. The global annual mean thermal skin temperature correction calculated [Van Scoy et al., 1995] using a Rayleigh wind speed distribution is $\Delta T_c = 0.28$ °C. Unlike the thermal skin, the warm layer cannot be colder than the underlying water due to gravitational stability constraints; we exclude here salinity variations affecting density. Typically, ΔT_w can vary from 0→2 °C. In some regions of the ocean, ΔT_w could be expected to offset ΔT_c such that $T_s = T_m$; however, their diurnal temperature cycling are both in phase: as the warm layer warms, the thermal skin will also warm (as it is usually colder, in fact this means the thermal skin will become less cold) and, hence, the thermal skin correction will become less significant. We note here that attempts to quantify the effect of geographical and temporal variability in ΔT_c on global air-sea CO₂ transfer [Robertson and Watson, 1992; Van Scoy et al., 1995] used thermal skin temperature corrections derived from monthly average meteorological variables; all diurnal variability in ΔT_c , which necessarily exists [Fairall et al., 1996; Schluessel et al., 1990], was not accounted for. In this paper we shall only investigate the influence of the warm surface layer on sea-surface temperature (Equation 1) and its subsequent effect on air-sea CO₂ exchange. The more general problem, which we cannot discuss here as we do not have the necessary measurements, includes both the diurnal variability in ΔT_w and ΔT_c .

We may write the flux of CO₂ gas (Q) at the air-sea interface as

$$Q = K_T \alpha (p_a - p_w) \quad (2)$$

where $K_T = K_T \{U_{10}, Sc\}$ is the gas transfer 'velocity' typically parameterised [Liss and Merlivat, 1986; Wanninkhof, 1992] in terms of wind speed at 10 m height (U_{10}) and Schmidt number (Sc), defined as the ratio of kinematic viscosity of water to molecular diffusivity of CO₂; $\alpha = \alpha(T_s, S)$ is the solubility of CO₂ in sea water of salinity S [Weiss, 1970]; and p_a and p_w are the partial pressures of CO₂ in the air and in the water.

A thermally trapped warm surface layer of typically a few meters deep will not equilibrate sufficiently with the atmosphere to affect the dissolved CO₂ concentration because dissolved CO₂ is strongly buffered by dissolved inorganic carbon species. Hence the total CO₂ concentration and total alkalinity in this trapped layer can be considered to remain constant. Experimentally, the change in CO₂ partial pressure as a function of temperature at constant total alkalinity, total CO₂ concentration and salinity is found to be 4.23 % °C⁻¹

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