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Marine Chemistry 98 (2006) 100–108

MARINE CHEMISTRY

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Aqueous CO_2 gradients for air–sea flux estimates

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Received 27 August 2005; received in revised form 30 August 2005; accepted 1 September 2005
Available online 2 November 2005

Abstract

The concentration of gaseous carbon dioxide (CO_2) in surface seawater is a fundamental control on the CO_2 flux between the ocean and atmosphere. However, the concentration gradient in the aqueous mass boundary layer determines the magnitude and direction of the flux. The gradients of CO_2 in the aqueous mass boundary layer cannot be measured directly and are usually inferred from partial pressures or fugacities of CO_2 (f_{CO_2}) in the air and water. In addition to the f_{CO_2}, the temperatures at the top and bottom of the aqueous mass boundary layer must be known to determine the thermodynamic driving force of CO_2 gas transfer. Expressing the gradient in terms of the aqueous CO_2 concentration, $[CO_{2aq}]$, also avoids some conceptual ambiguities. In particular, expressing the CO_2 as a fugacity, which is defined relative to the gas phase, when the gas exchange rate is controlled in the aqueous mass boundary layer often leads to errors in interpretation with respect to changes in boundary layer temperature. As a result the enhanced CO_2 flux caused by the cool skin effect appears to be overestimated. Apart from the difficulties estimating the temperature at the top and bottom of the aqueous mass boundary layer, the temperature dependence of solubility and fugacity of CO_2 is uncertain to the degree that it can bias air–sea CO_2 flux estimates. The CO_{2aq} at the surface, $[CO_{2aq0}]$, is at equilibrium with the atmospheric CO_2 level. As $[CO_{2aq0}]$ is strongly temperature dependent, it will be significantly higher at high latitude compared to low latitude, while atmospheric CO_2 levels show much less of a gradient.

Keywords: Chemical oceanography; Carbon system; Partial pressure; Fugacity; Aqueous concentration; Air–water gas transfer

1. Introduction

Quantification of atmospheric CO_2 controls is a high scientific priority because of the ecological and economic consequences of rising atmospheric CO_2 levels. Several national and international science goals outline the need to constrain the oceanic sources and sinks (e.g. Sarmiento and Wofsy, 1999; Bender et al., 2002). Currently about 1.5 ± 0.4 10^{14} mol CO_2 (≈ 1.7 10^9 metric ton C) is absorbed by the ocean every year making it the largest sustained sink of excess atmospheric CO_2 resulting from fossil fuel burning (Houghton et al., 2001). The magnitude and direction of the gas flux between the ocean and atmosphere varies interannually, by season, and by region. For adequate projections of future CO_2 levels, improved knowledge of the air–sea flux is critical. Atmospheric CO_2 levels need on average to be about 2% (approximately 6 μatm) greater than the oceanic partial

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doi:10.1016/j.marchem.2005.09.003

pressure of CO_2 to cause an annual uptake of 1.5 10^{14} moles such that this estimate is susceptible to small biases in the concentration gradient.

The goal of several international programs is to decrease the uncertainty in regional air–sea CO_2 fluxes (Doney et al., 2004). The main focus of these efforts is to quantify surface water CO_2 levels to estimate seasonal timescales for global air–sea fluxes. As part of this effort, improved knowledge of the processes controlling the air–sea CO_2 gas transfer must be made. The issues surrounding the conventional way of expressing the air–sea CO_2 fluxes with a bulk parameterization and the concentration gradient in terms of a partial pressure or fugacity are addressed. Since processes in the aqueous mass boundary layer control the gas transfer of CO_2 the concentration gradient is subsequently better expressed in terms of the aqueous concentration, CO_{2aq}. While the two quantities are simply related through a solubility coefficient, the solubility coefficient at the top and bottom temperatures of the aqueous mass boundary layer should be used to obtain the correct flux. This is seldom done.

The flux parameterization is described in terms of CO_{2aq} and compared with the conventional expression. The focus of this note is on microscale environments with changing physical surface conditions. The analysis suggests that the cool skin effect should have about 80% less of an influence on air–sea CO_2 fluxes than previous studies suggest as the mass boundary layer is significantly thinner than the thermal boundary layer. The annual surface water CO_2 climatology of Takahashi et al. (2002) is presented in terms of CO_{2aq} to illustrate the difference between the f_{CO_2} and CO_{2aq} on a global scale. Expressing the thermodynamic driving force of air–sea CO_2 fluxes in terms of $[CO_{2aq}]$ rather than f_{CO_2} or p_{CO_2} decreases the ambiguity in flux calculations.

2. Discussion

2.1. Theoretical framework

The flux of gaseous constituents across an air–water interface is defined in terms of a bulk parameterization as:

$$F = k\Delta C \tag{1}$$

where k is the gas transfer velocity and ΔC is the concentration difference between the air and surface water over the relevant boundary layer. For insoluble gases, or slightly soluble gases such as CO_2, transfer across the aqueous boundary is the rate-limiting step for air–sea gas transfer (Liss, 1983). The flux across the aqueous mass boundary layer for CO_2 is expressed as:

$$F = k\left(\left[CO_{2aqw}\right] - \left[CO_{2aq0}\right]\right) \tag{2}$$

where $[CO_{2aqw}]$ and $[CO_{2aq0}]$ are the aqueous CO_2 concentrations at the bottom and the top of the aqueous mass boundary layer, respectively. CO_{2aq} is the sum of dissolved CO_2 and H_2CO_3, the undissociated hydrated form of CO_2 (Stumm and Morgan, 1981). In seawater $\approx$99.9% of CO_{2aq} is in the dissolved form (Soli and Byrne, 2002). The $[CO_{2aq0}]$ is controlled by the concentration of CO_2 in the atmosphere and temperature at the top of the boundary layer, and to a lesser extent salinity. The $[CO_{2aqw}]$ is a function of the temperature, salinity, alkalinity (T_{Alk}) and total inorganic carbon (T_{CO_2}) content of the seawater.

The flux of CO_2 between the ocean and atmosphere is commonly presented in terms of the fugacity, or partial pressure, difference between surface water and air rather than as concentration difference across the interface:

$$F = kK_0(f_{CO_{2w}} - f_{CO_{2a}}) = kK_0\Delta f_{CO_2} \tag{3}$$

where K_0 is the solubility, and $f_{CO_{2a}}$ and $f_{CO_{2w}}$ are the fugacity of CO_2 in air and surface seawater, respectively. The fugacity is the partial pressure corrected for non-ideality of the gas with respect to molecular interactions between CO_2 and air. The values for fugacity of CO_2 and corresponding p_{CO_2} are very close in magnitude with f_{CO_2}=(0.9956 p_{CO_2}) at 0 °C, and f_{CO_2}= (0.9970 p_{CO_2}) at 30 °C (Weiss, 1974) (see Appendix A for the expression of the fugacity correction). The product of K_0 and Δf_{CO_2} is often referred to as the thermodynamic driving force of the flux.

Combining Eqs. (2) and (3) yields: $f_{CO_{2w}}=K_0^{-1}$ CO_{2aqw} and $f_{CO_{2a}}=K_0^{-1}$ CO_{2aq0}. It is in this conversion where the problem lies in the calculated air–sea flux. These conversions are only valid if K_0 does not vary over the aqueous mass boundary layer. This is seldom the case. In particular, since K_0 is a function of temperature, this approximation can lead to biases in the estimation of air–sea CO_2 fluxes with a temperature gradient across the aqueous mass boundary layer.

The correct expression of the flux in terms of f_{CO_2} is:

$$F = k(K_{0w}f_{CO_{2w}} - K_{0s}f_{CO_{2a}}) \tag{4}$$

where K_{0w} is the solubility at the base of the aqueous mass boundary layer and K_{0s} is the solubility at