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Abstract

Air-sea gas exchange is an important process in the geochemical cycling of carbon dioxide (CO_2). The air-sea flux of CO_2 is determined in part by the physical forcing functions, which are parameterized in terms of the air-sea transfer velocity, k_L. Past studies have attempted to correlate k_L with wind speed, U (e.g., Liss and Merlivat, 1986; Wanninkhof, 1992). Because strong winds occur in ocean regions thought to be important sources or sinks of CO_2, accurate knowledge of K_L at high U is important in estimating the global air-sea flux of CO_2. Better understanding of the physical processes affecting gas transfer at large U will increase the accuracy in estimating k_L in ocean regions with high CO_2 fluxes. Increased accuracy in estimating k_L will increase the accuracy in calculating the net global air-sea CO_2 flux and provide more accurate boundary and initial conditions for global ocean carbon cycle models.

High wind speeds are associated with the presence of whitecaps, which can increase the gas flux by generating turbulence, disrupting surface films, and creating bubble plumes. Bubble plumes will create additional turbulence, prolong the surface disruption, and transfer gas to or from individual bubbles while they are beneath the surface. These turbulence and bubble processes very effectively promote gas transfer. Because of this, Monahan and Spillane (1984) postulated that breaking waves, if present, will dominate non-whitecap related gas exchange. Under this assumption, k_L will increase linearly with increasing fractional area whitecap coverage, W_C. In support of this, Asher et al. (1992) found k_L measured in a whitecap simulation tank (WST) was linearly correlated with bubble plume coverage, B_C (the laboratory analog of W_C). Further evidence supporting the large effect of breaking waves on air-sea gas fluxes is given by the results of Wallace and Wyrick (1992) and Farmer et al. (1993). However, it is not definitively known how the presence of breaking waves and bubble plumes affect the dependence of k_L on Schmidt number, Sc, and aqueous-phase solubility, α. Knowledge of this dependence is necessary to determine the best method for parameterizing k_L in the presence of breaking waves.

The effects of whitecaps on air-water gas exchange could be studied in detail if k_L could be measured for reproducible breaking waves for different gases. In the research described here, k_L values for invasion and evasion of CO_2, oxygen (O_2), helium (He), sulfur hexafluoride (SF_6), and dimethyl sulfide (DMS) through clean and surfactant-influenced (SI) water surfaces were measured in a tipping-bucket WST. Reproducible, simulated breaking waves were generated in the WST by releasing a known volume of water vertically onto the tank water surface from a tipping bucket. The bubble populations in the WST are similar to bubble populations measured in the ocean (Asher and Farley, 1995) and the WST can generate B_C values of up to 0.77%. The WST and the characteristics of the bubble plumes generated in it are described in detail in Asher and Farley (1995).

All measurements were made in seawater that was filtered and sterilized using a flow-through ultraviolet sterilizer. This procedure removed particles, helped prevent biologically produced bubbles, and reduced water surface contamination. Prior to the start of each experiment, accumulated surface contaminants were removed by vacuuming the water surface. For comparison, SI water surfaces were generated by adding 1 ppmv of the soluble surfactant Triton X-100 to the WST. Salinity in the WST was measured by refractometry to be 30 *psu*.

The measurements of k_L for evasion through a cleaned water surface, $k_{L,E}(C)$, show that $k_{L,E}(C)$ is linearly related to B_C. Furthermore, the data show $k_{L,E}(C)$ is very sensitive to small changes in B_C even for the relatively soluble gases CO_2 and DMS. For these two gases, an increase in B_C from 0% to 0.77% increases $k_{L,E}(C)$ by a factor of seven for CO_2 and three for DMS. Similarly, k_L for invasion through a cleaned water surface, $k_{L,I}(C)$, was found to be linearly related with B_C. Invasive transfer velocities also were very sensitive to small changes in B_C with $k_{L,I}(C)$ for CO_2 showing an increase with increasing B_C similar to that observed for $k_{L,E}(C)$.

Bubble-mediated gas transfer models indicate that the gas flux due to bubbles decreases as α increases (Memery and Merlivat 1985; Woolf and Thorpe, 1992), suggesting that bubble plumes generated by breaking waves will be of little importance in the air-sea exchange of CO_2. However, the WST measurements show that the simulated breaking waves are very effective at increasing both $k_{L,E}(C)$ and $k_{L,I}(C)$ for CO_2. The sensitivity of $k_{L,I}(C)$ and $k_{L,E}(C)$ for soluble gases to small changes in B_C demonstrates that bubble transfer processes are not the only mechanisms by which breaking waves increase the gas flux. The turbulence generated by the plunging water and rising bubbles must make a significant contribution to the overall k_L measured in the WST. In agreement with Kitaigorodskii (1984), extending this conclusion to oceanic conditions suggests that the turbulence generated by oceanic breaking waves could be an important air-sea transfer pathway even for a relatively soluble gas such as CO_2.

Models of bubble-mediated gas transfer suggest that if the bubble gas flux is a significant fraction of the net gas flux, $k_{L,I}(C)$ measured at a particular B_C will be larger than $k_{L,E}(C)$ measured for the same gas at the same B_C (Memery and Merlivat, 1985; Woolf and Thorpe, 1992). Furthermore, this invasion-evasion asymmetry will be a function of α with the asymmetry increasing as α decreases. The WST data support this hypothesis, the ratio of $k_{L,I}(C)$ to $k_{L,E}(C)$, R_{IE}, calculated for transfer of SF_6, O_2, and CO_2 decreased as α increased when bubbles were present in the WST. In the absence of bubbles, R_{IE} was equal to unity, and no significant invasion-evasion asymmetry was observed.

Transfer velocities measured for invasion and evasion through SI water surfaces, $k_{L,E}(SI)$ and $k_{L,I}(SI)$, respectively, were also found to be linearly correlated with B_C. The presence of the surfactant caused a significant reduction in both $k_{L,E}(SI)$ and $k_{L,I}(SI)$ compared to $k_{L,E}(C)$ or $k_{L,I}(C)$, respectively, for the range of B_C studied here, the maximum reduction in k_L occurred at B_C=0%. Although the effect of the surfactant is largest when the water surface is not disrupted by breaking waves, the data show that soluble surface active compounds can decrease k_L even in the presence of breaking waves. R_{IE} calculated using $k_{L,I}(SI)$ and $k_{L,E}(SI)$ for SF_6 and O_2 shows that invasion-evasion asymmetry seen in the cleaned-surface case is also found in the SI data. Because this asymmetry is caused by bubble-mediated transfer processes, the similarity in the behavior of R_{IE} for transfer at cleaned and SI surfaces suggests that the presence of a soluble surfactant does not drastically decrease the importance of the bubble-mediated gas flux.

Using the results from the gas transfer measurements, an empirical parameterization has been developed that can be used to estimate k_L in the WST from B_C, Sc, and α. Based on the modelling studies of Memery and Merlivat (1985) and Keeling (1993), k_L is partitioned into a component due to mechanically generated turbulence, k_M, a component due to bubble plume turbulence, k_T, and a component due to bubble-mediated transfer, k_B. For conditions where the gas is far from equilibrium, this expression has the form

$$k_L = (A_M + B_C(A_T - A_M))\,Sc^{-n} + B_C\left(\frac{a_1}{\alpha} + b_1\,\alpha^{-m_1}\,Sc^{-n_1'}\right) \qquad (1)$$

where A_M and A_T are constants determined by the mechanically generated and whitecap-generated turbulence, respectively, and n=1/2 for transfer through a cleaned surface or n=2/3 for transfer through an SI surface. The constants a_1 and b_1 are functions of water surface cleanliness and flux direction (i.e., gas invasion or evasion) and the exponents m_1 and n_1' are functions of water surface cleanliness. The set of coefficients A_M, A_T, n, a_1, b_1, m_1, and n_1' were determined by nonlinear optimization of Equation 1 to the data for $k_{L,E}(C)$, $k_{L,I}(C)$, or $k_{L,E}(SI)$.

Comparison of $k_{L,E}(C)$ estimated using Equation 1 and B_C, Sc, and α with $k_{L,E}(C)$ measured in the WST showed the overall accuracy of Equation 1 was ±10% for B_C in the range 0% to 0.77% for the gases studied. Equation 1 was able to predict $k_{L,I}(C)$ with an overall accuracy of ±5% for the same range of B_C. Finally, $k_{L,E}(SI)$ could be estimated with an accuracy of ±10% using Equation 1. The accuracy of the model-predicted k_L values is within the experimental uncertainty of the direct measurements of k_L in the WST for all three cases. This shows that Equation 1 does an excellent job of describing the functional dependence of $k_{L,E}(C)$, $k_{L,I}(C)$, and $k_{L,E}(SI)$ on B_C, Sc, and α for the conditions present in the WST.

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