J10.3 TEMPERATURE SENSITIVITY OF A MICROMETEOROLOGICALLY-BASED AIR-SEA GAS TRANSFER PARAMETERIZATION

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1. INTRODUCTION

The air-sea exchange of climate relevant compounds, and, in particular carbon dioxide, has come under increased scrutiny due to the continued uncertainty surrounding the mass sequestration of these gases into the world's oceans and due to the potential consequence of atmospheric increases of these compounds on the Earth's climate. Although measurement techniques are improving, comprehensive open-ocean estimation of the air-sea flux of CO_2 presents significant difficulties from a ship. Mesoscale and larger-scale models could supply reasonable regional-to-global scale estimations of the total gas transfer, provided that an accurate small-scale parameterization of the interfacial gas flux is incorporated into the model. The perfect parameterization would accurately portray all of the physical mechanisms of gas transfer, including surface processes (influence of waves, microscale and larger-scale wave breaking, interfacial thermal structure, etc), sub-surface processes (bubbles and mixing), and micro-meteorological influences (atmospheric surface-layer turbulent structure, wind gustiness, etc). Much of the physics of gas exchange and the relative importance of each physical process remain unknown, but it is imperative that progress in the development of accurate gas transfer parameterizations and in the continued improvement of measurement technology must work in parallel.

2. THE FAIRALL PARAMETERIZATION

Ideally, the air-sea gas transfer parameterization will require reasonably-available variables as inputs. That is, the algorithm should only require input variables which can be readily measured over relevant scales from *in situ* or remote sensors. In addition, the model should compute the gas transfer velocity within the context of the relevant environmental variables and processes (radiative and turbulent fluxes, wind speed, wave state, surface current, air-sea temperature difference, near-surface water thermal structure, etc). Fairall et al. (2000) have presented in the literature one such micrometeorologically-based air-sea gas transfer parameterization, and this scheme is based on the well-known COARE Bulk Flux Algorithm (Fairall et al., 1996a). Work is on-going to make improvements to the Fairall parameterization, and the most recent undertaking is to focus on the sea surface temperature influence to the modeled gas transfer. A number of possible sea "surface" temperatures inputs exist: subsurface (3-5 meters) water intake temperature (for example, into a thermosalinigraph), the warm-layer temperature (from a floating thermistor or modeled from the 5-meter temperature), or a radiometrically-measured skin temperature (e.g., the cool skin). The molecular conditions near the interface, including the interfacial skin temperature, control the mass flux. Thus, any other measured temperature input to the algorithm requires a model of the thermal structure up to the skin surface (Fairall et al., 1996b).

The Fairall air-sea bulk gas transfer parameterization makes use of turbulence scaling theory applied to both fluids, and matches the fluid models at the interface where the suppression of the smallest turbulent eddies is accomplished via viscous dissipation. Other effects, such as bubble mediation and wave breaking, have only been addressed in a cursory fashion due to the complex nature of these physical forcings.

3. GAS FLUX

A common bulk expression of the air-sea flux of carbon dioxide (or any gas), **F**, is

$$\mathbf{F} = \mathbf{k}\alpha(\mathbf{fCO}_{2w} - \mathbf{fCO}_{2a}), \quad \mathbf{(1)}$$

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where $\mathbf{k}$ is the gas transfer velocity, $\boldsymbol{\alpha}$ is the gas solubility, and $\mathbf{fCO_2}$ is the fugacity of carbon dioxide in the bulk water and air, respectively. The solubility is a function of both temperature and salinity and can be empirically described such as in Wanninkhof (1992), Table A2. The solubility for CO_2 varies by a few percent per degree around 20 C (Weiss, 1974). The gas transfer velocity can be conceptualized as analogous to the traditional transfer coefficients in bulk turbulent flux parameterizations. This quantity has recently been expressed as a quadratic and cubic function of wind speed (**U**) in Wanninkhof (1992) and Wanninkhof and McGillis (1999), respectively, and it also has a Schmidt number ($\mathbf{S_c}$) dependence

$$\mathbf{k = k(Sc^{n}, U^{m})} \qquad \textbf{(2)}$$

where '**n**' changes from -0.67 for a smooth surface to -0.4 for a surface characterized with bubbles, and '**m**' has been empirically determined to be 2 or 3.

In most ship-based measurement situations, the water-side mixing ratio is measured by drawing continuous bulk (subscript '**w**') water samples into a headspace equilibrator (Wanninkhof and Thoning, 1993). Typically, this sample comes from a water intake in the forward hull of the ship at a depth of 3-5 meters. The air–side sample (from a height of approximately 10 meters) and headspace mixing ratios are then measured through a non-dispersive infrared (NDIR) detector, and the measurement is converted to fugacity. Given direct measurement of the gas flux (McGillis et al, 2000, McGillis et al, 2000) coincident with air and sea gas mixing ratio measurements, one can use Equation **(1)** to determine the gas transfer velocity, and this quantity has been used to develop simplified wind-speed dependent gas exchange models (Wanninkhof and McGillis, 1999).

Upon closer inspection, the flux is more accurately expressed in terms of the bulk and interfacial solubilities as in

$$\mathbf{F = k_s(\alpha_w fCO_{2w} - \alpha_s fCO_{2a})}, \qquad \textbf{(3)}$$

where the subscript '**s**' indicates the transfer velocity and solubility are computed at the skin temperature and salinity. Equation **(3)** assumes that mass is conserved (i.e. there are no chemical reactions), which is a simplification, as shown below. Most measurements of the bulk water fugacity are made below the warm-layer. In fact, this expression ignores the warm-layer effect in the ocean (Fairall et al, 1996), and we desire that the water-side fugacity and solubility be computed at the surface, as the interfacial characteristics so strongly affect the gas flux. For example, cool skin temperature depression could range from 0.1 to 0.4 degrees (Fairall et al, 1996), and warm layer elevation under light winds could be as large as 2-3 degrees in the tropics. This thermal structure from the bulk water up to the surface will certainly alter the flux. For the sake of physical accuracy in the parameterization, we will express the flux in terms of the interfacial characteristics.

There are other thermal influences on the flux of the gas, including the effect of the warm layer (and/or cool skin) on the fugacity of CO_2 dissolved in seawater (Takahasi et al, 1993) via the carbonate reaction. This requires a deviation from the mass conservation assumption, so that the surface fugacity is expressed in terms of the bulk fugacity through an empirical relationship

$$\mathbf{fCO_{2s} = fCO_{2w}(1 + 0.0423\Delta T)}, \qquad \textbf{(4)}$$

where $\mathbf{\Delta T = T_w - T_s}$. This percentage change with temperature was determined at a reference temperature of 20C, and it also includes the effect of solubility, whose temperature dependence is empirically formulated from Weiss (1974) or Wanninkhof (1992). A quick computation of the solubility at 20C reveals that the effect of temperature on the solubility accounts for approximately 2.7% of the thermal variability. Therefore, we have chosen to maintain the structure of our expression of the flux as in **(3)** with the addition of the small temperature correction to the mass due to the carbonate reaction as follows:

$$\mathbf{F = k_s \alpha_s \left[fCO_{2w} \frac{\alpha_w}{\alpha_s}(1 + 0.015\Delta T) - fCO_{2a} \right]}. \qquad \textbf{(5)}$$

This expression is more accurate and provides a statement of the flux in terms of the measured fugacities and bulk water temperature, along with the estimate of skin temperature. The COARE algorithm models the skin temperature from measurements within or below the warm-layer from which the surface solubility can be computed. Alternatively, the algorithm allows for input of direct measurement of the radiometric (skin) temperature, if it is available. In addition, the algorithm models the depth of the warm layer, which can be used to determine whether the fugacity measurement has been made within or below the layer. An additional thermal correction is necessary to the measurements in the conversion from mole fraction to fugacity (Ward et al., 2002), but we will not include those details here.

The current version of the Fairall parameterization also provides an estimate of the surface gas transfer velocity expressed as the sum of the influential physical resistances, which include the molecular and turbulent components on both sides of the interface. Additional transfer velocity terms arise under higher wind regimes as a result of bubble mediation and wave breaking, and these components are parameterized after Woolf (1997), although other treatments are being contemplated. No considerations are given to the effect of biological processes or to surfactants (Frew, 1997), although these environmental forcings are recognized to be potentially significant.

4. APPLICATION OF THE PARAMETERIZATION

The Fairall gas transfer parameterization was applied to data collected during the GasEx-1998 and GasEx-2001 experiments, both of which were conducted from the NOAA Ship *Ronald H. Brown*. These two cruises are landmarks for high quality direct measurement of carbon dioxide fluxes from over the open ocean (McGillis et al, 2001), and were also designed to provide a platform for gas transfer process studies. Data collected from the cruises and input into the model included: wind speed (corrected for ship maneuvers), air temperature, air specific humidity, sea surface temperature, downwelling solar flux, downwelling IR flux, height of the measurements, and latitude. Additional data, such as wave information, rainrate, atmospheric boundary layer depth, etc, were included where available. Measurements of the atmospheric and sea CO_2 fugacities were obtained from the permanent 'underway' system on the *Brown* (Wanninkhof and Thoning, 1993).

Directly-measured carbon dioxide fluxes were obtained from the Woods Hole Oceanographic Institution's closed path NDIR system (McGillis et al 2001), but these data were unavailable at this writing. Although there are wide variety of complex processes which contribute to gas exchange, a comparison of the Fairall parameterization and the directly-measured fluxes may be enlightening.

5. RESULTS, CONCLUSIONS, FUTURE WORK

The Fairall parameterization was run using both GasEx experimental data sets, with and without the warm-layer and cool-skin parameterizations from the COARE code. The sea surface temperature applied in all cases was the output from the thermosalinigraph, the intake of which is located 5 meters below the surface. Equation (5) was applied, and the differences in the resultant fluxes are shown in Figures 1 and 2. Although the CO_2 flux increase due to the warm-layer and cool-skin parameterizations is shown to be modest, it is noted that the bulk-skin temperature difference (**ΔT**) for the experiments only ranged from approximately -0.3 to 0.3 degrees. In addition, the warm-layer and cool-skin effects offset to some extent. The flux difference from application of the warm-layer model will be proportionally higher for larger bulk-skin temperature differences and may represent a significant source of error when integrated over basin-scales. Observations in light winds on the tropical oceans show that the bulk-surface temperature difference can range up to a few degrees, which affects the solubility ratio and the **ΔT** in Equation (5).

Further work toward improvements to the model include the closer investigation of the near-surface temperature structure in the water (Ward et al 2002), the sensitivity and accuracy of the model to that thermal structure, and comparison of the model output fluxes to the coincident directly-measured CO_2 fluxes (McGillis et al, 2001).

There are complex processes occurring in the oceanic surface layer, including biological activity, surfactants, wave breaking and bubbles, etc. It is expected that these processes play a significant role in gas exchange, but considerable progress remains to be made in order to accommodate more appropriate parameterizations of these effects into the model. It is anticipated that progress in all aspects of gas exchange may contribute to the improvement of the parameterization in the future.

6. REFERENCES

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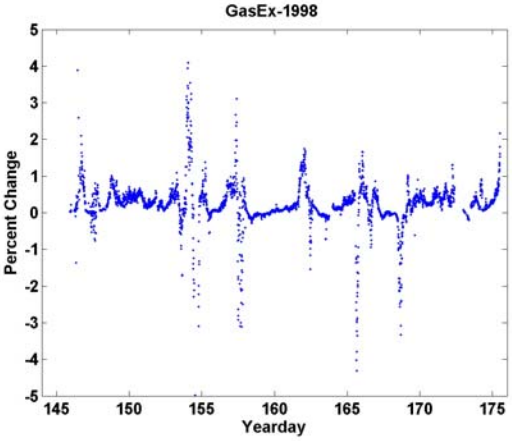

Figure 1. **Percent change in GasEx-98 CO2 flux due to inclusion of the warm-layer model in the COARE parameterization.**

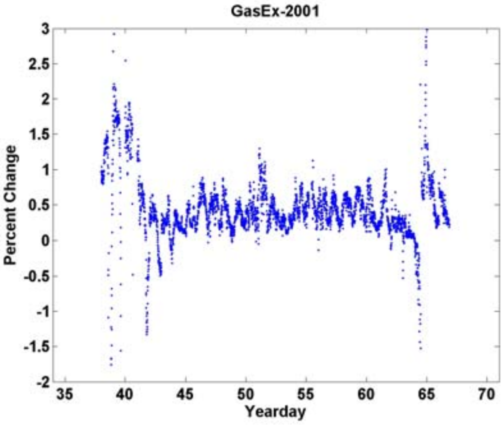

Figure 2. **Percent change in GasEx-2001 CO2 flux due to inclusion of the warm-layer model in the COARE parameterization.**