J6.4 MARINE STORM IMPACTS on BUBBLES and AIR-SEA EXCHANGE of GASES

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1. Introduction

Given the difficulty of making useful measurements at high wind conditions, this study attempts to shed some light on air-sea gas exchange under winter storm conditions based on the real measurements at Station Papa. Our preliminary analyses show that increasing gas transfer rates events are coincident with increasing wind speed and deeper bubble penetration depth, but this process also depends closely on sea state, such as fetch and duration. Moreover, the sudden increase of gas transfer, compared to the more gradual recoveries phase exhibits a quite asymmetric pattern. Wave breaking has a big influence on the gas transfer velocity during peak storm periods. While O_2 and N_2 gases fluxes are generally invasive, their sudden invasiveness with onset of storm conditions, and gradual bounce back afterwards is also very asymmetric.

Air-sea gas exchange is a complex physical-biochemical process, primarily controlled by the air-sea difference in gas concentrations and exchange coefficient or transfer velocity, which determines on how quickly a molecule of gas can move across the ocean-atmosphere boundary. Of particular importance to gas exchange, especially for poorly soluble gases such as oxygen (O_2) and nitrogen (N_2), is the relative contribution of bubbles due to breaking waves (Woolf and Thrope, 1991; Woolf, 1993, 1997; Asher et al., 1996). Generally speaking, gas transfer is augmented by bubbles (Woolf, 1997; Keeling, 1993), but factors such as the degree of supersaturation associated with small bubbles and transfer velocity caused by these processes are not yet known enough (SOLAS Science Plan, 2004).

As a preliminary step in better understanding the gas exchange under high wind speeds, a 6-day long storm case with 2-day-persistent-wind-speed greater than 15 m s^{-1} in January 2004 is analyzed. Our particular focus is on the gas transfer with and without bubble mediation under storm conditions.

2. Data and Methods

2.1 Data

Starting from September 2002, two years of data from C- SOLAS (Canadian Surface Ocean and Lower Atmosphere Study) Northeast Pacific mooring deployed at station Papa (50°N, 145°W) has been recovered. This allows for studies of air-sea gas exchange processes in open ocean, especially for high wind and sea states, which are quite rare.

The related meteorological and wave field parameters are provided by a coupled meso-scale atmosphere model MC2 and operational ocean wave model WW3 (Perrie *et al.*, 2004). Comparison of simulations and observations at buoy 46004 (50.93°N, 135.87°W) and station Papa indicates that the coupled model generally is quite consistent with observed data, and therefore appropriate for our mooring site.

2.2 Gas transfer velocity and wave-breaking

Given the uncertainty of direct gas transfer velocities (hereafter k_0), the Wanninkhof and McGillis (1999) parameterization (hereafter WM) is used in our study,

$$k_0 = 0.0283\, U_{10}^3\; (S_c / 660)^{-1/2} \tag{1}$$

in terms of U_{10} and the Schmidt number S_c, which was verified for winds up to 15 ms^{-1} in the open North Atlantic (McGills et al., 2001). According to a recent comparison of gas transfer velocity on sea-state-dependence by Woolf (2005), relatively high transfer velocities (including those

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simulated by WM) coincide with a mature sea. These conditions are typical of seas at station Papa, as demonstrated by simulated and observed winds and significant wave heights (SWHs) at buoy 46004.

The mechanism by which wave breaking enhances gas transfer is uncertain, and may involve bubble-mediated gas transfer (Woolf, 1997), or the influence of turbulent plumes in the upper ocean layer (Monahan and Spillane, 1984, Zhao et al, 2003). Quantitative estimates of bubble-mediated transfer are not yet accurate, and few studies have related bubble formation and distribution to characteristics of the gas transfer velocity. It has been suggested that a fraction of the transfer scales with the measured coverage of these plumes, e.g. the optically measured whitecap coverage (Woolf, 1997, 2005; Hare et al., 2004). In this study both these two mechanisms are considered.

The breaking-wave generated bubble-mediated gas transfer velocity (in terms of solubility and fraction of whitecap coverage) is taken Woolf (1997)'s form

$$k_b = W\,\mathbf{V}\alpha^{-1}[1+(\boldsymbol{e}\alpha\ S_c^{-1/2})^{-1/n}]^{-n} \qquad (2)$$

where W is whitecap fraction, α is the Bunsen solubility coefficient and **V**, ***e*** and *n* are empirical constants from GasEx-1998, respectively 14, 1.2 and 4900 cm/h (Hare et al., 2004). Although the original W in (2) is expressed in terms of only wind speed (Monahan and O'Muircheartaigh, 1980), we use a scheme by Zhao and Toba (2003),

$$W = 3.88\times10^{-7} R_B^{1.09} \qquad (3)$$

$$R_B = u_*^2 \ / \ \upsilon_a\, \omega_p \qquad (4)$$

where ω_p is wave spectrum's peak frequency, and υ_a is the kinematic viscosity of air, together with friction velocity u* they constitute a form of Reynolds number, R_B, for wind waves. When R_B>1000, visible breaking occurs (Zhao et al, 2001). The total gas transfer velocity is taken to be a sum of the two contributions (Woolf, 2005)

$$k_{T1} = k_0 + k_b \qquad (5)$$

while the gas transfer velocity related to wave breaking (hereafter 'K_{T2}') is Zhao et al. (2003)

$$k_{T2} = 0.13\ R_B^{0.63} \qquad (6)$$

Although K_{T2} is proposed for relatively soluble gas, such as CO_2, in which the bubble process can be negligible, it is one of few gas transfer velocities to consider the wave breaking explicitly. Here it is loosely considered as a baseline for comparison with K_{T1}.

2.3 Gas fluxes

The gas flux between air and sea is a diffusive process, which is expressed as

$$F = -k(C_a - C_w) \qquad (7)$$

where C_a is the dissolved gas concentration in equilibrium with the atmosphere which depends on solubility and atmospheric pressure, and C_w is the surface layer dissolved gas concentration. Gas fluxes with and without wave breaking influence can be estimated, with direct transfer velocity K_0, and (wave breaking) transfer velocities K_{T1} or K_{T2} in (7),.

3. Results

3.1 Observed gas and upper ocean conditions

The time series in Figure 1 were low-pass filtered (with a 24 h cut-off) to remove tide and diurnal signals. This shows that from day 350 to 380, with decrasing winter temperatures (Fig. 1b) and increasing mixed layer depth (MLD) (Fig. 1c), the observed O_2 and N_2 gas concentration at 21 m depth (Fig. 1a) gradually increased because of solubility dependence on temperature and salinity. Two instances of rapid increase of gas concentration occurred. The first sharp increase happens at day 361 and lasts for 3 days, followed by a 5-day oscillatory recovery, associated with the temperature fluctuations (Fig. 1b). Wallace and Wirick (1992) noted that the sudden increase in gas transfer and more gradual recovery tend to exhibit a quite asymmetric pattern, which could be explained by the rapid gas invasion as a result of pressurized air bubbles driving several meters below the sea surface, compared to the more slow diffusion across the air-sea surface. By comparison, the second event is from day 369 to day 370, followed by a 2-day gradual decreasing period, which then levels off in a relatively symmetric manner.

Checking the trend of normalized wind speed (Fig 1a) and the bubble penetration depth (BPD) (Fig. 1c), it can be seen that both increasing gas transfer events are coincident with increasing winds and deeper BPD, particularly the second event with winds in excess of 15 ms^{-1} wind speed and maximum BPD at 23 m. It is notable that before day 361, high wind events occurred, but the

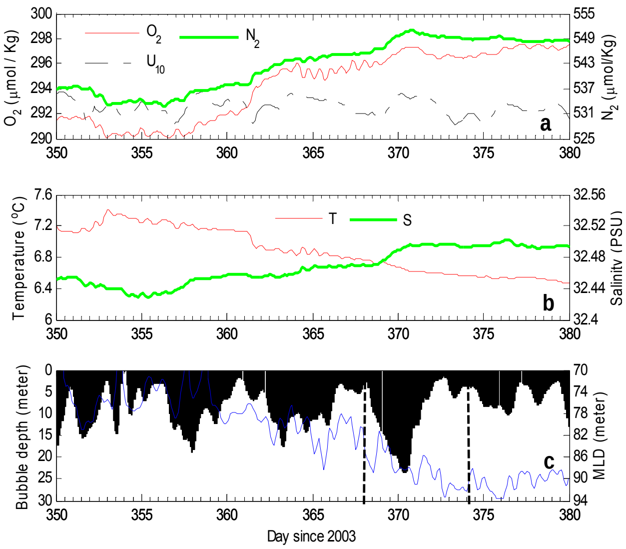

Figure 1. Time series of observed, at 21 m, (a) O_2, and N_2 concentrations, and U_{10} wind speed (normalized via 291+U*0.3/Umax so as to use O_2 scale); (b) ocean temperature and salinity at 21 m; and (c) bubble penetration depth (shaded) and mixed-layer depth (solid line).

gas concentrations do not change significantly, compared to the two events occurring after day 361. Possible reasons include shorter high wind durations, or net community consumption related to the relatively higher temperatures and shallower MLDs. Some studies (Woolf, 2005; Wanninkhof, 1992) suggest that sea state has a big influence on the gas exchange.

3.2 Storm impacts on gas transfer velocity

During the storm peak, from day 370 (Jan. 5th, 2004) to 371 (Jan. 6th, 2004), winds greater than 17 ms^{-1} last for 24 hours (Fig. 2a), with SWH ~to 7 m. This increases the non-dimensional wave-breaking parameter R_B (divided by 5000), and the white-cap fraction is up to 8% (equation 3).

The WM gas transfer velocity for oxygen is about 30-40 cm/h lower than that of Zhao et al (2003) (Fig. 2b). Of particular interest is that K_{T1}, is comparable to K_{T2}. Although they are considered from different mechanisms, the resultant total gas transfer velocity is unexpectedly close. Thus, in practical applications it is difficult to distinguish the transfer mediated by turbulence and bubbles because both are proportional to the wind (Zhao et al, 2003). This suggests that gas transfer is dependent on wave breaking, and whether it is primarily due to turbulence or bubble-mediated exchange, it should scale with whitecap coverage (Woolf, 2005).

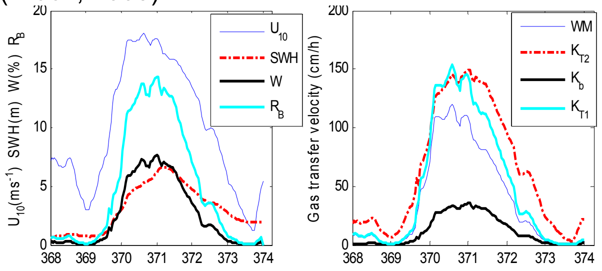

Figure 2. (a) Simulated wind speed, significant wave height (SWH), whitecap fraction (W), and wave breaking parameter R_B/5000 during storm period shown; (b) Calculated gas transfer velocities for oxygen, WM from equation (1), K_b from (2), K_{T1} from (5), and K_{T2} from (6).

3.3 Estimated gas flux

Because the mixed-layer (Fig. 1c) is much deeper than 21 m, and no observations are available above 21 m, the gas concentrations measured at 21 m are used to estimate an apparent air-sea flux.

Coupling K_0 and K_{T1} from (1) and (5), solubility, simulated atmospheric parameters, observed gas concentration into (7), the direct (denoted F_0) and bubble-mediated gas fluxes (denoted F_{0+b}) across the air-sea surface are estimated. Generally, both O_2 and N_2 gases fluxes are invasive during storms (Fig. 3a), and the maximum transfer happens during the strong winds when bubble clouds penetrate deeply. With wave-breaking induced transfer, the maximum increase in gas flux is ~ 20% for N_2, and 25% for O_2. As assumed in section 2.3, the 21 m depth gas concentrations respond instantaneously to the air-sea surface, which may give an overestimation in fluxes.

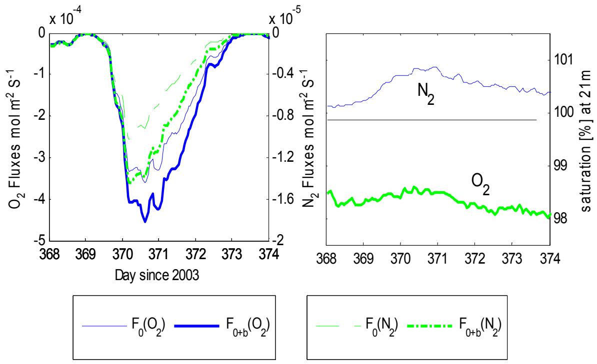

Figure 3. Estimated direct flux (F_0) and the flux bubble-mediated included (F_{0+b}) shown in (a), and (b) observed gas saturation levels.

When breaking wave-generated bubbles are taking into consideration, a supersaturation of the upper ocean (denoted as Δ) tends to be forced due to injection of small air bubbles, and the gas exchange between large bubbles and ambient water. This is a far more complicated process. Woolf and Thorpe (1991) developed a hybrid model including diffusive and bubbled-induced effects as,

$$F_{0+b} = -(k_0 + k_b)(C_a(1+\Delta) - C_w) \qquad (8)$$

where Δ is a function of U_{10}. This implies that gas fluxes will be increased due to the fractional supersaturation induced by bubbles. However, in this special case, the nitrogen flux would increase, while oxygen flux would decrease a few percent, because nitrogen is ~ 1% supersaturated, while oxygen is about ~2% under saturated (Fig. 3b).

4. Conclusions

In this study, air-sea gas exchange in station Papa under winter storm condition based on the C-SOLAS measurements in 2003 and 2004 is studied. We show that increasing gas transfer events in high wind and deepening BPD events. This process also depends closely on sea state. Moreover, the sudden increase of gas transfer and more gradual recoveries exhibits a quite asymmetric pattern. Continuing big uncertainties are the role of sea state and bubble processes, related to wave breaking

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