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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimation of bubbled-mediated air/sea gas exchange from concurrent DMS and CO_2 transfer velocities at intermediate-high wind speeds" *by* Thomas G. Bell et al.

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This paper discusses an interesting dataset of field gas transfer experiments where the air-sea fluxes of CO2 and DMS were measured using direct-covariance methods. The authors reduce the data to get at the bubble-mediated fraction of the total gas transfer velocity by assuming that differences in Schmidt-number normalized total gas transfer velocities for the two gases will give the Schmidt-number normalized bubble gas transfer velocities. This relation is given in Equation 5. Then, it is proposed that the two bubble transfer velocities can be scaled using two different relationships for

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bubble gas transfer (one by myself and co-workers, and one by D. Woolf).

The approach is novel, but I think the authors are glossing over a potential problem in that in the system they are studying, CO_2 is an invasive flux (air-to-ocean) and DMS is an evasive flux (ocean-to-air). My hunch is that Equation 5 is only strictly true when both gases are far from equilibrium *and* the flux is in the same direction. Problems arise in applying Equation 5 for a mixed system, where one gas is invading and one is evading, because the bubble gas flux is not the same, even when normalized to a common diffusivity/solubility. In the case of invasion, the bubble overpressure drives more gas than expected (based on the bulk air-ocean concentration difference) into the water. For evasion however, the bubble overpressure acts to decrease the net gas flux.

This means, at least for my parameterizations, that the functionality of the relationships that determine the dependence on solubility (which is the main difference between the transfer velocity for bubble-mediated processes and transfer across a wavy, unbroken surface) is not the same for invasion and evasion (see Asher et al., 1996, JGR-Oceans). Woolf gets around this issue by defining a diffusivity/solubility-dependent equilibrium supersaturation, which will not be the same for DMS and CO_2, and should be taken into account (I think) when applying Equation 5.

It isn't clear to me at this point whether or not Equation 5 is incorrect, or just needs to be qualified that it only holds in the specific case when the two bulk air-sea concentration differences (for CO_2 and DMS) are far from equilibrium. However, one thing is clear from looking at the material in the supplements, is that using the Asher et al. (2002) relationship for both CO_2(invasion) and DMS (evasion) is not correct. The Asher et al. (2002) relation is only for invasion. For evasion, there is a separate equation in Asher and Wannninkhof (1998, "The effect of bubble-mediated gas transfer on purposeful dual gaseous-tracer experiments." Journal of Geophysical Research 103(C5): 10,555-510,560) that should be used instead. However, I think the authors need to consider whether or not their approach might be flawed from the outset due to the mismatch in flux directions.

Other than a few minor comments and technical details I've listed below, the paper is good and I think the results are interesting. My main comment above also should not be seen as a fatal flaw. Provided the authors can justify Equation 5, and their derivation of f (equation 6), I think this paper could be published with relatively few changes.

Minor comments: Line 54: "These processes include ..." Comment: Buoyancy effects are not a process. It might be better in this sentence to say something like "These processes include diffusion, surface renewal, and bubble-mediated transport. In turn, turbulence can be generated by wind stress, wave-induced mixing, buoyancy currents, and wave breaking." Or something like that anyway.

Line 56: "A variety of theoretical, laboratory, and field ..." Comment: I don't think this sentence is strictly true. My opinion is we have a fairly good understanding of the factors that affect gas exchange from a phenomenological standpoint (the authors list them just a couple of sentences earlier). What we lack is how to determine which of those processes are important under a given set of circumstances. Most of this comes from the fact it is challenging to measure the things we know affect gas exchange in the field, at least at the scales over which these things control gas transfer.

Line 60: "Gas transfer via bubbles (k_bub) ..." Comment: It would be good to define k_bub here. The point is that there are a couple of different ways to do this, you can go the Memery and Merlivat (Memery, L. and L. Merlivat (1985). "Modeling of the gas flux through bubbles at the air-water interface." Tellus, Ser. B 37: 272-285) approach and use the bulk air-water concentration difference and accept that k_bub for invasion and evasion are different (e.g., I used this approach in Asher et al. (1996, JGR-Oceans)) or you can redefine the air-water concentration difference in terms of how bubbles would affect the equilibrium and have a common k_bub (but then it might get complicated relating k_bub for invasion and evasion) as done by Woolf (1997).

Line 78: "These measurements typically show DMS gas transfer velocities that are lower and exhibit more linear wind speed dependence than those estimated for CO2

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based on dual tracer studies (e.g. Bell et al., 2015; Yang et al., 2011; Goddijn-Murphy et al., 2012)." Comment: I think the authors should be clear here that there are no CO_2 measurements from dual-tracer studies. There are DT measurements for SF_6/He, which get related to CO_2 through diffusivity. Then there are EC measurements for CO_2. Comparison of the DT-derived CO_2 transfer velocities with CO_2 transfer velocities produced by EC measurements of CO_2 fluxes shows relatively good agreement. It is the transfer velocities produced by EC measurements of DMS fluxes that show different behavior.

Line 87: Comment: maybe want to note that they agree when normalized to a common diffusivity.

Line 126: "The air side gas transfer 127 contributes about 5% on average to the total resistance for DMS." Comment: The air-side resistance fraction is a function of wind speed. Does this 5% increase as U increases? COAREG must reproduce this, it was measured by McGillis et al. a while back.

Line 161: the relation in the text showing $k_w = k_{int} + k_{bub}$. Comment: I wonder if maybe it is time to stop writing this as a general expression (I know, I am guilty of this as well). What is generally true is that the total gas flux is equal to the sum of interfacial flux and the bubble flux. Saying the overall transfer velocity is equal to the sum of the two transfer velocities really only works if the concentration difference is far from equilibrium. Work through David's relations from the 1997 paper and you'll find they are a bit convoluted in terms of how exactly the pieced (his Delta term) fit together to make a coherent physical picture. If you start by assuming it is the fluxes, not the transfer velocities, which sum linearly, the assumptions required to get to the various relations proposed are more easily understood.

Technical Comments:

1. Multiple citations are not in any recognizable order. Sometimes they are chronological, sometimes alphabetical. I don't remember what the ACP style guide says, but I

am sure it is not "random."

2. Line 74: "... studies indicate a non-linear dependence ..."

Line 91: Shouldn't cite papers that are not published or submitted.

Line 175: The two f values are opposite from what is given in the supplement. Not sure which is correct, but it should be consistent (and correct).

Line 323: I know this is petty, but I don't think Woolf (1997) is based on laboratory data.

Equation 7: Figure caption says "cubic" and equation 7 is quadratic. Resolve this difference.

Line 384: The citation to Asher and Wanninkhof (1998) should be to Asher et al. (1996). If you really must cite Asher and Wanninkhof (1998) in this context, which you shouldn't, at least make it the other Asher and Wanninkhof (1998) paper that is directly relevant (see citation above).

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