

Interactive comment on “Measuring air–sea gas exchange velocities in a large scale annular wind-wave tank” by E. Mesarchaki et al.

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This paper describes a recent set of air-water gas exchange measurements in an annular wind-wave tank. The dynamic range of the gas tracers (14 gases, from rather insoluble to very soluble) and the wealth of supporting measurements (friction velocity, mean square wave slope, surfactants) make this a potentially very important study for resolving the complex physical processes involved in air-water gas exchange. This paper discusses the measurement techniques in detail and focuses on two end-member tracers (the sparingly soluble N₂O and the highly soluble methanol) to illustrate the performance of their system. This paves the way for a future (and likely more interesting) paper comparing transfer velocities of different tracers and examining the physics.

This paper is a useful contribution to the gas exchange community and suitable for
C782

publication after minor corrections. In general, I would like to see a bit more discussion on 1) how surfactants may suppress gas exchange, 2) aerodynamic resistance (or the lack of) and its affect on methanol transfer, and 3) k in low wind regimes and stability effects.

Specifics

p. 1645, line 3~5. On the waterside, small scale processes (e.g. surface renewal) also affect the rate of gas exchange, in addition to molecular diffusion. The rate of turbulent (aerodynamic) transport is an important limitation to the overall airside transfer velocity.

Line 8~9. Probably more accurate to say “Wind driven turbulence near the water surface and the resultant processes (surface stress...).”

Line 16. What are those poorly understood air-sea gas transfer regimes? Please specify.

A brief Introduction on surfactants and how they may affect gas exchange under varies wind speed/turbulence regimes (and appropriate references) would be welcomed here.

Paragraph starting from line 25. It is probably not necessary to dwell on the “drawbacks” of other techniques. Just say that these tracer techniques are made on fairly long time scales and generally applied to waterside controlled, inert tracers.

End of introduction: Can reiterate that results from the other gases measured will be presented elsewhere.

Section 2.1 Should mention that the gas tracers in the wind-wave tank are assumed to be inert (i.e. no in situ production or destruction).

P. 1652, line 2. Is it true that there is no concentration gradient in air? If there is a vertical gradient in horizontal wind velocity, doesn't it mean that there should be a gradient in airside concentration also? This gradient is likely very small for waterside controlled tracers. But for airside controlled tracers the gradient may be significant.

See my related comment near the end of this review.

p. 1652, line 11. Does the time constant of the equilibrator depend on the solubility of the gas? How long does it take to achieve equilibrium for the different gases studied here (e.g. methanol and N₂O)? A response time of 1 minute seems quite fast.

Working principles of the PTRMS and FTIR can be described in less detail.

p. 1655, line 7. What about the high solubility tracers? Are their calibrations linear?

p. 1656, line 23. This sentence is a bit unclear. Do the authors mean that the sensitivity (e.g. in counts/s/ppb) vs. m/z relationship is similar for both PTR-MS?

p. 1658, line 22. Bulk water?

p. 1661, line 5~15. This paragraph is rather awkward to read and has a number of grammatical mistakes. Suggest write.

p. 1662, line 3, “encompasses relatively large uncertainty” instead of “embraces a big uncertainty”

p. 1662, line 15. It was mentioned previously that capillary waves start to break above U_{ref} of 4.8 m/s. This seems not far from the U₁₀= 7.3 m/s here?

p. 1663. Line 5. Clearly surfactants do not reduce k and u*w in approximate equal proportion. Otherwise the k vs. u*w relationship would remain largely constant.

Line 10. Suggest changing this line to “The reduction in transfer velocity due to surfactants is the most apparent at low wind speeds. At high wind speeds and under more turbulent conditions the effect of surfactant seems weaker.”

Line 15. Seems superfluous and ungrounded to comment on surfactant effects beyond the wind speed range measured.

Line 25. Is U₁₀ here derived from u*w, or from U_{ref}?

p. 1664, line 1~3. Replace “and therefore” with “while” or “and”.

C784

Line 7~9. If quantifying k at low winds is one of the primary foci of these experiments, then you should discuss more about the discrepancies observed (and why your measurements might be more robust than previous estimates). For example, many K parameterizations are forced through the origin at U=0 m/s. Is that appropriate in light of your observations? Also, from your Table it looks like the water temperature was always lower than the airside temperature (i.e. stable atmosphere). At low wind conditions, convective driven turbulence is thought to be the main driver for gas exchange. How does stability affect your results? Also, any effect of stability on the exchange of soluble, airside controlled tracers?

Line 11. Plotting k vs. wind speed in log scale and discussing discrepancy in relative terms are a bit misleading here. A “smaller spread” at high wind speeds matters a lot more geophysically than the “huge disagreement in low wind speed.” What’s the spread in actual k units (e.g. cm/hr) at different wind speeds?

It would be good to see Fig. 10 and 11 in a linear scale as well.

Line 15. The Clark et al. (1994) results were from a river. Do the authors want to comment on why their results should agree with this parameterization? Also, what does the apparent consistency between the various parameterizations at intermediate wind speeds suggest about the influence of real surfactants over the open ocean? Where would the authors’ surfactant-affected kN₂O points lie on Fig. 10? It has been shown fairly conclusively that surfactants do suppress gas exchange in the lab (e.g. Frew et al. papers) and over the ocean (Salter et al. GRL 2011); the authors should cite these early results. To me, the important question now is what is the natural analog of, say 0.033 mg/L of Tirtion X-100? When are surfactants important in the real world?

p. 1664, line 17, “weakly soluble gases”

line 22. and elsewhere Yang et al. 2013

p. 1665, line 3. Is it true that there is no aerodynamic (turbulent) resistance in the

C785

wind-wave tank? Formulation from Hicks et al. 1986 (Duce et al.1991) predicts that for methanol, the airside diffusive transfer velocity (e.g. $1/R_2$) is about 25000 cm/hr at $U_{10} = 10$ m/s. The COARE model predicts an airside diffusive transfer velocity of about 10000 cm/hr at this wind speed. In comparison, your observed methanol transfer velocity is about 6000~7000 cm/hr at $U_{10} = 10$ m/s. I am guessing that there probably is some aerodynamic resistance in the wind-wave tank (but less than over the ocean). There is probably a weak vertical gradient in the air concentrations of airside controlled gases (i.e. it's not perfectly well mixed).

p. 1666, line 17. The aeoletron isn't the ocean. Better just say "air-water gas exchange measurements"

Fig. 9. Trends of k vs. u^*w for the clean and high surfactant case would be helpful to guide the eyes of the readers here. At the same ref wind speed, is the relative reduction in u^*w comparable to the relative reduction in k_{CH_3OH} due to surfactants? This might help to tease out the process with which surfactants affect airside and waterside controlled gases.

Table 2. Mean square wave slopes are included here but not plotted or really discussed in the manuscript. Is the k_w vs. mean square wave slope relationship consistent with and without surfactants? i.e. does mean square wave slope capture the effect of surfactants?

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