Interactive comment on “Measuring air–sea gas exchange velocities in a large scale annular wind-wave tank”

The authors would like to thank Dr. M. Yang for reviewing our manuscript and for the valuable comments and suggestions which have in many aspects improved the quality of this publication. Our responses are listed below.

Referee 1: General comment:

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 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 effect on methanol transfer, and 3) k in low wind regimes and stability effects.

<u>Answer</u>

We very much appreciate the helpful comments of Dr. Yang. His general points 1, 2 and 3 have been acted on and more discussion has been introduced in each case (see specific details below). Reading carefully the present review, it is clear that the referee would like more discussion concerning the complicated phenomena and mechanisms related to the gas exchange. Such discussions are long and are not in the scope of the current article. In depth investigations concerning the effect of the various parameters (e.g u^*, mss) on the gas exchange, the effect of surface layers, extra resistances etc. are planned for future publications. Our strategy for publication of this extensive dataset was to separate the method description/validation (this paper) from the full analysis (follow-up paper). This avoids a single paper which could be either unreasonably long or lacking in essential detail. We would like to remind the referee of the stated focus of the present <u>method paper</u>, which is the following:

- Providing a detailed description of an analytical method capable of:
  - ➢ Transfer velocity measurements of multiple tracers (covering a wide solubility and diffusivity range) in parallel
  - ➢ Transfer velocity measurements at various turbulent and water surface states.

- Demonstrate the efficacy of the proposed method by:
    - Presenting transfer velocity measurements of two contrasting tracers under different turbulence (Figures 7, 8) and water surface stages (Figure9)
    - Presenting the reproducibility of the proposed method (Figures 7, 8) as a result of 4 replicate experiments.
    - Compare the obtained results to previous lab and field measurements (Figures 10, 11).

The authors would like to maintain the focus of the present paper on the above, keeping additional physical discussions informative enough to describe the figures but concise.

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.*

Answer

According to the "two layer" model, the transport of gases across the boundary layers is controlled by molecular diffusion. Turbulent diffusion (or else transport) starts being significant once we have reached the upper part of the atmospheric boundary layer. We assume that this is what the referee meant and thank for the comment. It is indeed useful to add here a comment considering the turbulent transport in the air-space. The text has been improved and separated to a paragraph as following:

"The principles behind gas exchange at the air-sea interface have been reported in detail within previous reviews (Jähne and Haussecker, 1998; Donelan and Wanninkhof, 2002; Wanninkhof et al., 2009; Jähne, 2009; Nightingale, 2009). A simplified conceptual "two layer" model is generally accepted. The model assumes that close to the interface turbulent motion is suppressed and that the transfer of gases is controlled by molecular motion (expressed by the diffusion coefficient D). This leads to the formation of two mass boundary layers on both sides of the interface. In the upper part of the air-side mass boundary layer, turbulent transport becomes significant. Further away from the interface the significance of the air-side turbulent transport increases. In the water-side, due to lower diffusivities, molecular transport remains the controlling factor of the transfer. Depending on the solubility of the gas in question, its transfer could be restricted by one or both sides of the interface (i.e air-side and water-side controlled). "

- *Line 8-9. Probably more accurate to say "Wind driven turbulence near the water surface and the resultant processes (surface stress…)…"*

Answer

Thank you for the comment. In the revised version the sentence is rewritten as recommended.

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

Answer

To avoid confusion here, we rewrote the sentence as follows:

"Such studies aim to improve our understanding of air-sea gas transfer and provide new insights into the theoretical background."

The way our understanding of air-sea gas transfer is meant to be improved is defined in the previous sentence and the authors would prefer not to repeat this here.

"…The impact of wind driven mechanisms, surface films and diverse physiochemical tracer characteristics on the gas exchange rates can be studied in detail through transfer velocity measurements of individual species provided by the method proposed here. Such studies aim to improve our understanding of air-sea gas transfer and provide new insights into the theoretical background..."

- *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.*

The referee is right. We have added a few sentences here introducing surfactants and there effect on k.

"Surface films are also known to have a strong influence on the transfer velocity by inhibiting waves and decreasing the near surface turbulence (e.g Frew et al. (1990), Jähne and Haussecker (1998), Zappa et al. (2004), Salter et al. (2011)). To date, research on surface films (using different film thicknesses and types) and their effect on transfer velocity, is only in a very early stage"

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

Answer
Paragraph has been shortened.

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

Answer
The following sentence is added at the end of the introduction:

"Transfer velocity measurements of the rest examined tracers are going to be presented in a follow-up publication."

- *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).*

Answer
The word "inert" is introduced before the word "tracers" in the first paragraph of section 2.1

- *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.

Answer: See at 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.*

Answer
The time constant of the equilibrator does indeed depend on the solubility of the gas. The lower the solubility of the tracer, the longer the time until the equilibration is reached. The time constant was evaluated using a very low solubility tracer, namely hexafluorobenzene (α= 1.0) for which a constant of ~ 1min (more precisely between

1.2-1.3 min) was measured (see more in Krall, 2013). Since hexafluorobenzene has a similar solubility with the low solubility tracers used in this study (i.e N2O, isoprene etc.), a time constant of ~ 1min is expected for the low solubility tracers while even shorter time constants could be expected for the more soluble tracers.

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

Answer
Working principles have been shortened. The rest of the text has been reformed accordingly where necessary.

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

Answer
The water-side calibrations for the high solubility tracers were also linear. These calibrations though were not used in this study as the c_w values were needed only for the low solubility tracers (see section 2.2 water-side controlled tracers). For the high solubility traces, the calculation of the K_{ta} requires only the air-side concentration, c_a (see section 2.3 air-side controlled tracers). Because of this only the low solubility tracers are mentioned in the text.

As here pointed out, referring only to the low solubility tracers might confuse the reader and therefore we changed the text to include all tracers.

- *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?

Answer
The sentence is removed from the text.

- *p. 1658, line 22. Bulk water?*

Answer
Corrected to bulk water

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

<u>Answer</u>
Paragraph has been shortened and rewritten.

- *p. 1662, line 3, "encompasses relatively large uncertainty" instead of "embraces a big uncertainty"*

<u>Answer</u>
Text is changed accordingly.

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

<u>Answer</u> *Correct. We rephrased line 16 to point it out once more. Line 16 is changed to: "This sudden increase in the so far linear tendency can be attributed to various water surface effects (e.g initiation of capillary wave braking), which are not going to be discussed 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.*

<u>Answer</u>
The authors did not intend to confuse the reader in this way. The text in section 4.2 has been rewritten. We hope that the new formed sentences do not lead to such a misunderstanding.

- *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."*

<u>Answer</u>
The text of section 4.2 has been rewritten. Also the plot has been changed and the transfer velocities are now plotted against the u_{ref}. (See below the answer to the comment for Fig. 9).

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

Answer
Sentence has been removed.

- *Line 25. Is U10 here derived from u*w, or from Uref?*

Answer
Please see: Appendix B. The u_{10} is derives from the u^* using the provided equations.

- *p. 1664, line 1-3. Replace "and therefore" with "while" or "and".*

Answer: Corrected.

- *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?*

Answer: We thank the referee for the comment. Indeed, convective driven turbulence at low wind speeds is important and is missing from the discussion. As the referee commented, the case in our experiments was a stable atmosphere (water temperature lower that the air temperature). This means that here, no gas exchange due to convection was apparent. Though, the case in the open ocean, depending on the temperature and the light intensity conditions, can be different. A short comment on is included in the text providing an extra explanation for the large discrepancies observed at the low wind speed end. The discussion around k at low wind speeds is generally extended.

- *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.

Answer: The authors believe that the differences between the various parameterizations are clearly shown in the figures and there is no need of various extra numerical examples which, according to the authors, would complicate the text. As requested by both referees, a linear scale is added to both Figs. 10 and 11.

- *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?*

And

- *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 Triton X-100? When are surfactants important in the real world?*

Answer:
Here the authors would prefer to keep the focus on an overall comparison of the present study with previous ones, pointing out wind speed regimes with high uncertainties but also regimes where most of the studies are in agreement. In this way, the focus remains on the "problematic" low wind speed regime, a so far "new" regime, investigated by the proposed method. Further conclusions or speculations on why this study should agree or not with others studies, are not in the scope of this publication and would much better fit in a review paper for example.
In Fig 10, only clean surface N_2O transfer velocity studies are compared. No surfactant studies are included and therefore also not the surfactant affected points of this study. If the reader wishes to know where the surfactant affected kN_2O points would lie on Fig. 10, this is easy to estimate decreasing the presented data by the appropriate factor as (discussed in section4.2). A full discussion of the surfactant effect is included in the follow-up publication.
Surfactant citations are included in the introduction. Please see comment at the beginning of this review.

- *p. 1664, line 17, "weakly soluble gases"*

Answer: Corrected.

- *line 22. and elsewhere Yang et al. 2013*

Answer: The authors find it important to mention that Yang et al. 2013 refers to a field study as it is the only field study plotted in figure 11 and it is important for the reader to understand the “separation” between two k_{ta} groups (i.e model-field and tunnel). See also comment below.

- *p. 1665, line 3. Is it true that there is no aerodynamic (turbulent) resistance in the 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/R2) is about 25000 cm/hr at U10 = 10 m/s. The COARE model predicts an airside diffusive transfer velocity of about 10000 cm/hr at this wind speed. In comparison, you observed methanol transfer velocity is about 6000ı 7000 cm/hr at U10 = 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).*

Answer:

Wind profile measurements in the air-space of the Aeolotron facility (Bopp 2014) have shown that the wind profile starting from a few centimeters above the surface (~10 cm) and above is relatively constant. This is reported in the text ... “The well-mixed air-side space (at few centimeters height above the surface) ensures no concentration gradients and therefore concentration measurements independent of the sampling height.”

In the very first centimeters above the surface (surface - ~10cm), the wind profile shows an increasing gradient which could be roughly represented as logarithmic. This means that our ktCH3OH measurements possibly include an extra turbulence resistance attributed to the profile of the very first centimeters. A correction of the ktCH3OH accounting for an extra turbulent resistance (as described in Deacon 1977 for example) would reduce our ktCH3OH by a factor of 1.5-2, placing them close to the model and field studies (Fig.11). The same would happen if we were to correct the other tunnel measurement ((Liss 1973, Mackay and Yeun 1983) in the same way. Though, characterizing the air-side wind profile of a tunnel is difficult so much for this facility as also for the rest. The info provided, considering the air-space wind profile, height of air-space measurements, height of the inlet, etc., are not enough in order to accurately apply a turbulent resistant correction. To avoid invalid speculations, the authors prefer to present the ka parameterizations of the tunnel studies (Liss 1973, Mackay and Yeun 1983 and the present one) in their original form.

In Fig. 11, the presented ka parameterizations are consciously separated into two “color-groups” (tunnel (color) and model-field (grey-black)) corresponding to ka “with and without” the extra turbulent resistance.

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

<u>Answer</u>: Corrected.

- *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 kCH3OH due to surfactants? This might help to tease out the process with which surfactants affect airside and waterside controlled gases.*

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

<u>Answer</u>: In Fig. 9, the kt is now plotted against the u_{ref} in order to present a clearer effect for each wind speed setting. More discussion considering the effect of the surfactant on u* and mss and their relation to k is included in section 4.2. The mss reduction due to the surfactant is similar to the reduction in the transfer velocity of N_2O. This is also mentioned in section 4.2. The reader is referred to Table 2 for more information. Based on our dataset and the data analysis presented here, absolute correlations between k and the affected parameters are invalid. The process under which each parameter affects the gas transfer need further investigation and is going to be presented in the follow-up publication.