Author's reply to 'Interactive comment on "Air-sea gas exchange at hurricane wind speeds" by Kerstin E. Krall and Bernd Jähne' by Byron Blomquist

August 29, 2019

The authors thank Mr. Blomquist for his thorough and helpful comments. A point by point answer to his comments can be found below.

Computation of u_{10}

> Reviewer's comment: However, I would like to see a bit more detail on the assumptions involved in deriving an open ocean-equivalent 10 m wind speed and u* from wind speed measurements in the wind tunnel(p.12).

We now explain this in more detail in the manuscript. To this end we will add our co-workers from Kyoto (Naohisa Takagaki) and Miami (Andrew Smith) as co-authors, because they made the measurements and greatly helped with computing u_{10}. We also found a mistake in converting between $u_{*,a}$ and $u_{*,w}$, and decided to use Donelan et al. (2004) (lab measurements of C_D) instead of Powell et al. (2003) (field measurements of C_D) to convert measured wind speeds in Miami to u_* and u_{10}. This slightly changes the relationships $k_x(u_{*,w})$ and the model parameterization equations, but not our findings. Further details and an in-depth description of the measurement procedure can be found in Takagaki et al. (2012) and Donelan et al. (2004).

Separation of total gas transfer velocity into the components used in Eq. 10.

> Reviewer's comment: I don't fully understand how the parameters defined on p.16 (ks600, kc600 and kr) were obtained from the measurements. Was kc600 determined using only data for SF6 and CF4 (and only SF6 in seawater), as mentioned on p.18 and are these results shown in Fig.7b? Were these then applied as fixed values in a two- parameter fit to data for all gases to obtain ks600 and kr in Fig. 7a,c?

Each wind speed is treated separately. The fit routine does not know u_* or u_{10}. Input parameters are: all k_{meas}, of one wind speed condition, Sc and α calculated at the water temperature k_{meas} was measured at. In a first step, the fit routine minimizes $(k_{\text{tot}}\text{-}k_{\text{meas}})^2$ using a standard least squares algorithm (`scipy.optimize.curve_fit` in python) where

- k_{meas} is the set of all measured k at one specific wind speed condition, and
- k_{tot} is calculated from the corresponding physico-chemical tracer properties α and Sc using Eqn. 10 with the free and to be optimized parameters k_{c600}, k_{s600} and k_r.

In the next step(s), the condition given by equation 16 is looked at. If it is fulfilled, the fit routine commences and outputs k_{c600}, k_{s600} and k_r from step 1. If the condition Eqn. 16 is not fulfilled, the fit is repeated, however the parameter space is reduced for k_{c600}, with the maximum allowed value of k_{c600} being $k_{c,\text{max}} = k_{meas,T,600} - k_{s600}$ where $k_{\text{meas},T,600}$ is the highest measured, Schmidt number scaled transfer

velocity of either SF_6 or CF_4. This second fit yields a new set of k_{c600}, k_{s600} and k_r, for which the check according to equation 16 is performed again. This is repeated until the condition is satisfied, and the fit routine commences with the results k_{c600}, k_{s600} and k_r from the last iteration step.
This is repeated for each wind speed condition of each of the campaigns separately.
$k_c(\alpha)$-curves as well as plots showing a comparison between k_{meas} and $k_{modeled}$ are shown in the appendix below.

The parameter $k_{c,600}$

> Reviewer's comment: There's potential confusion with the notation for kc600, defined on P.16 as a constant(maximum) value for bubble transfer at a given u*, because kc is also the second term in Eq.10 which could be measured under conditions where Sc=600, but would not be the same as kc600 defined on p.16 since it depends on gas solubility. I suggest using a different notation for the fit parameter representing the maximum limiting value of kc.Perhaps results for kc can also be shown on a plot similar to Fig.2, where the 'kc600' parameter is indicated as the value of kc at the low solubility limit, where the curve is flat?

The definitions are indeed consistent. Maybe this line of reasoning helps:
Starting from Eqn. 9,

$$k_c = \frac{1}{\alpha} k_r \left[1 - \exp\left(-\frac{\alpha}{\alpha_t} \right) \right],$$

assuming that the exponent α/α_t is small, we can calculate the Taylor series up to the second term,

$$\exp\left(-\frac{\alpha}{\alpha_t} \right) = 1 - \frac{\alpha}{\alpha_t}.$$

Inserting this into Eqn. 9 above immediately cancels α, so that k_c indeed does no longer depend on α for small α. Then, replacing α_t with its definition given in Eqn. 8 yields

$$k_{\mathrm{c,low}\,\alpha} = k_{\mathrm{c},600} \left(\frac{600}{\mathrm{Sc}} \right)^{n_b}$$

which is the definition of $k_{c,600}$ in the limit of low solubilities given in Eqn. 6 and also again given on P16. Also have a look at the $k_c(\alpha)$-curves in the appendix below, which show a flattening for the low solubilities. Maybe the confusion comes from the attempt to apply Schmidt number scaling to k_c as given in Eqn. 9 for a gas with a solubility close to, equal or larger than α_t to arrive at something like a CO_2-equivalent bubble surface transfer velocity, which one might also be tempted to also call $k_{c,600}$. However, since k_c as given in Eqn. 9 does depend on the solubility, Schmidt number scaling is not permitted, so that

$$k_c \left(\frac{Sc}{600} \right)^{-n} \neq k_{c,600}$$

for gases with a solubility close to, equal or larger than α_t.

Comparison with other wind-wave tank experiments

> Reviewer's comment: I'm surprised the authors do not present a detailed comparison with results from Rhee et al. 2007, which is a similar wind-wave tank gas transfer study and should be more directly comparable to this work than the field studies.

Rhee et al. (2007) is, among other studies, rather irrelevant for our work, because 1) their highest measured wind speed is 13 m/s, and 2) their means of bubble generation (submerged aerators) is very different from ours (wave breaking induced bubbles only). Therefore such a comparison is not meaningful. In the introduction, we refer, of course, to the two previous lab studies in the Kyoto high wind speed facility: Iwano et al. (2013, 2014) and Krall and Jähne (2014).

Comparison with Mischler's bubble tank experiments and difference between DMS and CO_2

> Reviewer's comment: The absence of detectable bubble transfer below u*w=5.8 m/s for all gases is certainly unexpected, and to me a sign that something is very wrong here. For example, from the information presented in Fig.2 (Mischler, 2014) we expect kc for CO2 (alpha=0.78@ 20°C) and kc for DMS (alpha=12 @ 20°C) to differ by more than a factor of 10.

Figure 1 shows the modeled k_c for DMS and CO_2 in salt water:

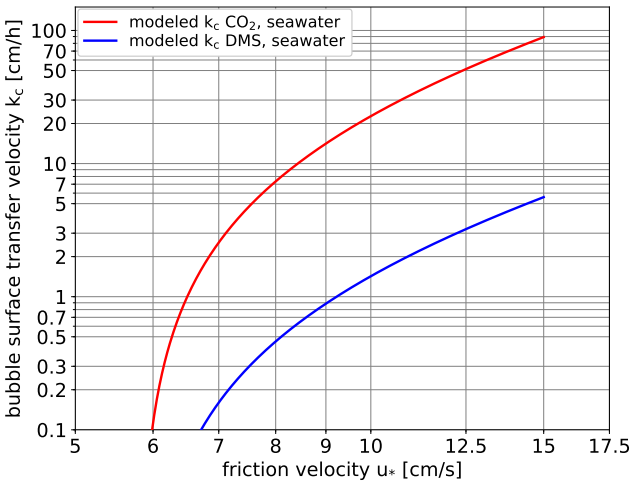

Figure 1: Modeled k_c for DMS and CO_2 in salt water

Both are, as expected, different by more than a factor of 10. However, since k_c for DMS and CO_2 are very small compared to the surface transfer velocity, this difference can hardly be spotted in Fig. 10, where we show the total modeled k of DMS and CO_2. This finding is in perfect agreement with Mischler (2014), who measured pure bubble-induced gas exchange in a special bubble tank.
The reviewer could have easily produced a graph like this for any gas by using the model parameterization equations for $k_{c,600}$ and k_r given in the appendix of the manuscript together with Eqns. 8 and 9 and computed the difference in k_c for DMS and CO_2 for himself.
To summarize, when there are bubble effects, we do indeed see the correct spacing between DMS and CO_2. Nothing is wrong with our data or the fit.

Missing bubble-induced gas exchange at moderatly high wind speeds

> Reviewer's comment: The absence of any difference in transfer rate at moderately high wind speeds among gases covering a broad solubility range is an indication that something is wrong in the determination of kc or that the experimental design is unable to simulate mechanisms of gas transfer at these wind speeds at sea. This result is certainly contradicted by field evidence from several studies showing a generally linear increase in k for DMS at wind speeds of 10-20 m/s and a roughly quadratic increase for a less soluble gas like CO2 over the same interval.

The reviewer's argument is only partially true. Field measurements show a rather confusing picture. While the results of Blomquist et al. (2017) show significantly higher gas transfer velocities for CO_2 than for DMS, the results of Zavarsky (2018) do not (Figure 2). Why is this the case and why are the DMS gas transfer velocities of Blomquist et al. (2017) almost a factor of two lower than those of Zavarsky (2018)? Also, why are gas transfer velocities measured using dual tracer techniques using the very low solubility tracers He and SF_6 (which translates to very large expected bubble contribution) generally much lower than CO_2 transfer velocities measured with eddy covariance (see the compilation of field measurements in Garbe et al. (2014, Fig. 2.10)), even at wind speeds as high as 15 m/s?

Dependency on sea state respectively wave age

> Reviewer's comment: I don't see obvious errors in the theoretical model developed by the authors, which is generally similar to prior treatments in the literature. I suspect the unique conditions in the wind-wave tank at high wind speeds are not comparable to the open ocean. Even an 'infinite fetch' design cannot simulate the wave spectrum in open ocean conditions, except perhaps under light winds, and thus cannot simulate large breaking wave crests and deep bubble plume penetration. I therefore wonder if the absence of bubble-mediated transfer at moderate wind speeds and the observed abrupt jump in the slope of gas transfer at wind speeds above 30 m/s are merely characteristics inherent to the wind- wave tank experimental design?
> I assume high wind interfacial conditions in the tank to correspond to a 'young' sea state, with very high surface stress and widespread coverage with small, choppy breaking waves. This condition is not common at sea except in a situation of very short fetch or a very rapid increase in wind speed, and in any case does not persist long before large breaking waves develop. It's therefore difficult to understand how these results apply to typical 'hurricane wind speed' conditions at sea. The authors should present a detailed analysis of these differences to provide some context for comparisons with field studies.
> *and later ...*
> Nevertheless, at moderate wind speeds of 10-16 m/s sampled under ideal conditions, kco2 from B2017 shows quite a bit of scatter and a high bias compared to other studies, with lower transfer rates observed in 'young' sea states and enhanced transfer in fully developed conditions or in 'old' seas when wind speed is declining but waves are still quite large. These effects are less pronounced for DMS. See Fig.6 in B2017. This implies sea state is a significant factor in the transfer of low solubility gases, and these subtleties are obscured by bin averaging. The comparison between kdms and kco2 likely depends on the specific sea state conditions, and the bubble transfer contribution to low solubility gases in a very 'young' sea state may be significantly reduced, which could be consistent with the kc result in this report.

The authors agree with the reviewer that air-sea gas transfer is not only related to the wind speed, but that the sea state, especially the wave age must be considered as well. But, again, current field results are quite confusing. As the reviewer mentioned, Blomquist et al. (2017) found lower gas transfer velocities in 'young' sea states than in 'old' seas for carbon dioxide and attributed this to higher bubble contributions at older seas. This finding is in strong contrast to estimates of air entrainment due to breaking waves by Deike et al. (2017). They found that the air entrainment is much lower at high wave ages. The effect is large, air entrainment scales roughly with the inverse wave age.
Our short-fetch experiment add results for very young wave ages, where the contribution of bubbles is low again. Therefore currently the issue of wave age dependency needs to be left open. Systematic measurements covering a wide range of wave ages are required.

DMS gas transfer

> Reviewer's comment: DMS is the high-solubility gas in this study (MA was omitted) and should represent interfacial transfer with minimal bubble-mediated contribution. The comparison to data from field studies in Fig.9 looks fairly good to me, despite the fact that there is little or no overlap in the wind speeds. Thus results for the first term in Eq.10, ks, seem roughly consistent with open ocean observations. Instances of suppressed DMS transfer noted in a few field studies are the exception and suggest we don't yet understand all the factors controlling gas transfer emphasis added. The effects of surfactants are an obvious factor that probably suppresses gas transfer, with some support from lab studies, but this has not been carefully examined under field conditions except at low wind speeds. Zavarsky et al. 2018 discuss the possible suppression of transfer by flow separation and angular differences in wind and wave direction.
> With respect to the comparison with results in B2017 (Fig.10 and p.23), I can make a few

clarifications. The B2017 cruise focused on high wind conditions with relatively few flux measurements at U10¡ 8 m/s, and these are generally under non-ideal conditions when the ship was moving at maximum cruise speed to reposition between storm events. So, we expect additional uncertainty or bias in the low wind speed results. Trends shown by the bin averages in Fig.10 are therefore misleading, and in any case the error bars for kdms and kco2 overlap at low wind speeds, so it's not meaningful to say results for the two gases differ by a factor of 3 at U10=3.4 m/s.

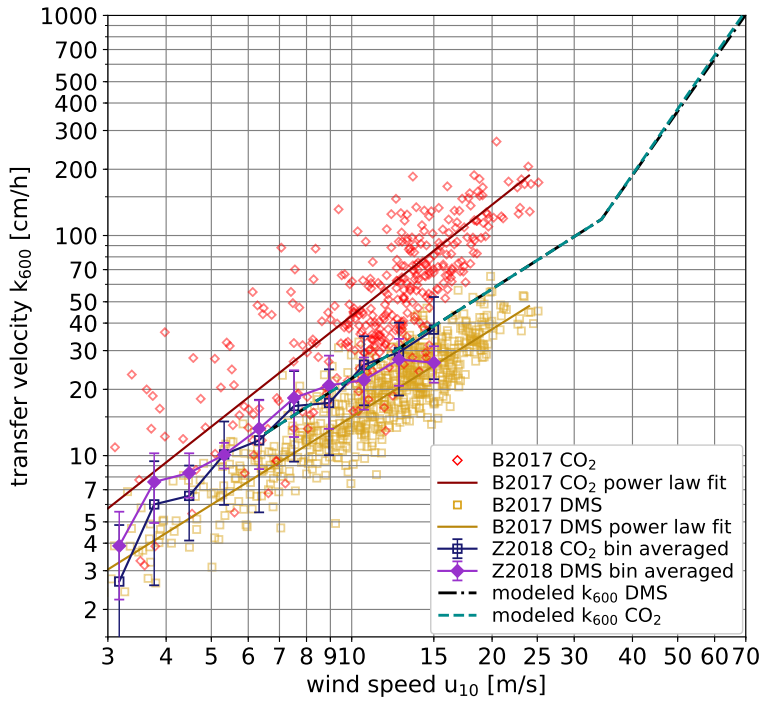

Figure 2: Comparision of DMS and CO_2 gas transfer velocities in a double logarithmic representation: eddy covariance measurements from HiWinGS by Blomquist et al. (2017) (B2017). Also shown are the CO_2 and DMS transfer velocities measured by Zavarsky et al. (2018) (Z2018). The output of the model presented in this paper for CO_2 and DMS is also shown.

We thank the reviewer for this clarification. However, if you plot the individual measurements instead of bin-averaged measurements (Fig. 2), the transfer velocities of carbon dioxide are still significantly higher down to 3 m/s wind speed. We will use then individual measuring points in a revised version of Fig. 10 instead of bin-averaged values, see Fig. 2.

Conclusions

Reviewer's comment: I think this is a carefully conducted study and well written report which explores the mechanisms of gas transfer in a wind-wave tank, but I struggle to understand the significance of these results with respect to conditions in the open ocean, especially at 'hurricane wind speeds'.
I don't agree with the conclusion in Sec.4.6 that rough correspondence between the wave-tank and open ocean data in Fig.11 shows the lab results are capturing the essential mechanisms, since the mechanistic details in each case could be significantly different (the physical details certainly are) and the rough agreement coincidental. As someone with a keen interest in this topic but limited experience with of wind-wave tank experiments I'd like to see a more thorough examination of these issues.

First a comment to the significance of our lab measurements for open ocean conditions. We have done the first systematic study at all in the wind speed range beyond 33 m/s u_{10}. So far only three data points

with huge error bars were available as shown in Figure 11 of our paper. In the wind speed range, we found a very steep increase of the gas transfer velocities even without the effect of bubbles, being associated to various rapid surface fragmentation processes at the free surface. We do not claim that this effect happens in the very same way at the open ocean, but it will happen also there, indicating that also the transfer of all water-side controlled gases will be enhanced significantly. This is an important new finding in our view for the global fluxes between ocean and atmosphere.

It is evident that gas transfer velocity - wind speed relations cannot be transferred from a wind-wave flume to the ocean. This is just as wrong as using empirical gas transfer - wind speed relations from a collection of field experiments. However, we insist that laboratory measurements are invaluable to identify the mechanisms of air-sea gas transfer. Laboratory measurements are generally much more precise and accurate than any current field measuring techniques. It is possible to use much more tracers simultaneously. And it is easy to perform systematic studies. It is not required to perform perfect simulations. This will not be possible. It is just necessary to identify and quantify mechanisms, which can then be adapted to open ocean conditions.

There were two serious limitations in the past: The limited wind speeds and only low-fetch conditions. The first limitation is already gone with the Kyoto High Windspeed Facility and the Miami SUSTAIN Facility. The second one can be overcome in annular facilities such as the Heidelberg Air-Sea Interaction Facility, the Aeolotron (Fig. 3).

Figure 3: Heidelberg Aeolotron: Due to the infinite fetch of the 10 m diameter facility, long and steep breaking wind waves can be generated, much larger than in any linear facility.

We have already modified the Heidelberg Aeolotron to perform experiments at higher wind speeds. With a number of new experimental techniques, which we have started to test this year, we are currently preparing experiments to cover an unprecedented range of wave ages in laboratory experiments and thus hope that we can make a useful contribution to solve the wave age dependency of air-sea gas exchange.

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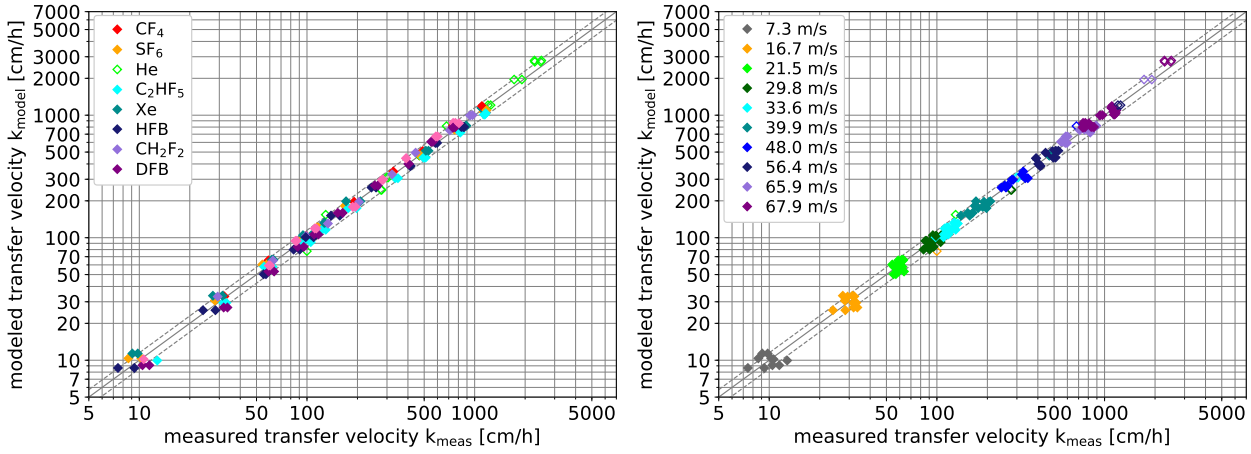
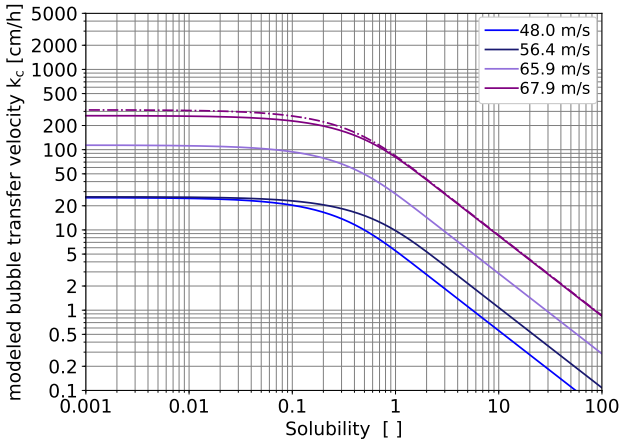
Appendix

The following plots will also appear in a supplement to the final revised paper.



(a) (b)



(c)

Figure 4: Kyoto freshwater experiment: Modeled vs. measured transfer velocities, colors corresponding to the tracers (a) and colors corresponding to the wind speeds used (b). The solid line marks perfect agreement, the dashed lines plus or minus 15%. He was excluded from the fit, therefore it is only shown here with open symbols. (c) bubble surface transfer velocity k_c in dependency of the solubility for the wind speeds, for which a bubble contribution was detected. The highest wind speed condition was repeated twice, one of the repetitions is shown as a dashed line, the other as a solid line.

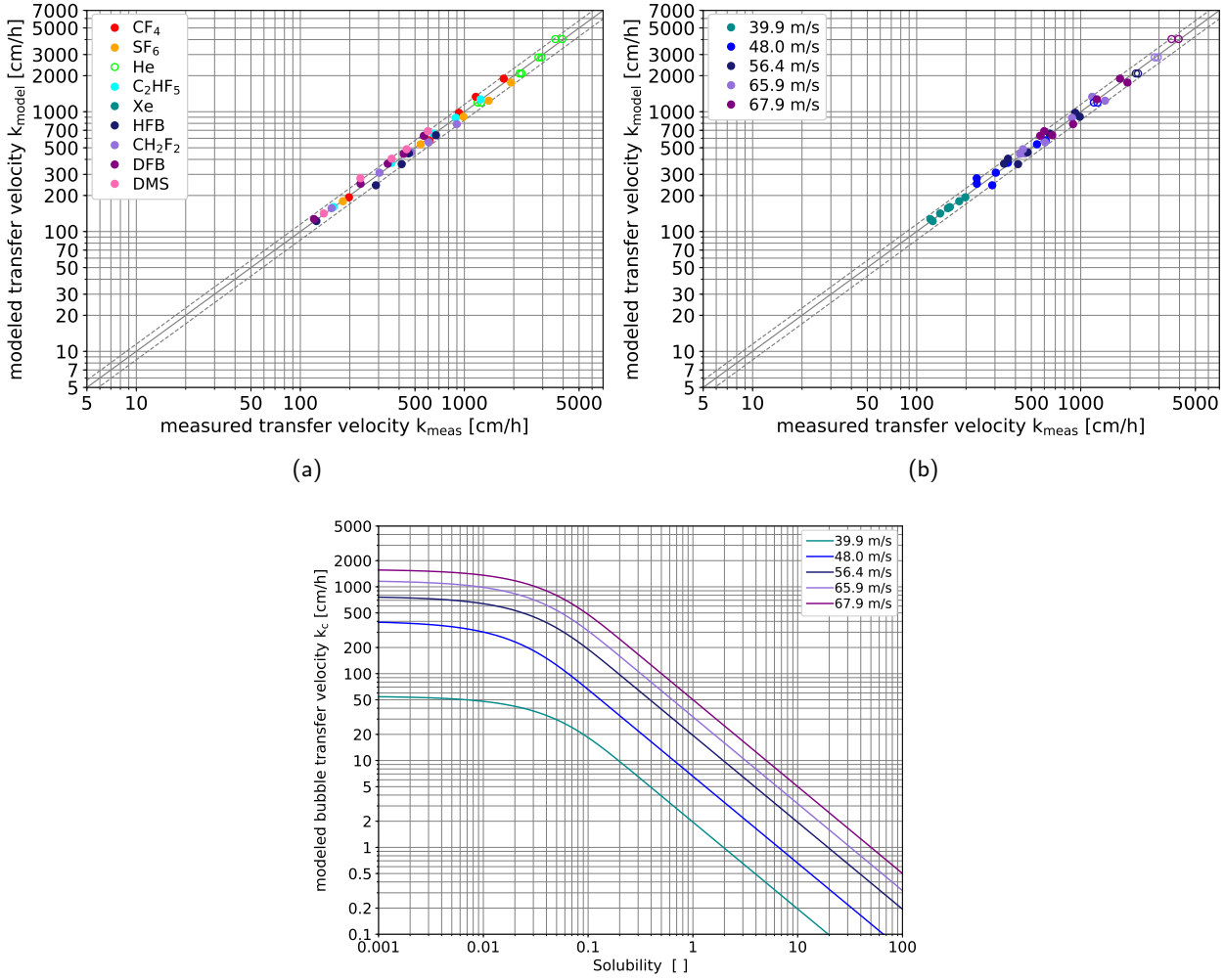
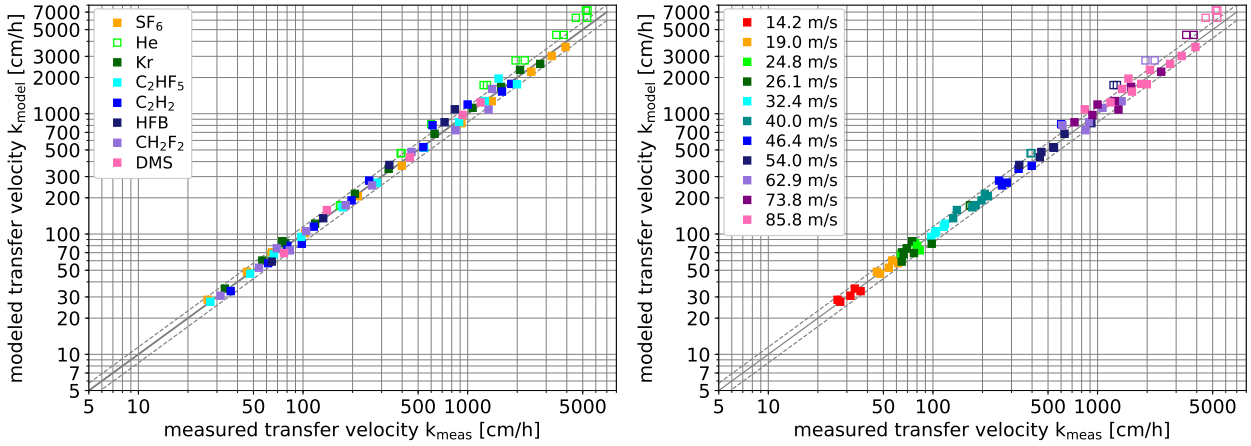
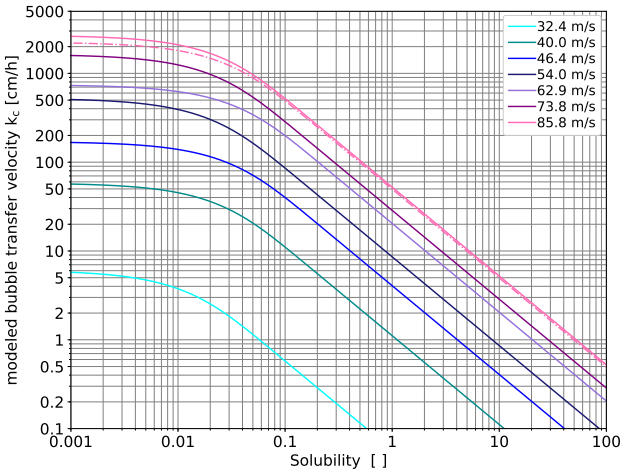


Figure 5: Kyoto seawater model experiment: Modeled vs. measured transfer velocities, colors corresponding to the tracers (a) and colors corresponding to the wind speeds used (b). The solid line marks perfect agreement, the dashed lines plus or minus 15%. He was excluded from the fit, therefore it is only shown here with open symbols. (c) bubble surface transfer velocity k_c in dependency of the solubility for the wind speeds, for which a bubble contribution was detected.



(a) (b)



(c)

Figure 6: Miami seawater experiment: Modeled vs. measured transfer velocities, colors corresponding to the tracers (a) and colors corresponding to the wind speeds used (b). The solid line marks perfect agreement, the dashed lines plus or minus 15%. He was excluded from the fit, therefore it is only shown here with open symbols. (c) bubble surface transfer velocity k_c in dependency of the solubility for the wind speeds, for which a bubble contribution was detected. The highest wind speed condition was repeated twice, one of the repetitions is shown as a dashed line, the other as a solid line.