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Air–sea gas exchange at wind speeds up to 85 $m\,s^{-1}$

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Model equations

These model equations are intended to be used for predicting the gas transfer velocity of any water side controlled gas (except very low Schmidt number Helium) in extremely short fetch conditions, e.g. in wind-wave tanks. They cannot be used in the field directly, since the onset of bubble mediated gas transfer and also the onset of the strongly turbulent regime might happen at different friction velocities in the field.

All $u_{*,w}$ in cm s^{-1}, all k in cm h^{-1}.
$k_{s,600}$ for fresh water and seawater:

$$k_{s,600} = \begin{cases} 3600/7.19\ u_{*,w}\ 600^{-0.5} & \text{if } 0.75 < u_{*,w} < 5.8 \\ 0.605\ u_{*,w}^{3.00} & \text{if } 5.8 \leq u_{*,w} < 15 \end{cases} \tag{1}$$

$k_{c,600}$ for fresh water:

$$k_{c,600} = \begin{cases} 0 & \text{if } 0.75 < u_{*,w} < 5.8 \\ 4.17(u_{*,w} - 5.8)^{2.20} & \text{if } 5.8 \leq u_{*,w} < 15 \end{cases} \tag{2}$$

$k_{c,600}$ for seawater:

$$k_{c,600} = \begin{cases} 0 & \text{if } 0.75 < u_{*,w} < 5.8 \\ 51.5(u_{*,w} - 5.8)^{1.82} & \text{if } 5.8 \leq u_{*,w} < 15 \end{cases} \tag{3}$$

k_r for fresh water and seawater:

$$k_r = \begin{cases} 0 & \text{if } 0.75 < u_{*,w} < 5.8 \\ 1.30(u_{*,w} - 5.8)^{1.75} & \text{if } 5.8 \leq u_{*,w} < 15 \end{cases} \tag{4}$$

More on the fit

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 for each used tracer calculated at the water temperature k_{meas} was measured at. In a first step, the fit routine minimizes (k_{tot}-k_{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 19 in the paper 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 19 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. For 10 wind speed conditions (low wind speeds with no bubble contribution) no iteration was required, 15 other wind speed conditions needed one iteration step. Only for three wind speed conditions (saltwater, Miami, highest wind speeds), up to 10 iterations were required.

Comparison between measured and modeled transfer velocities

Figures 1, 2 and 3 show comparisons between the measured and the modeled transfer velocities for the fresh water, seawater model and the seawater experiment, respectively. k_{model} was calculated using Eqn. 11 in the manuscript with the fitted parameters $k_{\text{s},600}$, $k_{\text{c},600}$ and k_{r}. Since Helium was excluded from the fit, it is shown here using open symbols. Please note that the transfer velocities measured span almost three orders of magnitude.

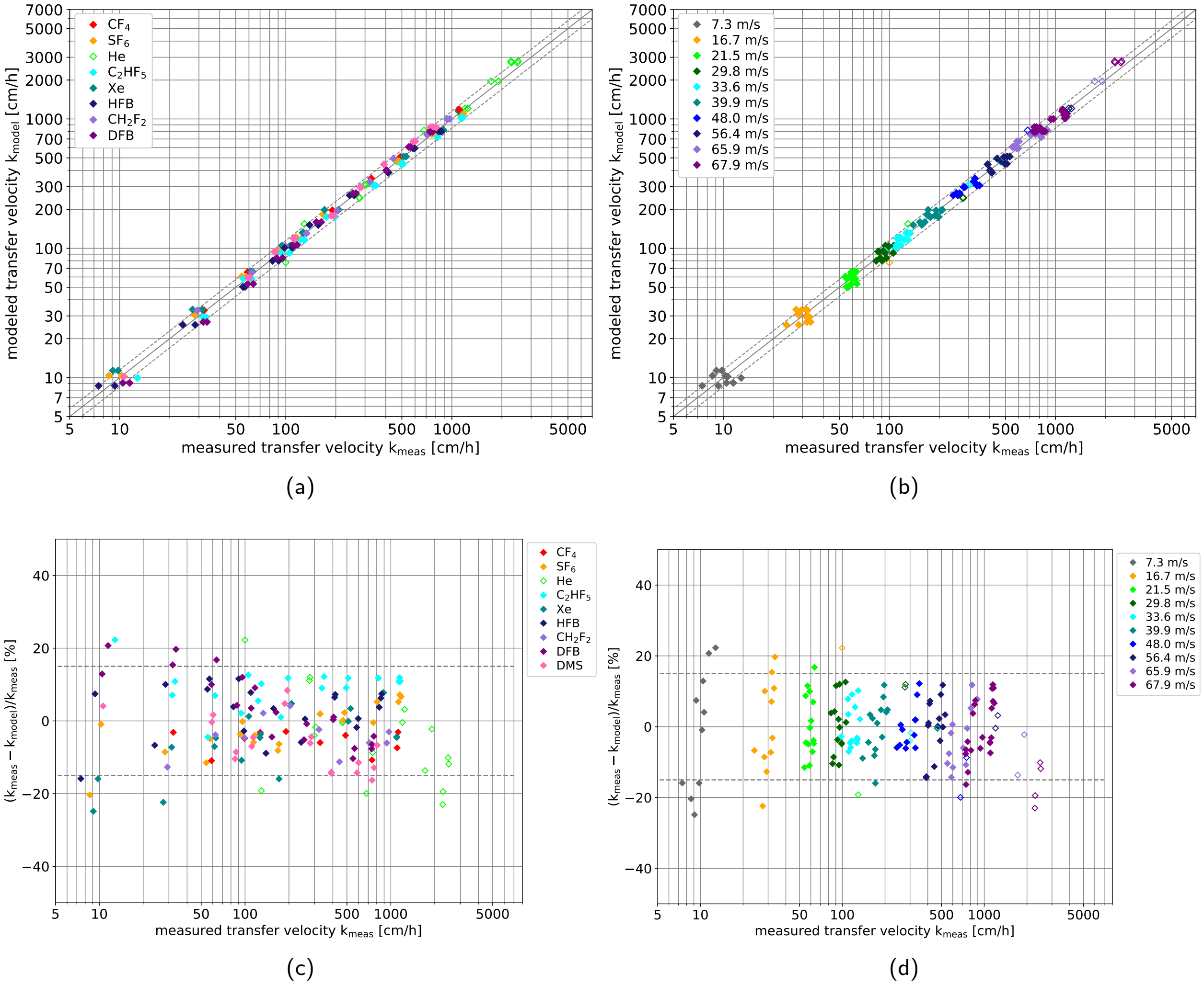
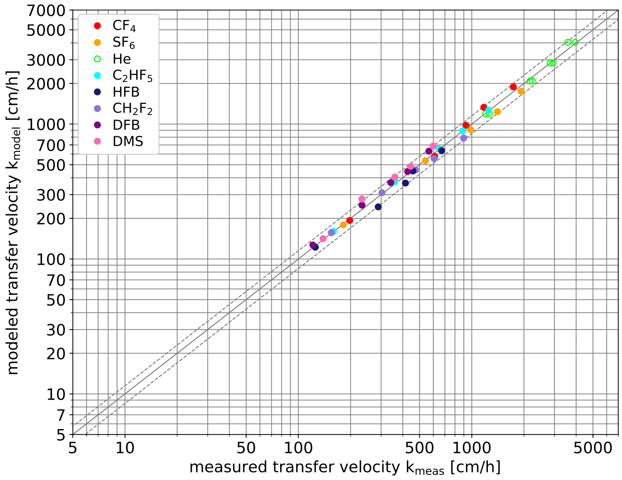
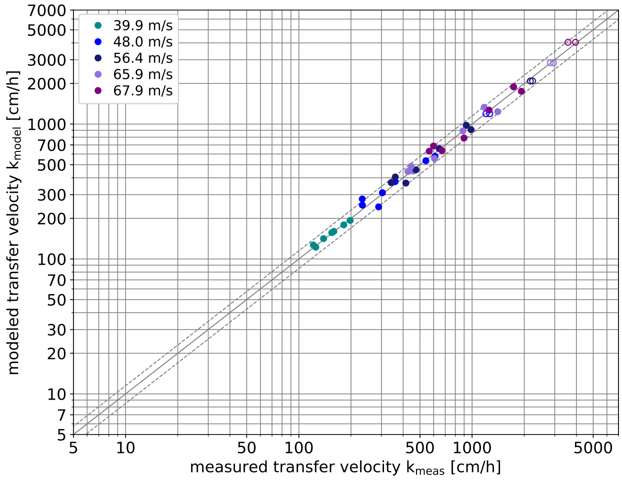


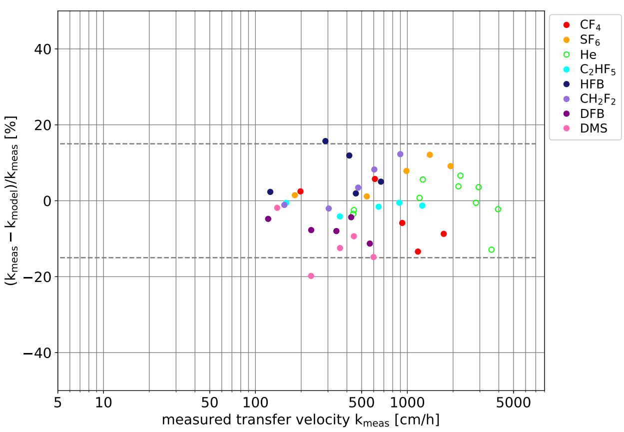
Figure 1: Kyoto freshwater experiment: Modeled vs. measured transfer velocities, colors corresponding to the tracers (a) and colors corresponding to the wind speeds used (b). The solid line marks perfect agreement, the dashed lines plus or minus 15%. (c) and (d) show the deviation between the measured and modeled transfer velocity in percent of the measured transfer velocity. He was excluded from the fit, therefore it is only shown here with open symbols.



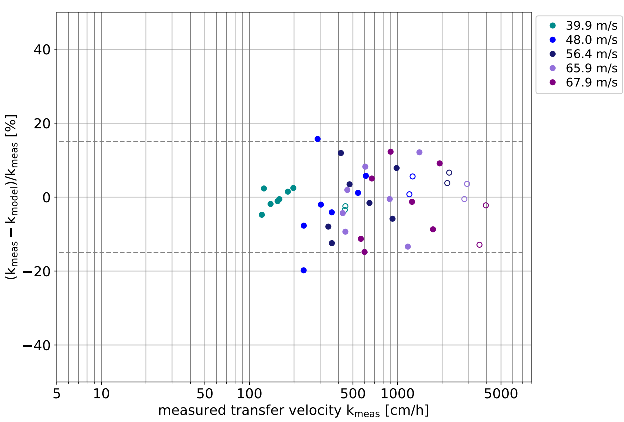
(a)



(b)



(c)



(d)

Figure 2: 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%. (c) and (d) show the deviation between the measured and modeled transfer velocity in percent of the measured transfer velocity. He was excluded from the fit, therefore it is only shown here with open symbols.

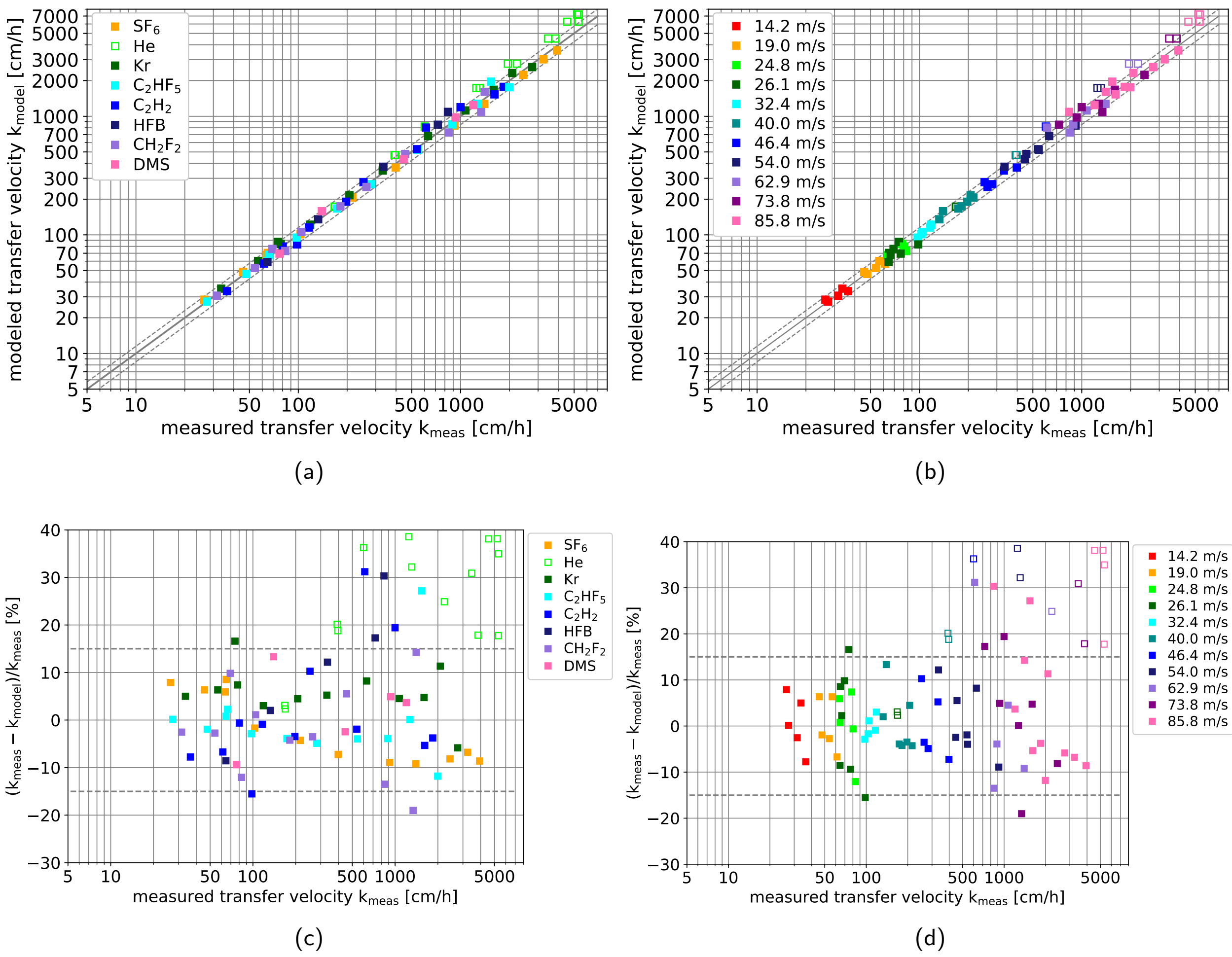


Figure 3: Miami seawater experiment: Modeled vs. measured transfer velocities, colors corresponding to the tracers (a) and colors corresponding to the wind speeds used (b). The solid line marks perfect agreement, the dashed lines plus or minus 15%. (c) and (d) show the deviation between the measured and modeled transfer velocity in percent of the measured transfer velocity. He was excluded from the fit, therefore it is only shown here with open symbols.

Modeled bubble surface transfer velocity k_c

Figure 4 shows the modeled bubble surface transfer $k_c(\alpha)$ curves for a tracer with Sc=600 according to Eqn. 10 in the manuscript (using Eqn. 9 as an expression for the transition solubility) using fitted values of $k_{\mathrm{c},600}$ and k_{r} for each wind speed condition in each of the experiments for which a bubble contribution was detected. The low solubility limit is equal to the parameter $k_{\mathrm{c},600}$. For solubilities higher than the transition solubility, the bubble surface mediated transfer k_c is proportional to the inverse solubility α^{-1}.

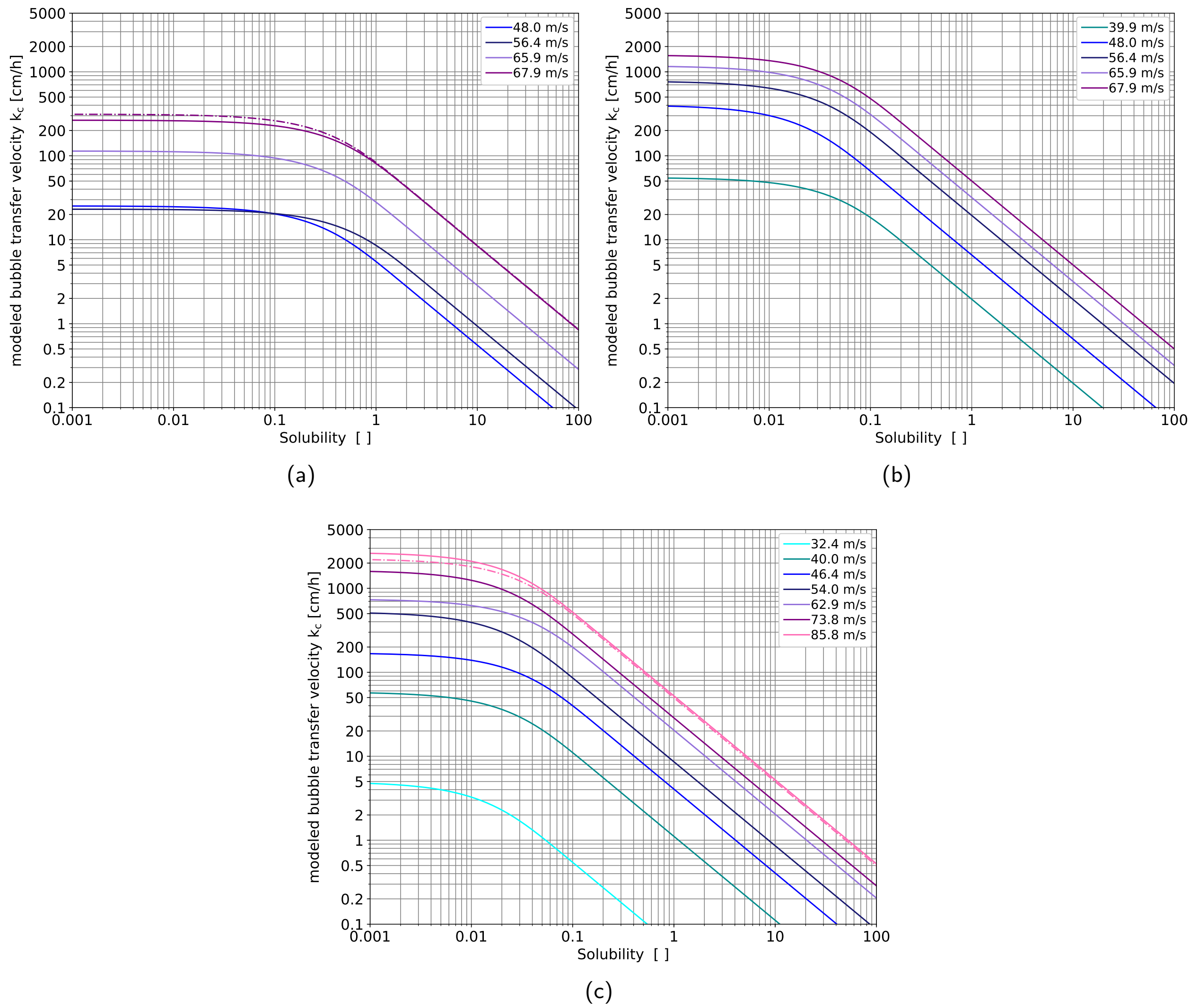


Figure 4: Bubble surface transfer velocities k_c calculated from fitted $k_{c,600}$ and k_r (Eqn. 10) in dependency of the solubility for the wind speeds, for which a bubble contribution was detected for the Kyoto fresh water experiment (a), the Kyoto modeled seawater experiment (b), and the Miami seawater experiment (c). For fresh water and seawater, the highest wind speed condition was repeated twice, one of the repetitions is shown as a dashed line, the other as a solid line.