A Comparative Lab Study of Transfer Velocities of Volatile Tracers with Widely Varying Solubilities

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Motivation and Goals

The solubility of volatile tracers in water has an important impact on the **gas transfer rates between the atmosphere and the ocean**. The velocity of the transport processes of **highly soluble tracers** is limited by diffusion in the **air sided** boundary layer, while the **water side** boundary layer affects the tracers with a very **low solubility**. Many **important environmental trace gases** (e.g. acetone, acetaldehyde, acetonitrile) are **driven by both processes**. The combination of these processes has not yet been investigated and the model that exists is very basic [1].

Background

Mass transfer through the air-sea boundary layer:

$$k = \frac{F}{\Delta c}$$

k: transfer velocity
Δc: concentration difference across the boundary layers
F: gas flux through interface

- interface can be considered as a two-layer film model
- bulk of each phase is well mixed by turbulence
- thin layers where the transport is driven by molecular diffusion
- at the interface is a jump in the concentration

$$c_{ws} = \alpha\, c_{as}$$ α : dimensionless solubility
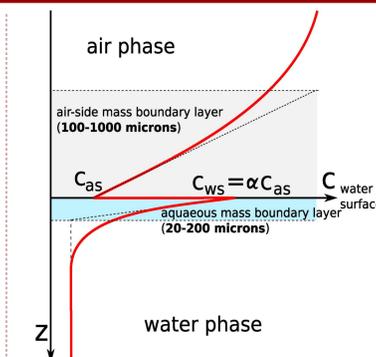
Example of a concentration profile of a tracer with the dimensionless solubility α ≈ 4.

Transfer resistance:

$$R = \frac{1}{k}$$

- adding two resistances R_{air} and R_{water} in air sided and water sided boundary layer is similar to resistances in electrical circuits:

$$R_{total} = \alpha\, R_{air} + R_{water} \qquad (1)$$

- unlike in electrical circuits, the tracers solubility needs to be taken into account [1].

Experimental Setup

In a pilot study at the *Aeolotron*, an annular wind wave facility, the transfer velocities of 16 tracers with with a solubility range of more then five orders of magnitude have been measured:

- the wind speed varied between 1.4 m/s and 8.4 m/s
- at the start of each new wind speed the facility was flushed with fresh air for twenty minutes to stabilze the conditions (e.g. waves)
- afterwards the facility was completly closed until the concentration equilibrium was achived for air sided tracers
- concentration time series of substances with low solubilities were measured by a fourier transform infrared spectrometer (FT-IR)
- concentration time series of the gases with high solubilities by a proton transfer reaction mass spectrometer (PTR-MS)
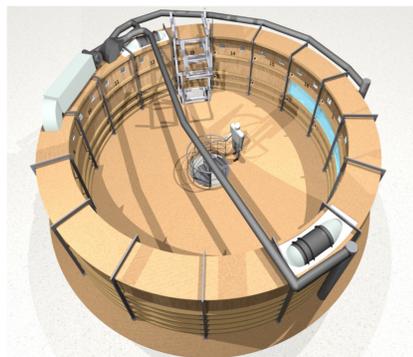
Rendered aerial view of the *Aeolotron,* the world's largest operational annular wind-wave facility.

Evaluation and Results

Air sided concentration time series of a high soluble tracer:
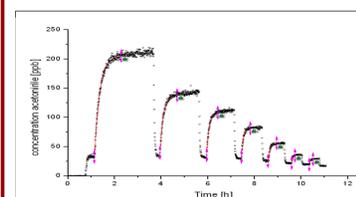
- an exponential fit yields the time constant
- by using a box model [2] and this time constant the transfer resistance is calculated

Air sided concentration time series of a low soluble tracer:
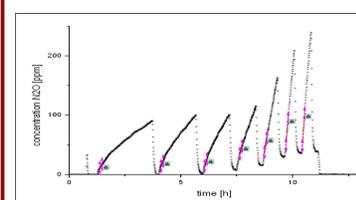
- a linear fit yields the temporal change of the tracer's air concentration
- by using a box model [2], this temporal change of the tracer's air concentration, the air concentration and water concentration of this tracer the transfer resistance is calculated

measured transfer resistance of tracers with low solubilities.

measured transfer resistance of tracers with high solubilities.

How to Determine Transfer Resistances

To determine the air sided transfer resistance of a tracer T:

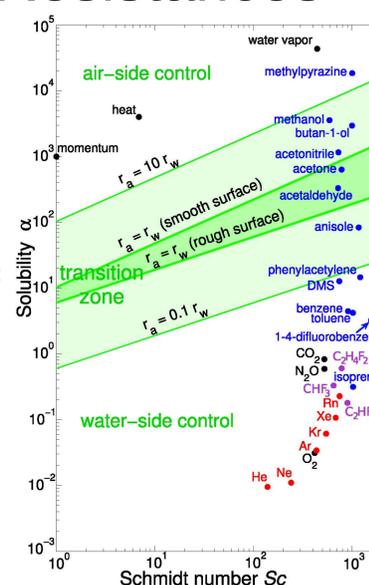$$R_{air}^{T} = \left(\frac{D^{HS}}{D^{T}}\right)^{n} R^{HS}$$

D: diffusitivy of trace gas
R^{HS}: resistance of a highly soluble substance (e.g. methanol)
n: Schmidt number exponent

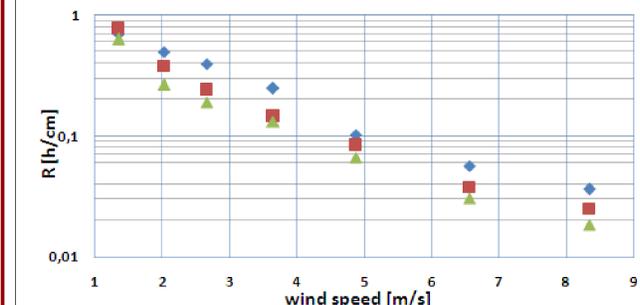**To determine the water sided transfer resistance of a tracer T:**

$$R_{water}^{T} = \left(\frac{D^{LS}}{D^{T}}\right)^{n} R^{LS}$$

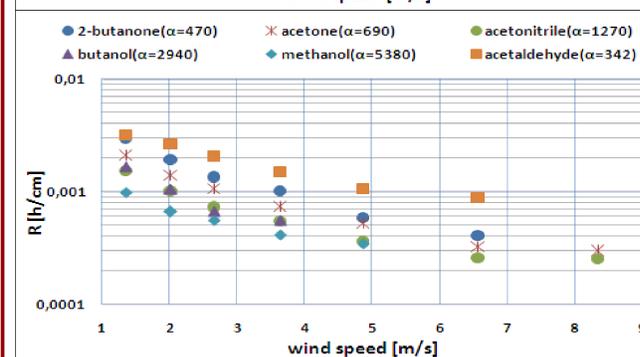R^{LS}: reistance of a low soluble substance (e.g. CHF_3)

- by adding the two calculated transfer resistances similar to equation (1) the total transfer resistance of the tracer T can be determined
- by comparing the calculated with the measured total resistance equation (1) can be proven

Outlook

- environmental parameters such as temperature and surfactant coverage will be varied in further experiments together with the Max Planck Institute for Chemistry, Mainz
- the new environmental conditions should then be included in equation (1)

References: [1] P. S. Liss and P. G. Slater. Flux of gases across the air-sea interface. Nature, 247:181–184, 1974.
[2] R. Nielsen. Gasaustausch - Entwicklung und Ergebnis eines schnellen Massenbilanzverfahrens zur Messung der Austauschparameter. Dissertation, Univ. Heidelberg, 2004.