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Air-Sea Gas Exchange under Nature-Like Surfactant Influence in the Lab

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Aims of this Study

Surface active material ("**surfactant**") on the water surface:
- modifies **near surface turbulence**
- hinders **wave formation** and
- **dampens waves**

all of this modifies the **gas transfer velocity** k

the goal is
- to **understand the physics** of gas transfer with surfactant influence
- to **accurately quantify** the gas transfer velocity with respect to surfactant coverage
- to develop a **physics based model** of gas transfer

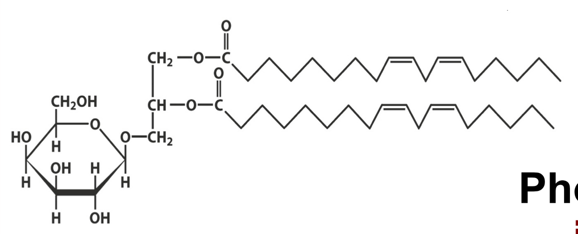
Surfactants

Surfactants are produced by:
- phytoplankton primary production (exudates: complex high-molecular weight polysaccharides)
- zooplankton grazing (digestion and by-products of ingestion ["sloppy feeding"])
- degradation products (degradation of exuded matter & dead organisms, chemical and microbiological)
- in coastal waters: terrestrial inputs (rivers, wet+dry)
- anthropogenic sources play a minor role.

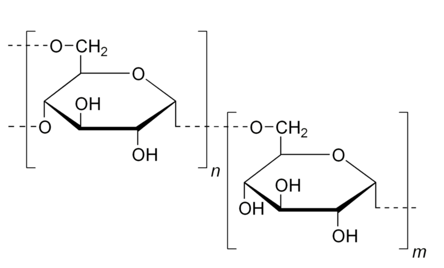
Surfactants are found almost everywhere on the water surface (Wurl et al. 2010).

these substances were chosen to model natural surfactants:

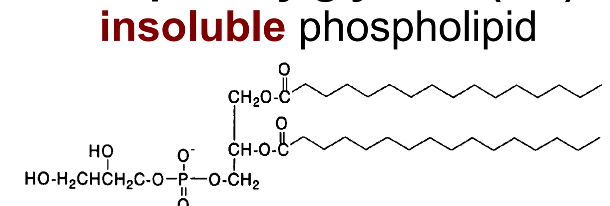
Mono-Galactosyl-Diacylglycerol (MGDG):
insoluble glycolipid



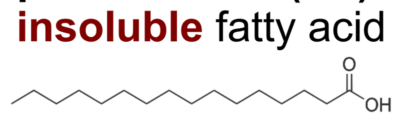
Dextran (D):
soluble polysaccharid



Phosphatidylglycerol (PG):
insoluble phospholipid

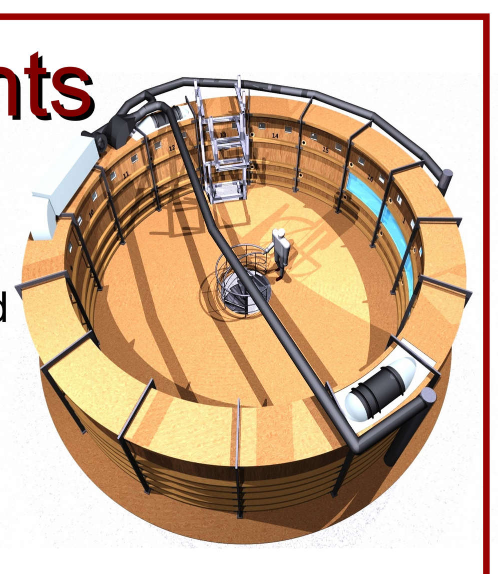


palmitic acid (PA):
insoluble fatty acid



More on the composition and distribution of natural surfactants can be found in:
Kattner and Brockmann, 1978; Zutic et al., 1981; Gašparovic et al., 1998; Gašparovic and Cosovic, 2003; Frew et al., 2006; Reinthaler et al., 2008; Tepic et al., 2009; Frka et al., 2011

The Experiments



were performed at the **AEOLOTRON** wind-wave tank

7 wind speeds between 1.7 and 14.8 m/s

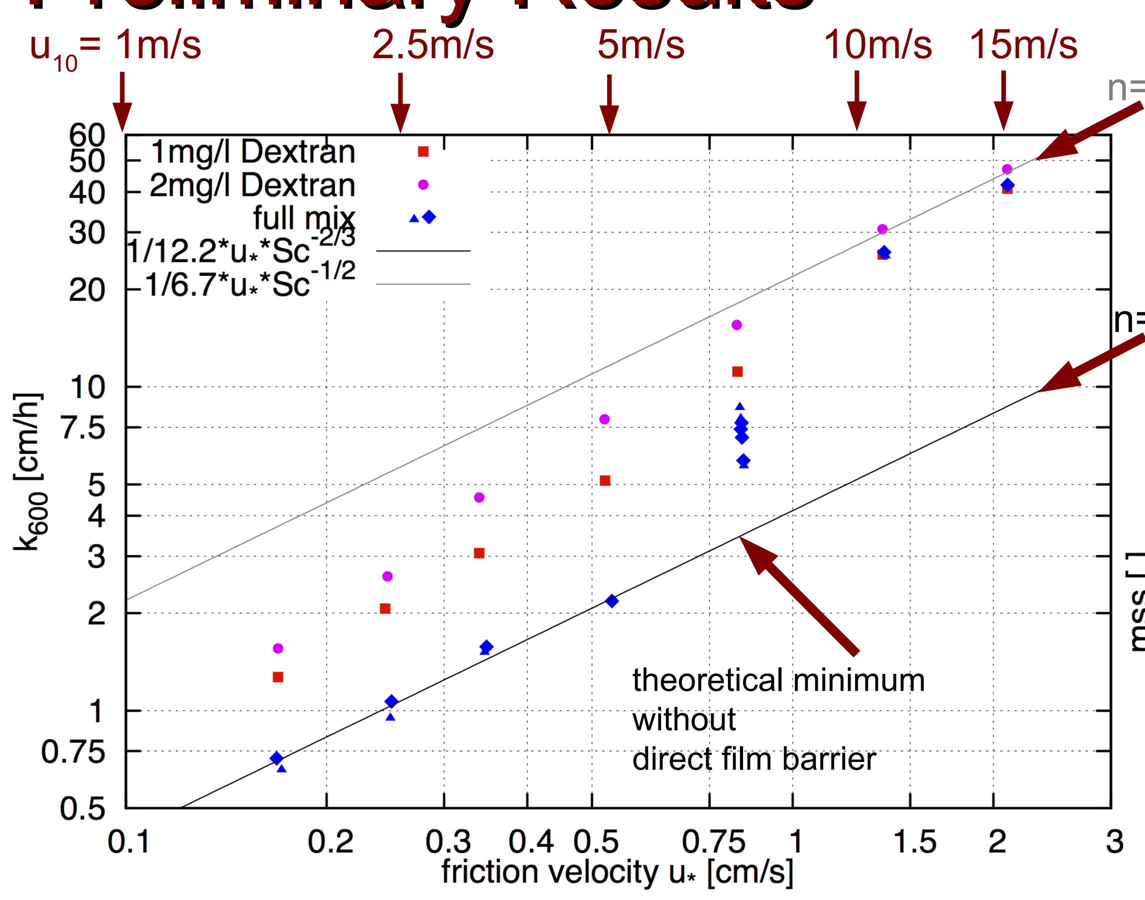
gas transfer velocities of 2 gases measured using FT-IR spectroscopy with a method described in Krall 2013

environmental conditions such as **mean square slope, friction velocity**, temperatures and humidity monitored

4 repetitions with different **surfactant conditions**:

1) 1mg/l Dextran (once)
2) 2mg/l Dextran (once)
3) **Full Mix:** 2mg/l Dextran + 5.3mg/m² MGDG + 2mg/m² PG + 0.4mg/m² PA (twice)

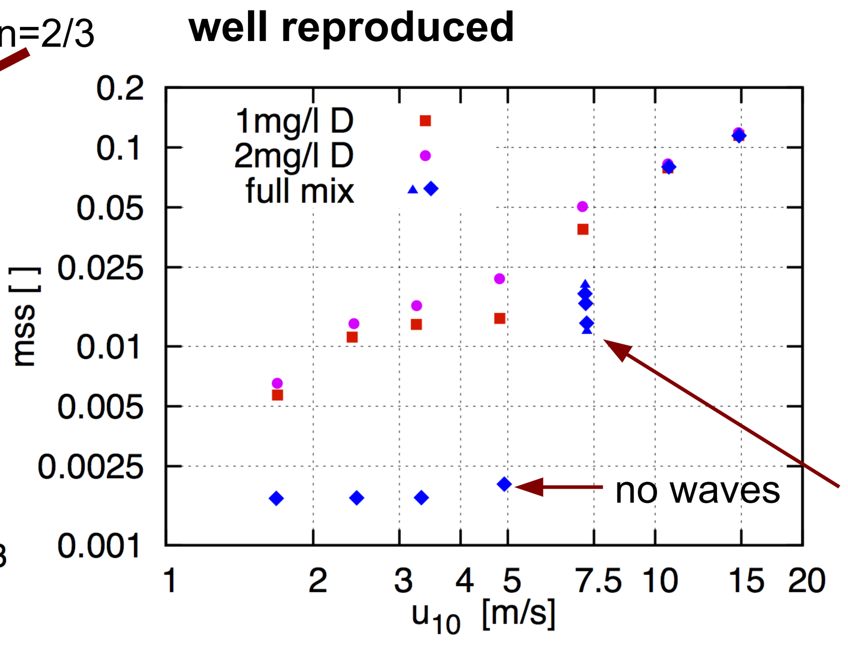
Preliminary Results



high variability with with up to **70% reduction in the gas transfer velocity** at the same wind speed for the different surfactant conditions

➡ gas transfer – wind speed relationships fail!

theoretical prediction of $k = \beta^{-1} u_* Sc^{-n}$
with n=2/3 for smooth and n=1/2 for rough water surface
well reproduced



the **mean square slope (mss)** is a wave parameter that describes the **"roughness"** of the water surface

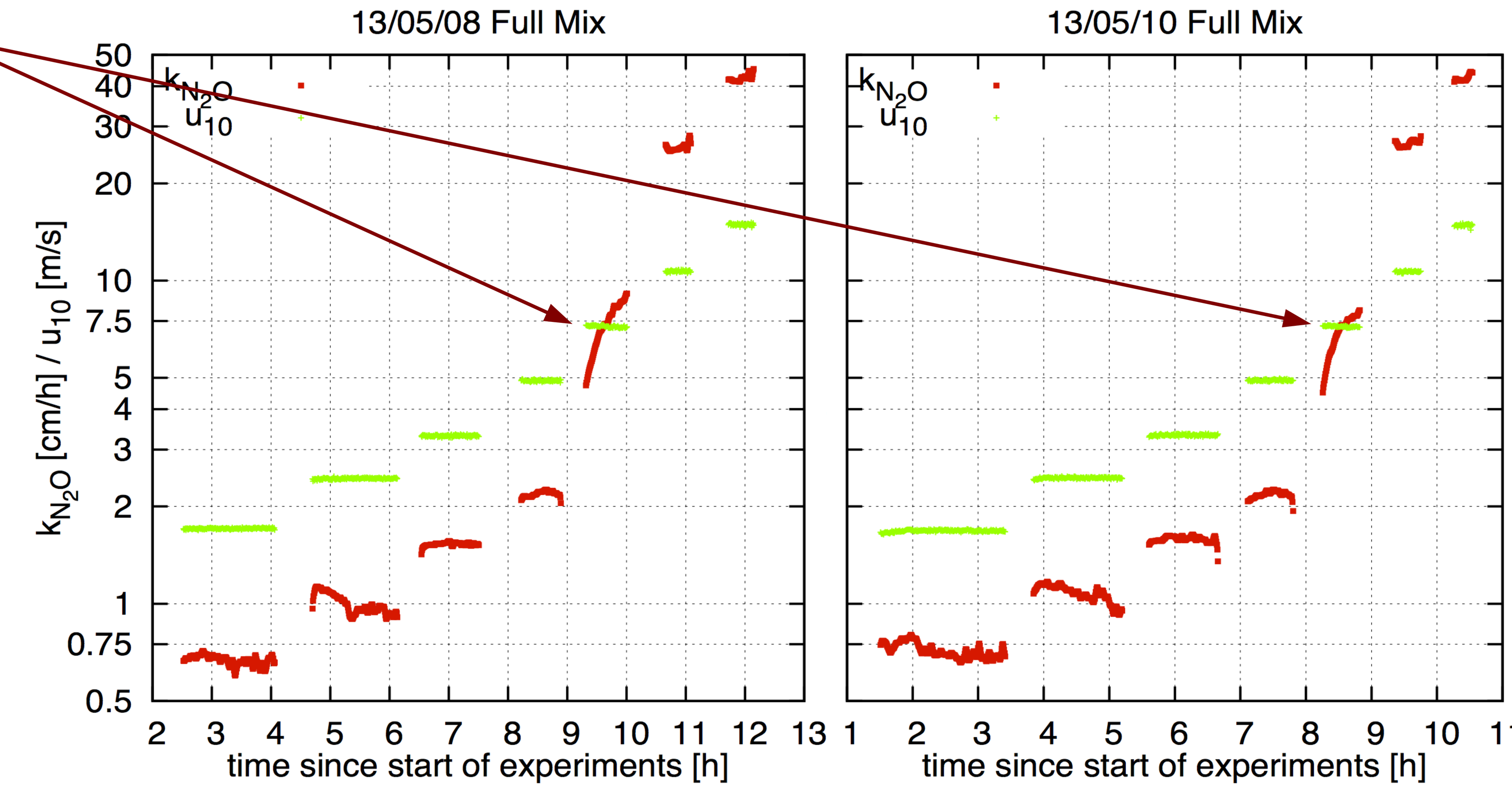
the full mix **suppresses waves** up to wind speeds of around **7 m/s**, where the first waves appear

at a **constant** wind speed **u_{10} of around 7m/s** the **gas transfer increased** by almost a **factor of 2** for the **Full Mix** cases

no such **increase** was seen for the **Dextran-only** cases

this indicates, that the **insoluble surfactant film** must have **ruptured** and was **mixed down** into the water bulk where it is ineffective in reducing gas transfer

this film rupturing is also seen in the mean square slope parameter



Comparison with a previous study using an artificial surfactant

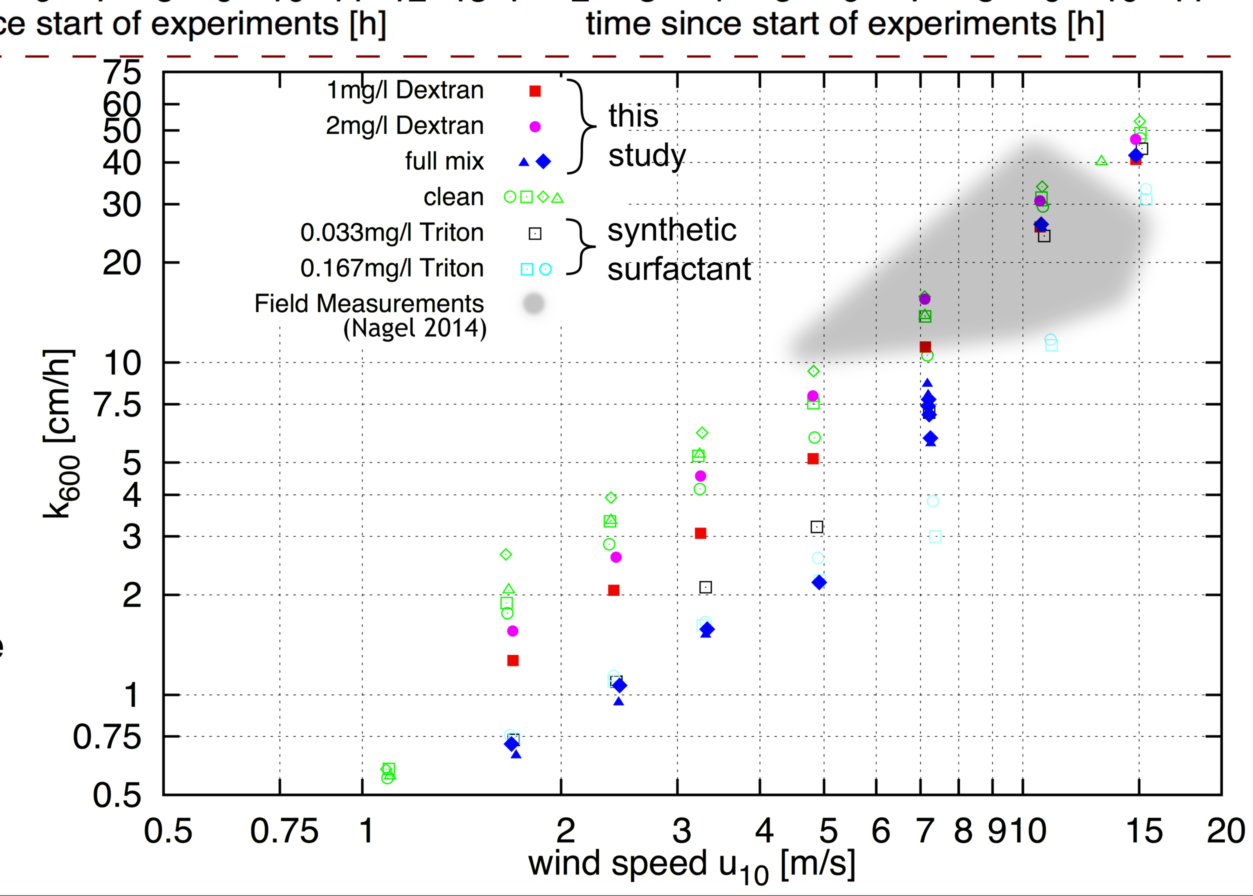
a **synthetic detergent (Triton X-100)** was used in **two concentrations** in a previous study in the Aeolotron

also, **clean conditions** were measured

Dextran alone has **little influence** on gas transfer

the **full mix** suppresses gas transfer velocity to the values observed with the **highest Triton X-100** concentration, but **surface film ruptures at lower wind speed**

for the **highest wind speeds**, **very little surfactant influence is seen**, even for the full mix cases



Conclusion & Outlook

gas transfer velocities with a nature-like surfactant mix were measured **for the first time** in the Aeolotron wind-wave tank

Dextran alone has little influence on the gas transfer velocity in the used concentration

the **full mix surfactant layer ruptured** at a wind speed of around **7m/s**

this **rupturing was seen** in the **transfer velocity** as well as in the **mean square slope**, which describes the water surface roughness

a **comparison with a previous study** using a synthetic surfactant shows **good reproducibility** of measured gas transfer velocities

the **amount of suppression** of gas transfer due to the full mix is **comparable to that of Triton X-100**

gas transfer velocities are **highly variable** at a fixed wind speed **depending on the surfactant coverage**
and therefore:
wind speed – gas transfer relationships do **not accurately describe gas transfer** under surfactant conditions

a **further study is needed**, where also surfactant parameters like **surface activity** is measured

the Aeolotron is equipped to measure with salty sea water, so it is **possible to use natural surfactant samples** collected from the ocean

combining all findings will lead to a **physics based model** of gas transfer

References: Nagel, L. **Active Thermography to Investigate Small-Scale Air-Water Transport Processes in the Laboratory and the Field**, 2014 (in prep.); Krall, K. E. **Laboratory Investigations of Air-Sea Gas Transfer under a Wide Range of Water Surface Conditions,** 2013; Sanja Frka et al. **Phytoplankton driven distribution of dissolved and particulate lipids in a semi-enclosed temperate sea (Mediterranean): Spring to summer situation**, 2011 (doi:10.1016/j.ecss.2011.04.017). Gašparovic et al. **Surface-active properties of organic matter in the North Adriatic Sea**, 2013 (dpi:10.1016/S0272-7714(03)00133-1); Gašparovic et al. **Contribution of organic acids to the pool of surface active substances in model and marine samples using o-nitrophenol as an electrochemical probe**, 1998 (dpi:10.1016/S0146-6380(98)00055-2); Kattner and Brockmann **Fatty-acid composition of dissolved and particulate matter in surface films**, 1978; Rheintaler et al. **Dissolved organic matter and bacterial production and respiration in the sea-surface microlayer of the open Atlantic and the western Mediterranean Sea**, 2008 (dpi:10.4319/lo.2008.53.1.0122); Tepic et al. **Multivariate statistical analysis of the distribution patterns of carbohydrates and surface-active substances in the northern Adriatic Sea**, 2009 (doi:10.1016/0304-4203(81)90004-9); Zutic et al. **Surfactant production by marine phytoplankton**, 1981 (doi:10.1016/0304-4203(81)90004-9); Wurl, O.; Wurl, E.; Miller, L.; Johnson, K. & Vagle, S. **Formation and global distribution of sea-surface microlayers.** Biogeosciences, 2011, 8, 121-135.
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