Investigating the mechanisms of air-sea gas exchange at hurricane wind speeds in wind-wave tunnel experiments

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Existing measurements
at hurricane wind speeds in the field

Existing measurements at hurricane wind speeds in the field


- Measurements in hurricane *Frances* 2004 using unmanned buoys
- Modeled
- Parameterizations developed for lower wind speeds
- Parameterization developed in McNeil&D’Asaro2007

\[ k_{\text{McN}} = 14 + a \cdot u_{10}^b \]

\[ a = 0.0002925 \ (-0.001215, 0.0018) \]
\[ b = 3.742 \ (2.415, 5.069) \]
The high speed wind-wave tank

length: approx. 15.7 m
flume width: 80 cm
water depth: 80 cm
air ‘height’: 80 cm
water volume: 10.0 m$^3$
air volume: 10.0 m$^3$
surface area: 10.3 m$^2$
$u_{10}$: 7.0-67 m/s (@6.5m fetch)
The high speed wind-wave tank

Wind increasing to 67 m/s
trace amount of Butanol modifies bubble size distribution by hindering coalescence here: 0.5 liters Butanol in 13,700 liters of water this is not enough to significantly change the surface tension
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Salt water model
Wind at 67 m/s
# Tracers

<table>
<thead>
<tr>
<th>Tracer</th>
<th>D  ([10^{-5}\text{cm}^2\text{s}^{-1}])</th>
<th>(\alpha) [ ]</th>
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<tbody>
<tr>
<td>SF(_6)</td>
<td>1.06</td>
<td>0.006</td>
</tr>
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<td>0.0095</td>
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![Graph showing solubility vs. Schmidt number](image)
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![Graph showing the relationship between solubility and Schmidt number](image-url)
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Hiden HPR-40 membrane inlet mass spectrometer
Measured transfer velocities with fresh water

How to compare this to other measurements?

Use Schmidt number scaling?
Schmidt number scaling

\[ \frac{k_A}{k_B} = \left( \frac{Sc_A}{Sc_B} \right)^{-\frac{1}{2}} \]

for partially air side controlled tracers:

\[ \frac{1}{K} = \frac{1}{k_w} + \frac{1}{\alpha k_a} \]

→ Schmidt number scaling is not applicable for partially air side controlled tracers

at high wind speeds:

\[ k = k_o + k_b \]

total transfer velocity  ‘direct’ transfer  bubble contribution

\[ k_b \text{ depends on } Sc \text{ and } \alpha \]

→ Schmidt number scaling is not applicable when there are bubbles

**turn this argument around:** differences found between gases after Schmidt number scaling to \( k_{600} \) can be attributed to either (partial) air side control or solubility dependent bubble effects!
Measured transfer velocities in fresh water scaled to $k_{600}$

methyl acetate has lower transfer velocities for all wind speeds

→ additional air side resistance!
Measured transfer velocities in fresh water scaled to $k_{600}$

![Graph showing measured transfer velocities vs. wind speed]

- $SF_6$
- He
- $Xe$
- $C_2HF_5$
- HFB
- $CH_2F_2$
- DFB
- DMS

Transferring velocities $k_{600}$ [cm/h] vs. wind speed $u_{10}$ [m/s]
Measured transfer velocities in fresh water scaled to $k_{600}$

Very small differences between gases at high wind speeds.

Weak bubble contribution in fresh water!
Measured transfer velocities in fresh water scaled to $k_{600}$ and friction velocity

Lab data sets:


Measured transfer velocities in fresh water scaled to $k_{600}$ and friction velocity

**Transfer velocity $k_{600}$ [cm/h] vs. friction velocity $u_{*,w}$ [cm/s]**

- SF6
- He
- Xe
- C$_2$HF$_5$
- HFB
- CH$_2$F$_2$
- DFB
- DMS
- HFB K2013
- DFB K2013
- CO$_2$ I2013

**Lab data sets:**

**Friction velocity $u_{10}$:** 35 m/s
Measured transfer velocities in fresh water scaled to $k_{600}$ and friction velocity

![Graph showing transfer velocities vs friction velocity](image)

- $u_{10}=35\text{ m/s}$

Lab data sets:

Measured transfer velocities
in fresh water scaled to $k_{600}$ and friction velocity

![Graph showing measured transfer velocities vs friction velocity](image)

- $u_{10} = 35 \text{ m/s}$

- A new regime of gas transfer starts at approx. 35 m/s, in which $k \propto u^3 \ldots u^4$

- Solubility dependent bubble mediated gas transfer is not the dominant cause of this increase!

Lab data sets:
Measured transfer velocities
in salt water model scaled to $k_{660}$

---

clear solubility dependency at high wind speeds!
Measured transfer velocities
in salt water model scaled to $k_{660}$ compared to field data

lab data comparable to field data indicates that all essential physical mechanisms governing gas exchange in the field are replicated in the lab

Bubble enhancement at $u_{10}=64\text{ms}^{-1}$

Fresh water compared with salt water model at 20°C

$$
Ef = \frac{k^{\text{swm}}_{660} - k^{\text{fw}}_{660}}{k^{\text{fw}}_{600}}
$$

Enhancement $Ef$ [%] vs. solubility []

- SF$_6$
- He
- C$_2$HF$_5$
- CH$_2$F$_2$
- HFB
- DFB
- DMS

Up to 95% enhancement of gas transfer in salt water model for CO$_2$ ($\alpha=0.83$) likely very weak bubble influence!
What about DMS? limited exchange velocities observed in the field

![Graph showing DMS transfer velocity vs. wind speed](figure_from: Bell, T. G.; De Bruyn, W.; Marandino, C. A.; Miller, S. D.; Law, C. S.; Smith, M. J. & Saltzman, E. S. Dimethylsulfide gas transfer coefficients from algal blooms in the Southern Ocean ACP, 2015, 15, 1783-1794)

**figure from:**
Vlahos, P.; Monahan, E.; B.J.Huebert & Edson, J.
Wind-dependence of DMS transfer velocity: comparison of model with recent southern ocean observations
What about DMS?
limited interfacial exchange observed in the field but not in the lab


no limit or plateau observed in our study!
Conclusions

Comparability between lab and field data confirms that the essential mechanisms are replicated in the lab at high wind speeds above 35 m/s:
- New regime with much steeper increase of the gas transfer velocity found in agreement with previous studies.

In fresh water:
- Bubble effects for all gases very small, likely negligible for CO₂.

In salt water model:
- Up to 95% increase in the gas transfer velocity found for the lowest solubilities.
- No increase found for solubilities above approx. 1, so bubble effects for CO₂ likely very small, even in salt water!

No limited transport velocity for DMS observed.

Next step: confirm this with real salt water.
Surface Tension of Butanol
measured with a bubble tensiometer at 22.5°C

pure water: 72.37mN/m @ 22.5°C

used concentrations of Butanol in this study: max. 35mg/l

Butanol does not lower the surface tension below that of pure water in the concentrations used in this study!

1-Butanol

10mg/l 100mg/l 1000mg/l 10000mg/l

1000
100
10
1
0.1
0.01

45
50
55
60
65
70
75

surface tension [mN/m]

bubble life time [s]
Water side mass balance
for an evasion experiment

Mass balance equation:
\[ \Delta m = m_{in} - m_{out} \]

Water side mass balance:
\[
V_w \dot{c}_w = -kA(c_w - \alpha c_a) - \dot{V}_w c_w
\]

Assuming \( c_a \approx 0 \) yields exponentially decreasing water side concentration:
\[
c_w(t) = c_w(0)e\left(- \left(\frac{A}{V_w}k + \frac{\dot{V}_w}{V_w}\right)t\right)
\]
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Fetch Dependency

Water Surface at the Wind Inlet at 67m/s with fresh water

wind

10cm