

Discussion Session SOLAS Open Science conference Kiel, September 2015:  
**Relationship between wind speed and gas exchange over the ocean:  
Which parameterisation should I use?**

*Session chairs:*

David Ho, U. Hawaii, Honolulu USA

Rik Wanninkhof, NOAA/AOML, Miami USA

*Rapporteur:*

Phil Nightingale, Plymouth Marine Lab, Plymouth UK

Attendance: approximately 40

Introduction

Wanninkhof provided a general introduction on approaches used to determine relationships between gas transfer velocity ( $k$ ) and wind speed ( $u$ ), henceforth called  $k$ - $u$  relationships/parameterizations. There are two widely approaches to development of such relationships (**Figure 1**):

1. Empirical fit to field or laboratory data

2. Using fundamental boundary layer physics. These are often adjusted to experimental data and often need tuning and/or adjustment parameters.

Both should be validated by global constraints (e.g. bomb  $^{14}\text{C}$  uptake).

Wind is mostly used as a predictor as it can explain  $\approx 80\%$  of the variance of  $k$  values in dual tracer (DT) studies. However, we need to remember that other factors are known to affect  $k$  (**Figure 2**) Wind products (CCMP and NCEP2) impact the derived  $k$ - $u$  relationships as well. Not only the absolute wind speeds but also the wind speed distribution is important. For instance global ocean  $\text{CO}_2$  fluxes show efflux at low wind and influx at high winds (see **Figure 3**).

When determining relationships between  $k$  and  $u$  from DT studies it is seldom that there are high (or low) winds for the duration of the interval over which  $k$  is determined. Therefore there are little DT data at high and low winds (i.e. outside 4- 14 m/s). However, curve-fitting techniques using a presumed functionality of  $k$ - $u$  can shed light on gas transfer at very high and very low winds if they occurred part of the time during the time interval of study.

Discussion

The discussion was freewheeling and included questions by the audience that were addressed by others in audience, the session chairs or rapporteur. Below are the salient points by topic.

*Functionality of the  $k$ - $u$  relationships*

Several basic questions regarding the developed relationships were posed including if there was any physical basis to the functionality of empirical equations. A linear relationship suggests that gas transfer follows a solid wall theory; a quadratic indicates that gas transfer follows wind stress while a cubic suggests that gas transfer is related to energy dissipation. A cubic expression is also often related to impact of bubbles on gas exchange. A polynomial expression such as proposed in Wanninkhof et al. 2009 (W-2009) can be interpreted as several of these processes controlling gas transfer.

*Wind speed distributions*

Some of the earlier parameterization distinguished between long and short term winds with different  $k$ - $u$  parameterization for each (e.g. Wanninkhof, 1992). This was necessary as there were no high-resolution wind speed products available at that time. This distinction is no longer needed as there are several wind products that provide high-resolution output (winds up to 4 times a day at 25 X 25 km resolution). The exact resolution depends on the scale of the study in that that the full frequency spectra of winds should be captured. If "short term winds" are not available for a study area the frequency distribution from e.g. a climatology can be used along with the associated non-

linearity factor  $(= (u_{\text{mean}})^2 / (u^2)_{\text{mean}})$ . All k-u parameterizations developed since 2000 are for short-term winds.

#### *Dual deliberate tracer (DT) studies*

Results from dual tracer study appear applicable for k-u relationships applicable to CO<sub>2</sub> exchange which at face value is surprising as the DT use <sup>3</sup>He and SF<sub>6</sub> that are both sparingly soluble and therefore more susceptible to bubble enhanced exchange than the more soluble gas CO<sub>2</sub>.

Laboratory experiments (Asher and Wanninkhof, 1995) and field studies (Nightingale et al., 2000), show that the DT approach yields a Sc dependence of 0.5 and agreement of results with global <sup>14</sup>C constraints confirm that the DT approach can be used for CO<sub>2</sub> fluxes. DT measurements have challenges. At high winds and high sea states it is difficult to obtain samples. DT requires time intervals from 0.5 to 4 days to get a reliable concentration difference. Because of different time and space scales of EC and DT measurements comparison of the methods is difficult.

There should be independent validation the DT approach with <sup>3</sup>He and SF<sub>6</sub> by using another gas/technique, especially at high winds and for a variety of gases. Ideally, a non-volatile tracer would be used in the DT technique but studies using spores (Nightingale et al., 2000) and dyes are not that accurate due to non-conservative nature of the non-volatile tracers and/or the high minimum detection limits. The studies are difficult to execute.

#### *Eddy correlation (EC) techniques*

Current advances in eddy correlation (EC) techniques show tremendous promise but it remains a tricky measurement with possible instrumental and calculation biases. Also, the EC approach measures a flux (over an sometimes ill-defined footprint) and concurrent surface water concentration measurements must be performed to determine the k. The older published EC kCO<sub>2</sub> data are often higher than the k derived from DT (Jacobs et al. 2002). In these cases CO<sub>2</sub> was measured in moist air requiring a large and uncertain Web correction (**Figure 4**). More recent, but presently unpublished, EC measurements agree with DT for CO<sub>2</sub> (Bell et al. pers comm). The EC kDMS (dimethylsulfide) is significantly lower than EC for kCO<sub>2</sub> that is attributed to bubbles affecting the k for CO<sub>2</sub> more than the k for DMS in line with the solubility of DMS being 10 times greater than that the CO<sub>2</sub> (Bell et al. 2013). Based on comparisons between DMS and CO<sub>2</sub> exchange in a wave breaking simulation tank (Asher et al. 1996) this suggest a very large contribution by bubble-mediated exchange. Some EC results for DMS show that k rolls over at high winds if bin averaged. However, when the data is not bin-averaged the anomalies are associated with a particular time period/location (**Figure 5**). This indicates that other factors than wind speed are impacting the DMS fluxes on local scales. The ability to determine k on 30-minute and sub-km<sup>2</sup> scale opens avenues to improve process level understanding on the factors impacting k. However, very small signal to noise of the EC measurements leads to large uncertainties in the point measurements and some type of averaging is required. Furthermore, the measurements require quality micrometeorological measurements and sensors with high frequency response (> 10 Hz).

#### *Gas transfer at low and high winds*

Aside from lack of measurements at high and low winds there are many unique environments that need better k values and improved parameterizations. In particular, we need more process level information for coastal studies, as wind speed by itself is not sufficient. There can be fetch, bottom boundary, and surfactant effects. Also, there is a need for coastal wind products that properly capture wind patterns on local scales including land/sea breezes and orographic winds caused by continental effects.

There is also a need to improve information on uncertainties in the measurements and their associated techniques. The 'real' uncertainties below 4 and above 12 m/s are not well constrained. The 5 % uncertainty for kCO<sub>2</sub> inferred from the full range of measurements is probably not applicable for high and low wind speeds. There are only few DT points available at high and low

winds (**Figure 6**) but the extremes carry a lot of weight in curve fitting. The error analysis should be redone using only DT measurements in the 4-12 m/s range.

#### *Satellite winds*

There is a need to better understand the forcing functions of  $k$ . Direct ocean 'measurements' instead of wind derived from 'products' such as backscatter is preferred. White caps, wave slope are difficult to measure. It can be done in a process study but difficult they are difficult to do routinely/operationally.

There is a need to consider uncertainty in satellite derived wind speeds and the impact of the large footprint of these measurements. Algorithms to convert from backscatter to wind speed are probably too simple. Footprint size and signal degradation means that high winds  $> 20$  m/s are routinely underestimated using common backscatter –wind speed conversions. The backscatter signal flattens out at high winds/sea states making them less sensitive. Recent research has shown that wind speed can be measured very precisely but this is not routine on most ships. Wind stress that is better related to surface conditions controlling gas transfer,  $u^*$ , can be measured using a sonic anemometer. Wind stress may be more accurately determined from satellites. Using the raw backscatter signal,  $\sigma_0$ , as an indicator of forcing is another base level approach that should be further investigated

#### *Gas transfer for soluble gases*

It is well known that soluble gases behave differently than  $\text{CO}_2$  but  $k$ - $u$  relationships derived from  $\text{CO}_2$  are commonly used for soluble gases. We need further regional studies studying gas transfer of more soluble gases. EC techniques may be a way forward for more soluble gases. Soluble gases will offer the opportunity to test the hypothesis that differences between DMS and  $\text{CO}_2$  are due to bubbles, as soluble gases have a limited bubble effect. The increased experience in using EC has improved precision, improved understanding of the measurements and reduced artefacts.

There currently are no tested  $k$ - $u$  relationships for soluble gases. The recommendation as to what to use to derive fluxes for soluble gases such as  $\text{CH}_3\text{Br}$  would be to use the NOAA-COARE model (**Figure 7**). The model requires at least two tuning parameters and requires knowledge of bubbles and their distribution with wind speed. These factors are poorly constrained and introduce an uncertainty in NOAA-COARE. For soluble gases this should be less of an issue as bubbles should not be an important contributor to the exchange of soluble gases. The COARE model has been used for ozone,  $\text{O}_3$  (Fairall et al. 2006), which for practical purposes has an infinitely high solubility in seawater (because of its very fast reaction time). Photolysis reactions producing  $\text{O}_3$  in the microlayer could impact surface concentrations and conversion of the measured EC flux to a  $k$ .

#### *Sea-air oxygen fluxes*

Little work has been done on determining the gas transfer of oxygen although it is an important gas in biogeochemical cycling and used to determine ocean anthropogenic  $\text{CO}_2$  uptake via atmospheric  $\text{CO}_2/\text{O}_2$  changes (Manning and Keeling, 2006). Some prelim work (Rutgerson, pers. com.) shows higher  $k_{\text{O}_2}$  than  $k_{\text{CO}_2}$  but questions remain how accurate the  $\text{O}_2$  concentration differences can be measured in the air with the EC technique considering the very high  $\text{O}_2$  levels in the atmosphere.

#### *From laboratory study to sea*

There was a discussion when/if laboratory results from fresh water can be extrapolated to seawater/oceans. There are many scaling issues that have to be addressed in this conversion as well as large differences in seawater and fresh water bubble populations

#### Recommendations

Several recommendations were offered by the session participants including:

- For gas transfer of CO<sub>2</sub> over the oceans the relationships proposed in Nightingale et al. (2000), Sweeney et al. (2007), Ho et al. (2006), and Wanninkhof et al. (2009) are recommended. They are very similar and fall within the overall uncertainty of DT measurements. The relationships by Liss and Merlivat (1986) Wanninkhof 1992 and McGillis et al. (2001) do not agree with current constraints.
- An updated summary Schmidt number and solubilities and adjustments in the canonical Wanninkhof 1992 relationship can be found in Wanninkhof (2014).
- Controlled studies on determining the effect of factors other than wind are urgently needed including the effect of bubbles, surfactants, boundary layer stability (air and water), and ice.
- An improved uncertainty analysis, particularly for EC measurements is necessary.
- Field and laboratory studies looking at the k-u parameterizations for soluble gases.

Figures:

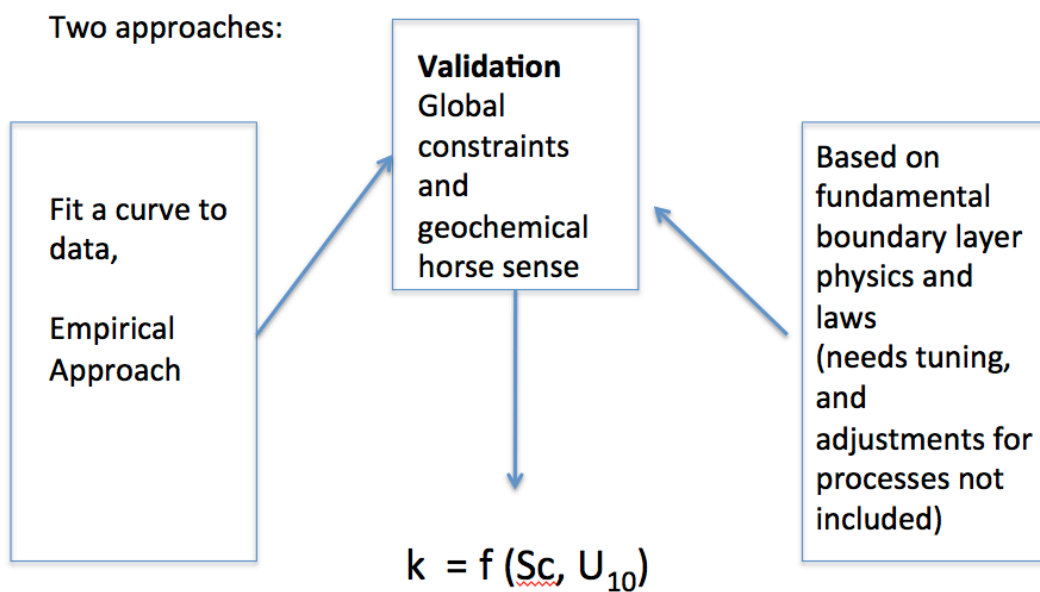


Figure 1.

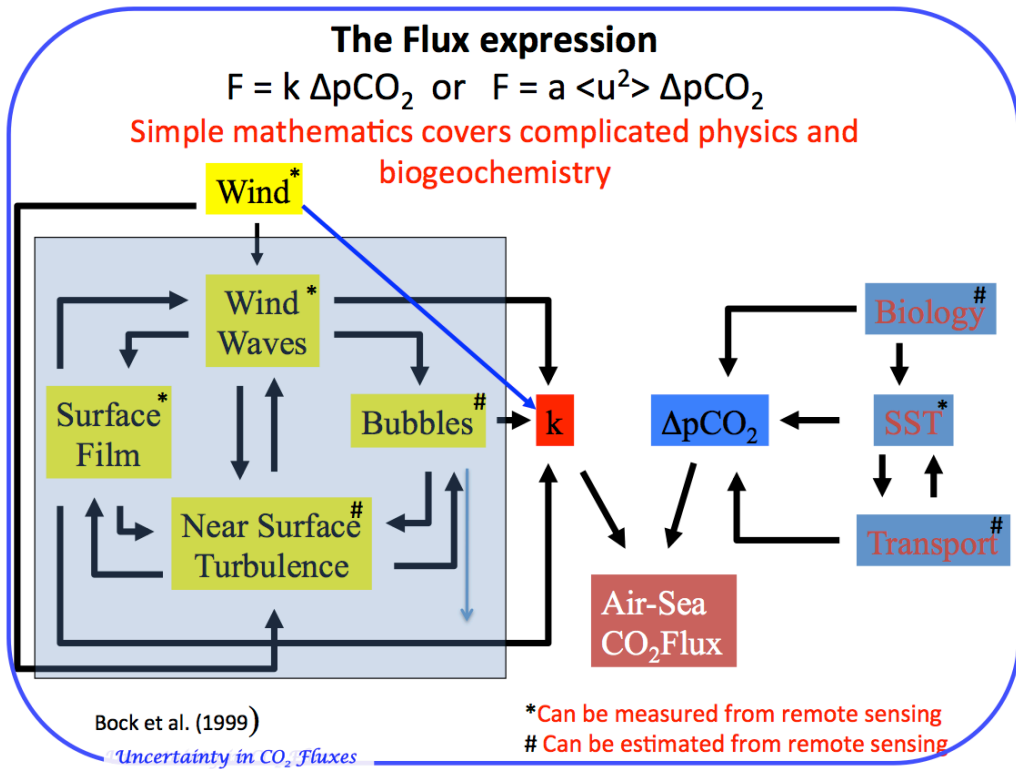


Figure 2.

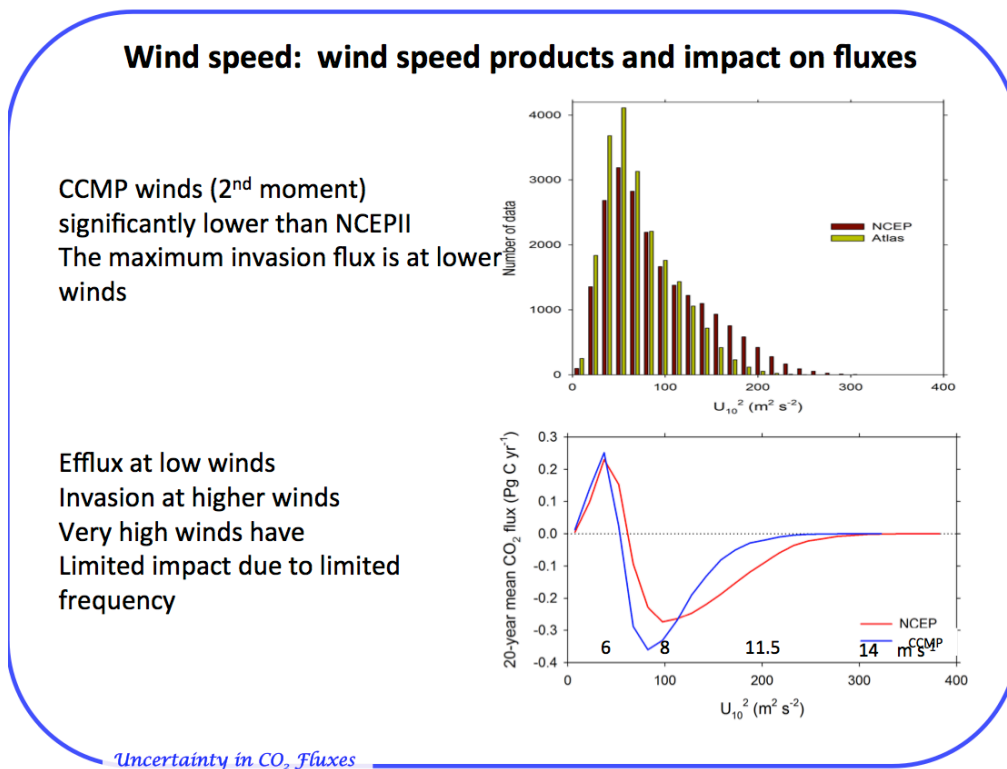
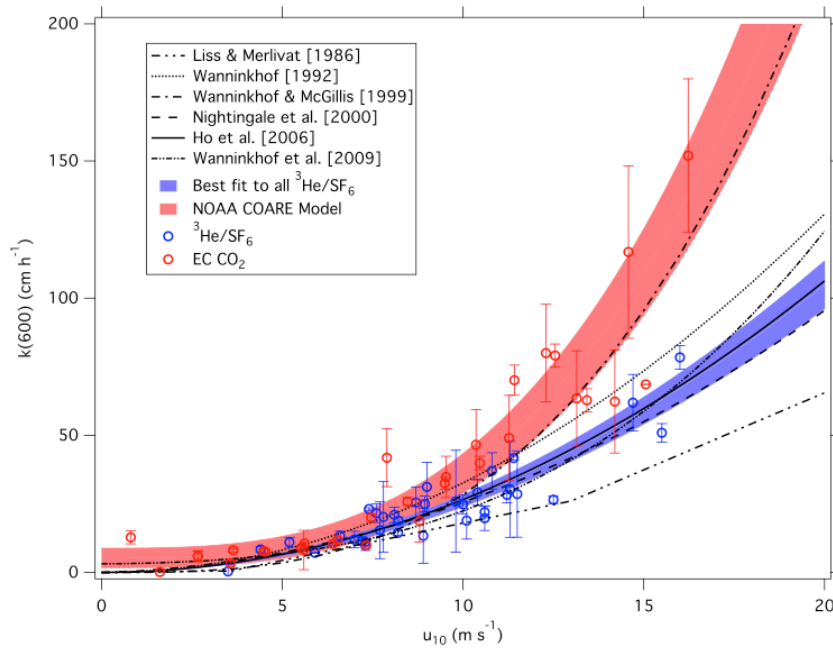


Figure 3.

# Comparison between $^3\text{He}/\text{SF}_6$ and $\text{EC CO}_2$



- Eddy covariance produces higher order (i.e., cubic) dependencies
- Deviation between  $^3\text{He}/\text{SF}_6$  dual tracer and  $\text{CO}_2$  eddy covariance most pronounced at higher wind speeds (i.e.,  $> 10 \text{ m s}^{-1}$ )

Figure 4.

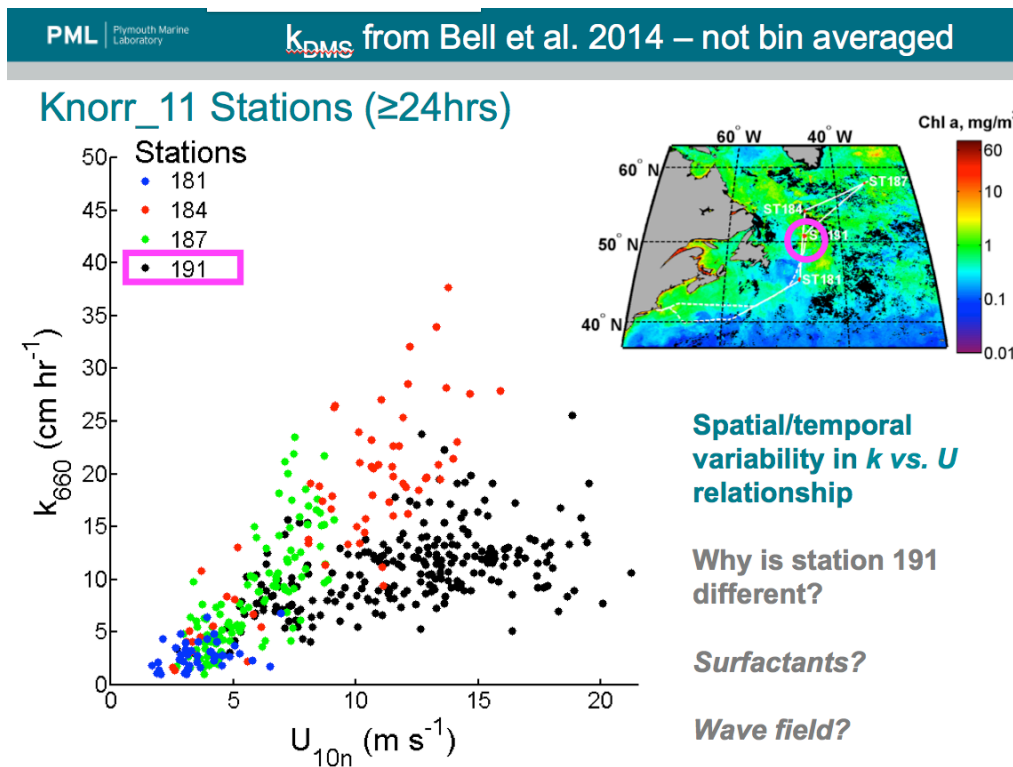


Figure 5.

Comparison of parameterizations with all  $^3\text{He}/\text{SF}_6$  data, including revisited GasEx-98 data

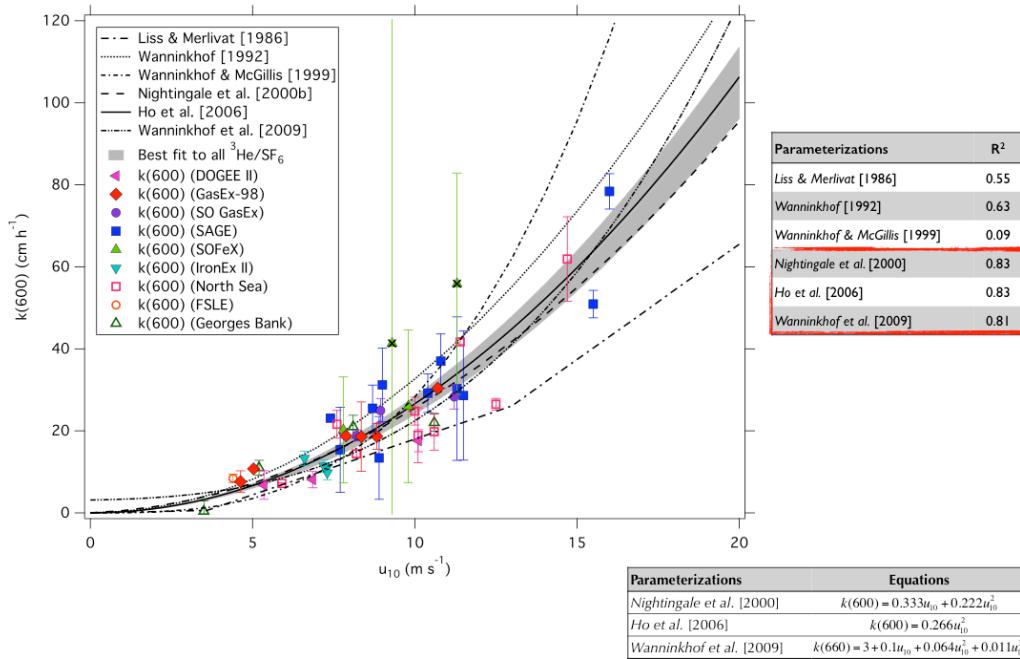
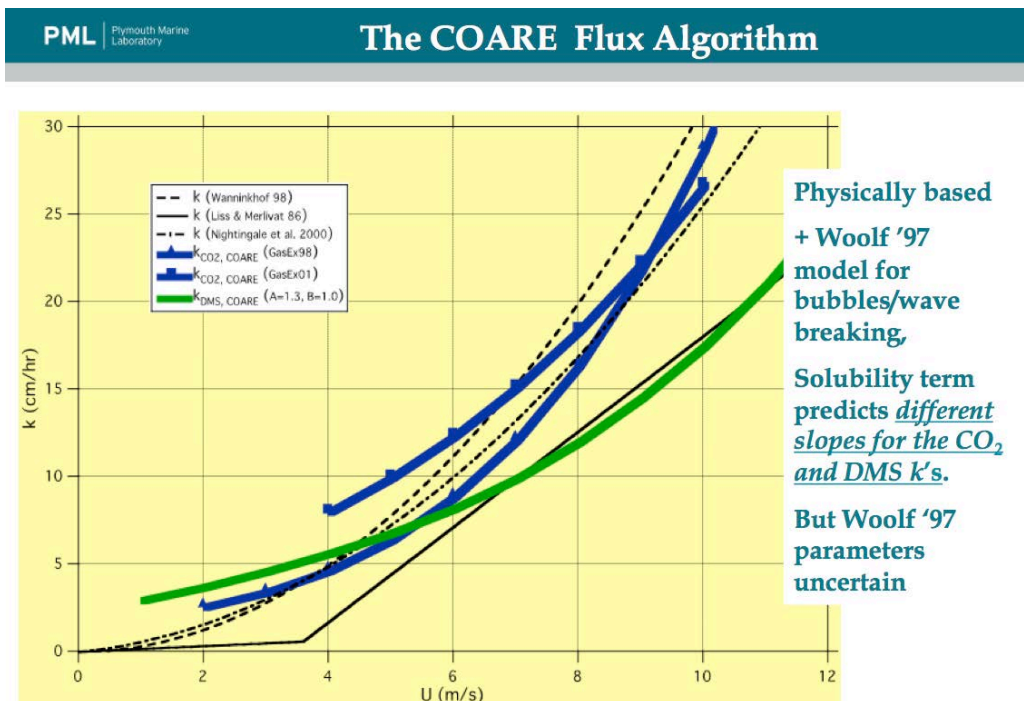


Figure 6.



Fairall et al. JGR 2011

Figure 7.

References:

Asher, W. E., and R. Wanninkhof (1998), The effect of bubble-mediated gas transfer on purposeful dual gaseous-tracer experiments, *J. Geophys. Res.*, *103*, 10555-10560.

Asher, W. E., P. J. Farley, B. J. Higgins, L. M. Karle, E. C. Monahan, and I. S. Leifer (1996), The influence of bubble plumes on air/seawater gas transfer velocities, *J. Geophys. Res.*, *101*, 12027-12041.

Bell, T. G., W. De Bruyn, S. D. Miller, B. Ward, K. Christensen, and E. S. Saltzman (2013), Air/sea DMS gas transfer in the North Atlantic: evidence for limited interfacial gas exchange at high wind speed, *Atmos. Chem. Phys. Discuss.*, *13*(5), 11073-11087, doi:10.5194/acp-13-11073-2013.

Ho, D. T., R. Wanninkhof, P. Schlosser, D. S. Ullman, D. Hebert, and K. F. Sullivan (2011), Towards a universal relationship between wind speed and gas exchange: Gas transfer velocities measured with <sup>3</sup>He/SF<sub>6</sub> during the Southern Ocean Gas Exchange Experiment, *J. Geophys. Res.*, *116*, C00F04, doi:10.1029/2010JC006854.

Ho, D. T., C. S. Law, M. J. Smith, P. Schlosser, M. Harvey, and P. Hill (2006), Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations *Geophys. Res. Lett.*, *33*, L16611, doi:10.1029/2006GL026817.

Jacobs, C., P. Nightingale, R. Upstill-Goddard, J. F. Kjeld, S. Larsen, and W. Oost (2002), Comparison of the deliberate tracer method and eddy covariance measurements to determine the air/sea transfer velocity of CO<sub>2</sub>, in *Gas Transfer at Water Surfaces*, edited by M. Donelan, W. Drennan, E. Saltzman and R. Wanninkhof, pp. 225-231, AGU, Geophysical Monograph 127, Washington, DC.

Fairall, C. W., L. Bariteau, A. A. Grachev, R. J. Hill, D. E. Wolfe, W. A. Brewer, S. C. Tucker, J. E. Hare, and W. M. Angevine (2006), Turbulent bulk transfer coefficients and ozone deposition velocity in the International Consortium for Atmospheric Research into Transport and Transformation, *J. Geophys. Res.*, *111*, D23S20, doi:10.1029/2006JD007597.

Liss, P. S., and L. Merlivat (1986), Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 113-129, Reidel, Boston.

Manning, A. C., and R. F. Keeling (2006), Global oceanic and land biota sinks from the Scripps atmospheric oxygen flask sampling network, *Tellus*, *58B*, 95-116.

McGillis, W. R., J. B. Edson, J. E. Hare, and C. W. Fairall (2001), Direct Covariance Air-Sea CO<sub>2</sub> Fluxes., *J. Geophys. Res.*, *106*, 16729-16745.

McGillis, W. R., J. B. Edson, J. E. Hare, and C. W. Fairall (2001), Direct Covariance Air-Sea CO<sub>2</sub> Fluxes., *J. Geophys. Res.*, *106*, 16729-16745.

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, *14*, 373-387.

Sweeney, C., E. Gloor, A. R. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof (2007), Constraining global air-sea gas exchange for CO<sub>2</sub> with recent bomb C-14 measurements, *Global Biogeochem. Cycles*, *21*(2), GB2015 doi:10.1029/2006GB002784.

Wanninkhof, R., W. E. Asher, D. T. Ho, C. S. Sweeney, and W. R. McGillis (2009), Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing, *Annual Reviews Mar. Science*, *1*, 213-244, 101146/annurev.marine.010908.163742.

Wanninkhof, R. (1992), Relationship between gas exchange and wind speed over the ocean., *J. Geophys. Res.*, *97*, 7373-7381.

Wanninkhof, R. (2014), Relationship between wind speed and gas exchange over the ocean revisited, *Limnol and Oceanogr: Methods*, *12*, 351-362, doi: 10.4319/lom.2014.12.351.