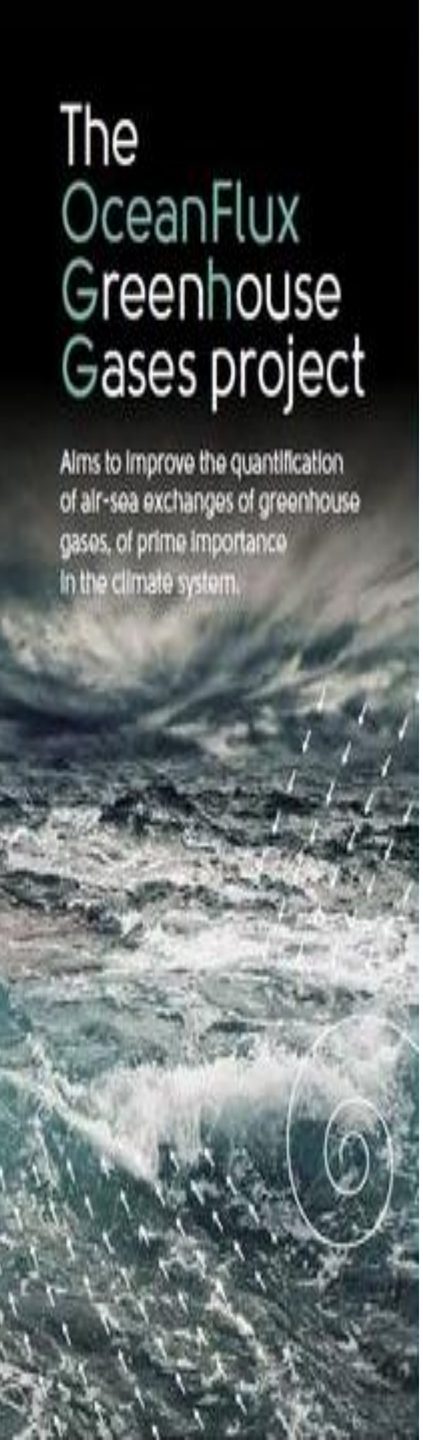


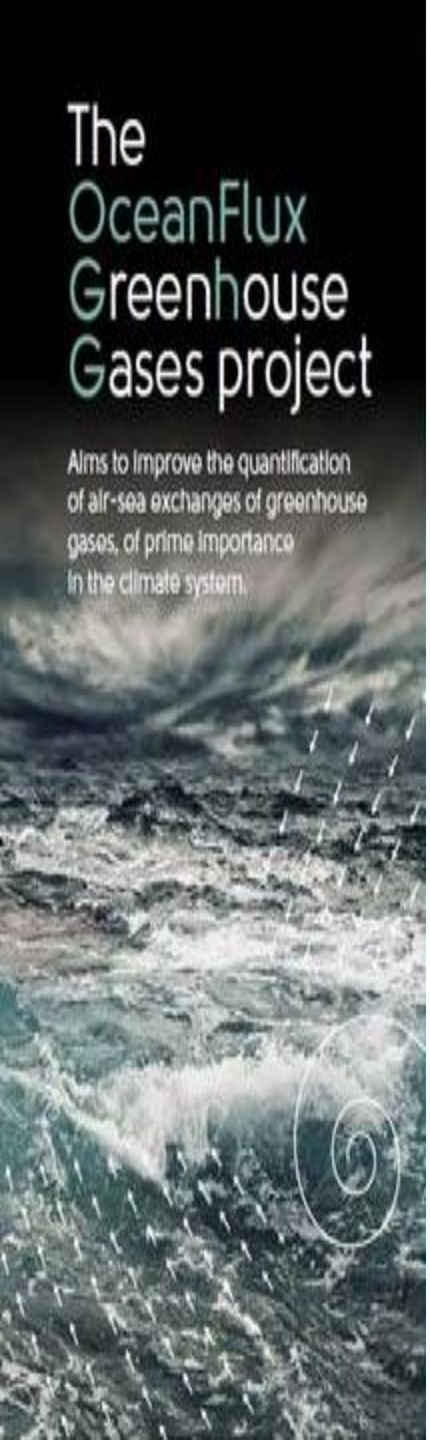
Parameterizing the bubble-mediated air-sea flux of a non-ideal gas, DMS

P. Vlahos[1,2], J. Liang[3] and E.C. Monahan[1]

[1]Departments of Marine Sciences &

[2]Environmental Engineering, University of Connecticut , Groton

[3]Applied Physics Laboratory, University of Washington, Seattle



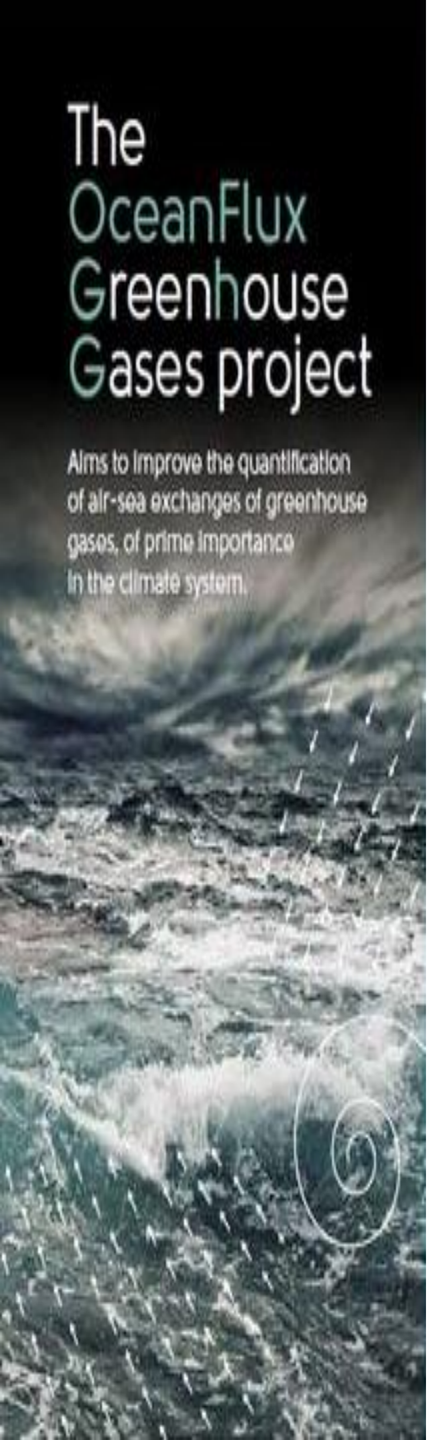
Bubble Effects

- Enhancement in gas transfer rate
- Equilibrium super-saturation condition [Woolf 1997]

- Physical-Chemical effects

  …..What are bubble effects for non-ideal gases such as DMS

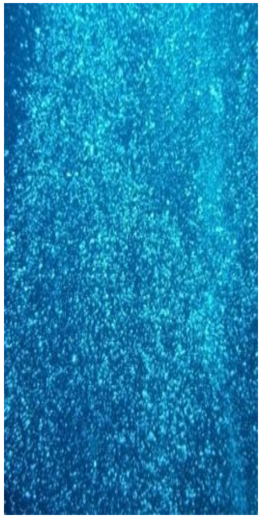
  - chemical properties may be useful in predicting bubble effects for non-ideal gases such as methylated sulfur species
  - Couple with air-sea bubble model



Addressing solubility in a bubbly surface ocean

In senescent conditions

$$C_{i,w} \approx \gamma_{i,\,w}^{-1}\, V_i^{-1}$$



At high wind speeds (>12 m/s)

$$C_{i,mix} \approx \gamma_{i,\,mix}^{-1}\, V_i^{-1} \approx (1\text{-}x_b)C_{i,w} + (x_b)\, K_H C_{i,w} + K_{b\text{-}film} C_{i,w}$$

$$\approx [(1\text{-}x_b)\gamma_{i,\,w}^{-1} + (x_b)\gamma_{i,\,b}^{-1} + \boxed{\Phi_B\, \gamma_{i,\,b\text{-}film}^{-1}\,]V_i^{-1}}$$

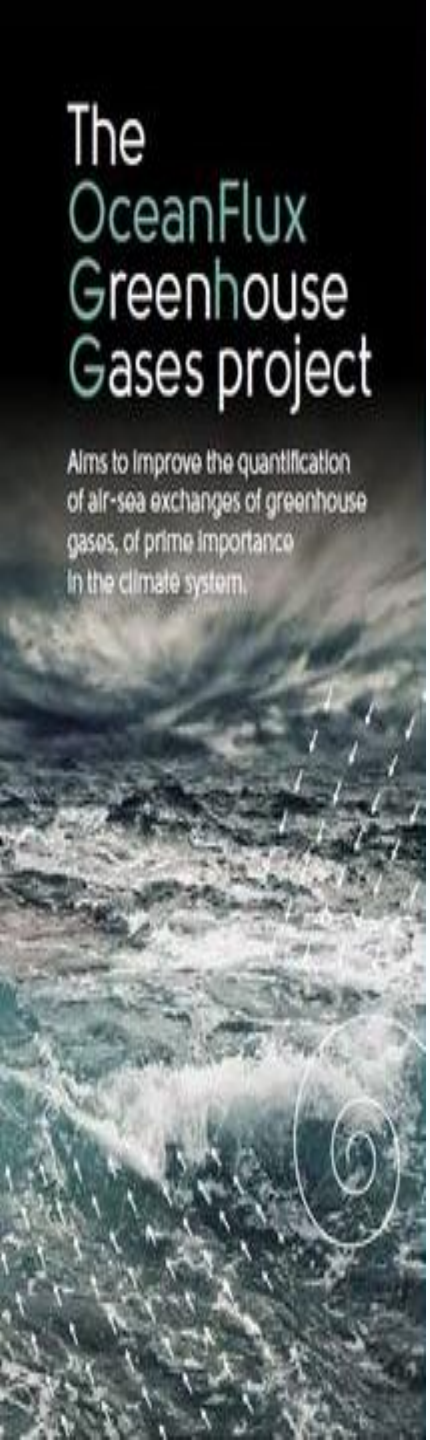
or

Where $\Phi_B = f(x_b) =$ bubble surface area per m^2

$\gamma_{i,\,j}$ = activity coefficient of substrate I in phase j

V_i = molar volume of substrate i in $cm^3 mol^{-1}$

X_b = volume fraction of bubbles in sample volume



Henry's Law Constant, K_{iH}

K_{iH} = vapor pressure/solubility

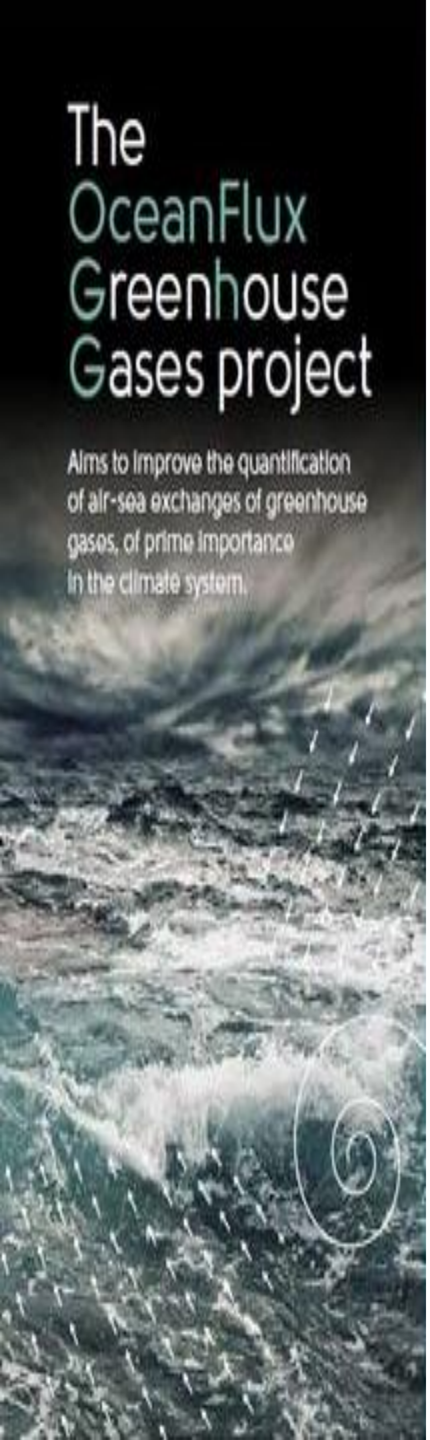
$$= \rho_i / C_{i,w}$$

$$= \gamma_{iw}, \rho_{iL} V_w$$

$K_i = K_{iH}/RT$ (dimensionless)

$$K_{i,mix} = K_i / (1 + (C_{mix}/C_w)\, \Phi_B)$$

↑ $K_{b\text{-}film}$

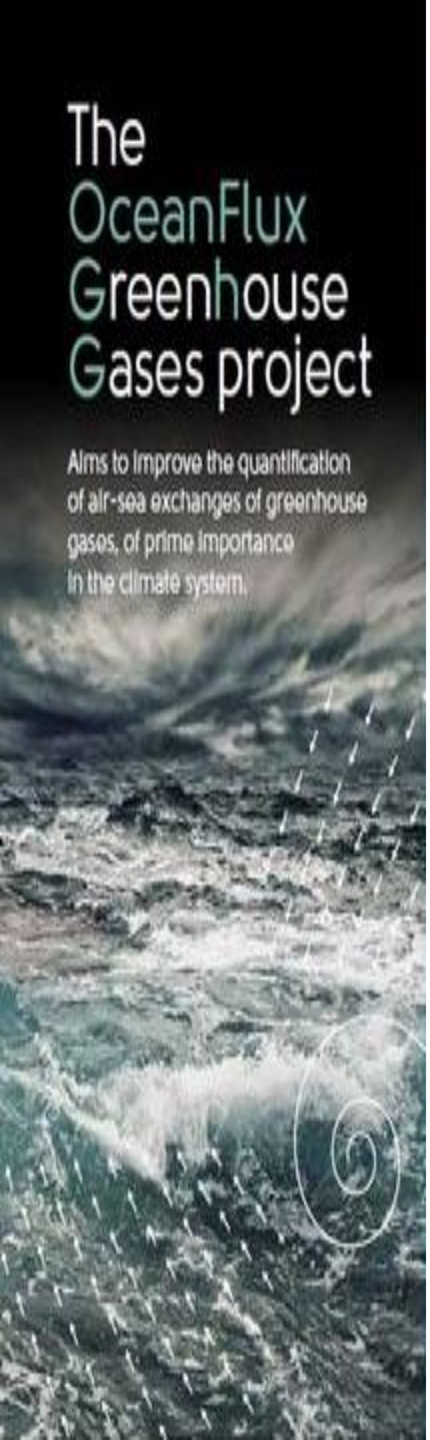


In terms of flux

$$Flux = k_i \, \Delta C_{AW}$$

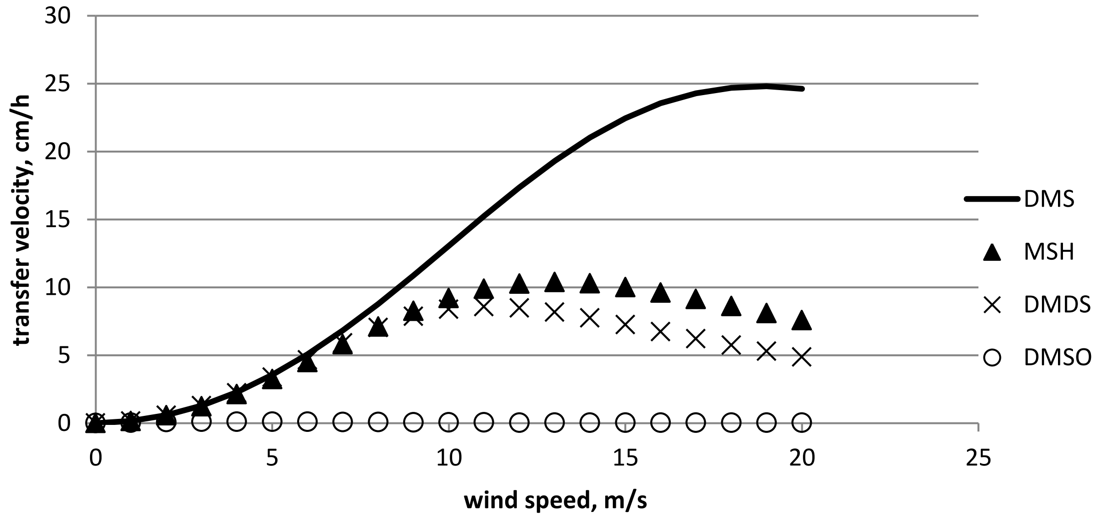
$$k_i = [1/(k_a K_{i,mix}) + 1/k_w]^{-1}$$

where $K_{i,mix} = K_i/(1+(C_{mix}/C_w)\,\Phi_B)$

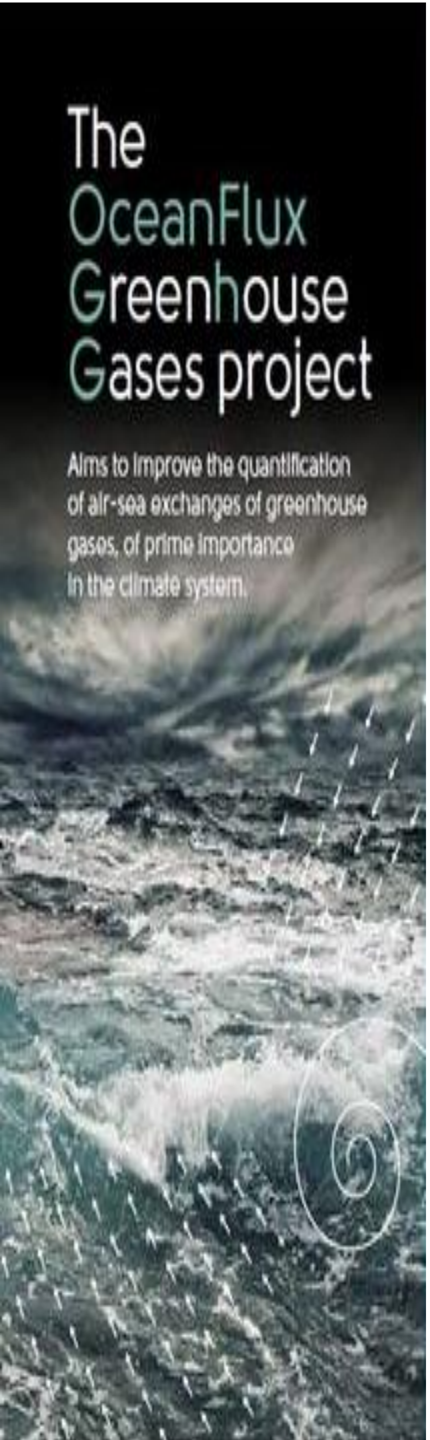


Predicted influence of wind speed on transfer velocities of surface active gases

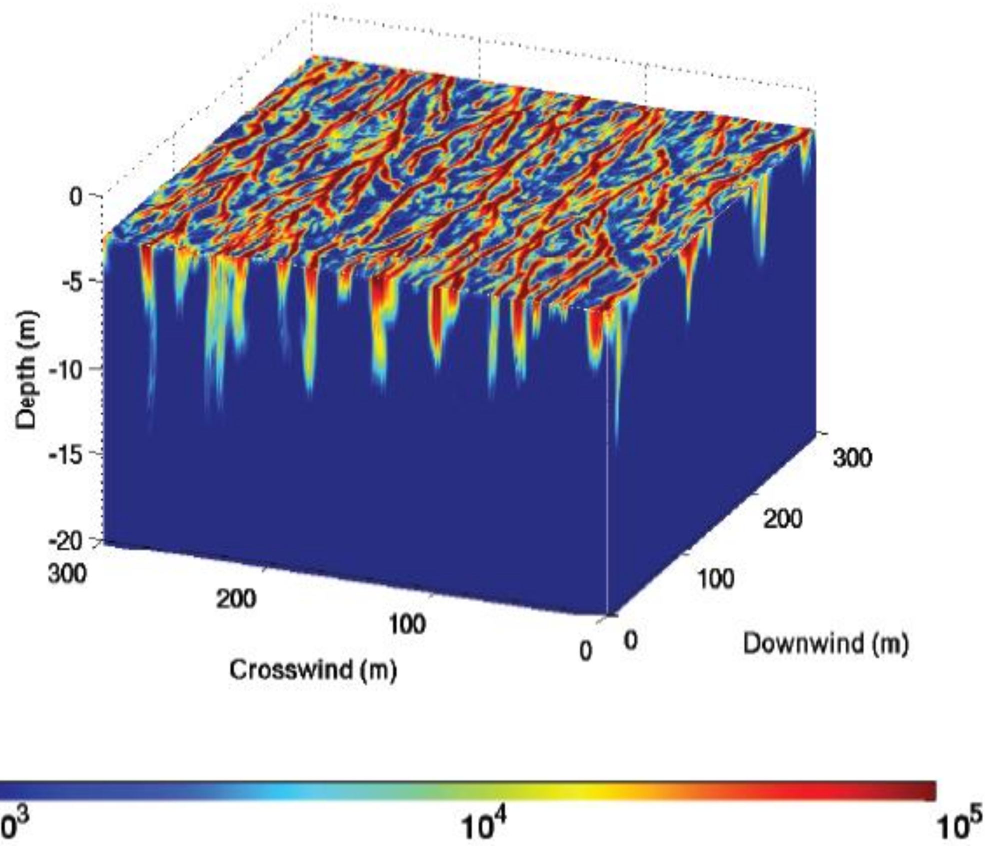
Compound	Chemical Formula	MWt , g/mol	Solubility, (mol/L)	K, (dimensionless, air/water)
MSH	CH_3SH	48.11	0.195	0.0115
DMS	C_2H_6S	62.13	0.355	0.08
DMSO	C_2H_6SO	74.12	miscible	5.25×10^{-7}
DMDS	$C_2H_6S_2$	94.20	0.0363	0.0428



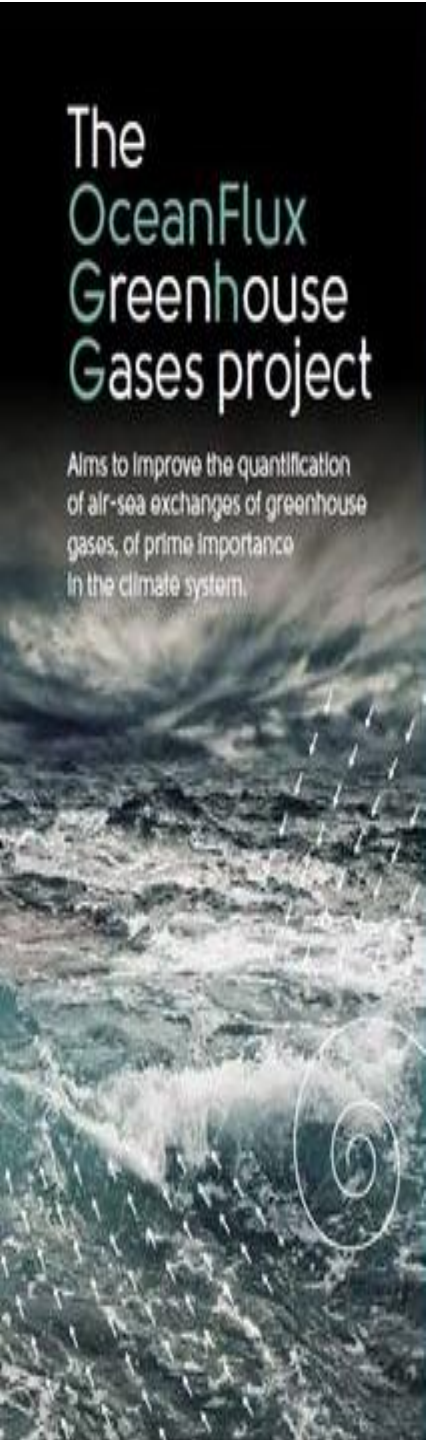
From Vlahos et al (2011), *Gas Transfer at Water Surfaces, 2010*



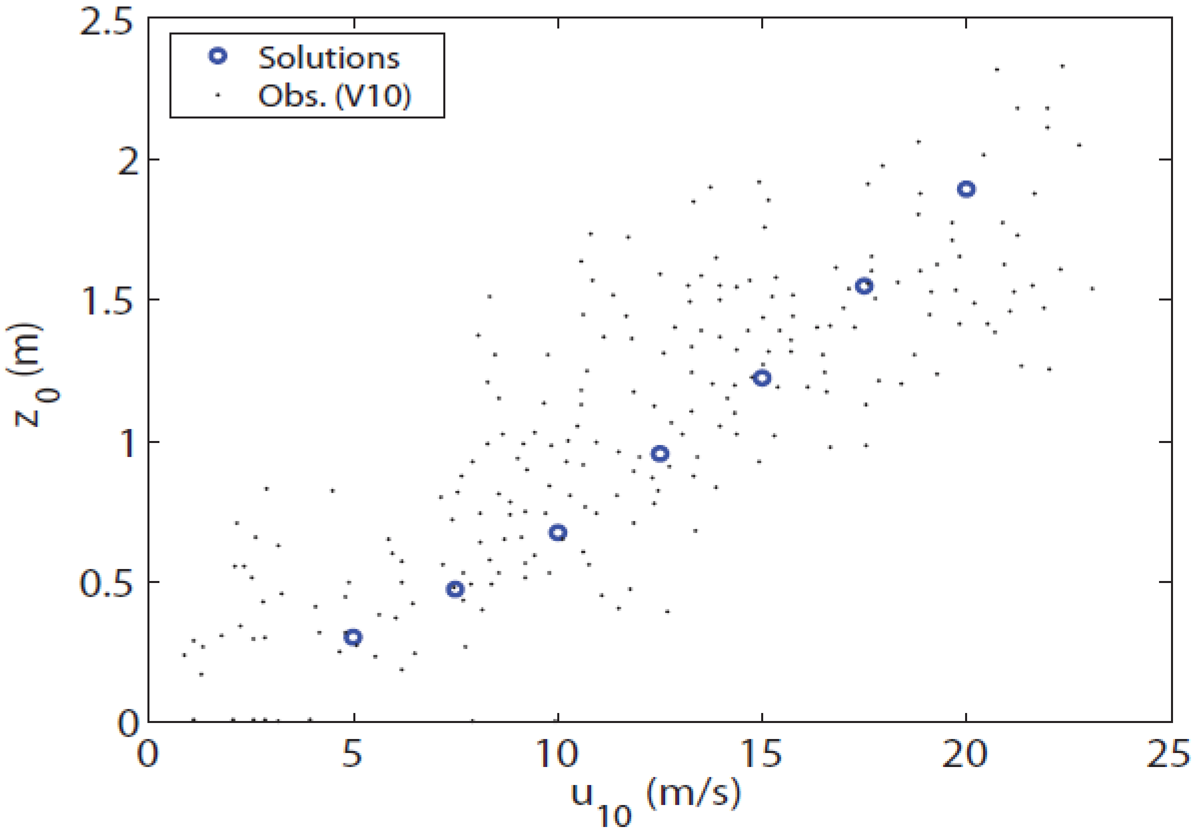
Liang et al. 2011, 2012, 2013



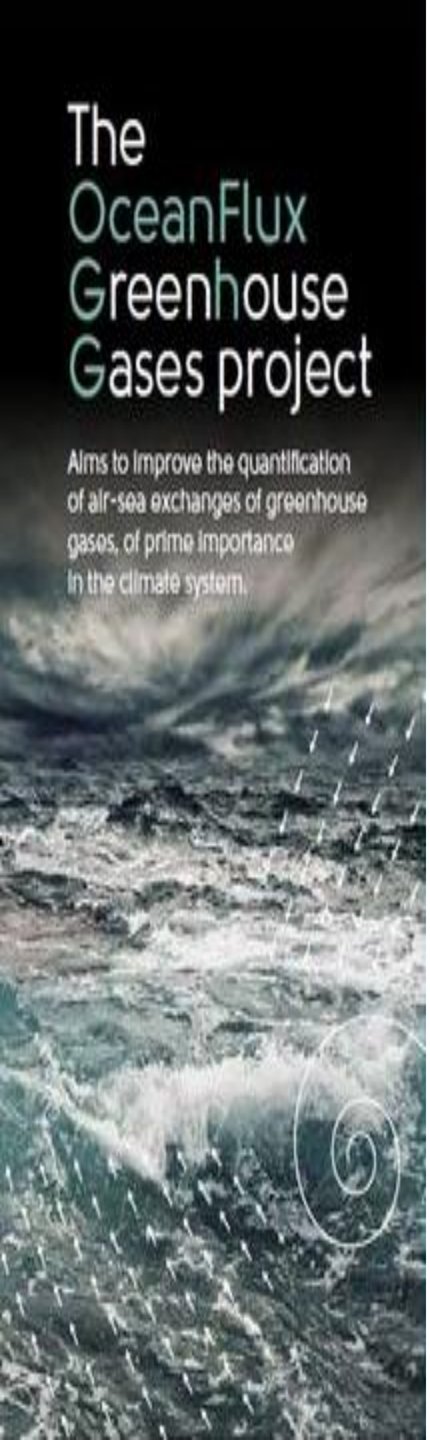
simulated total bubble number density
(number per m^3) at $u10$ = 17:5 m/s.



Liang et al. 2013

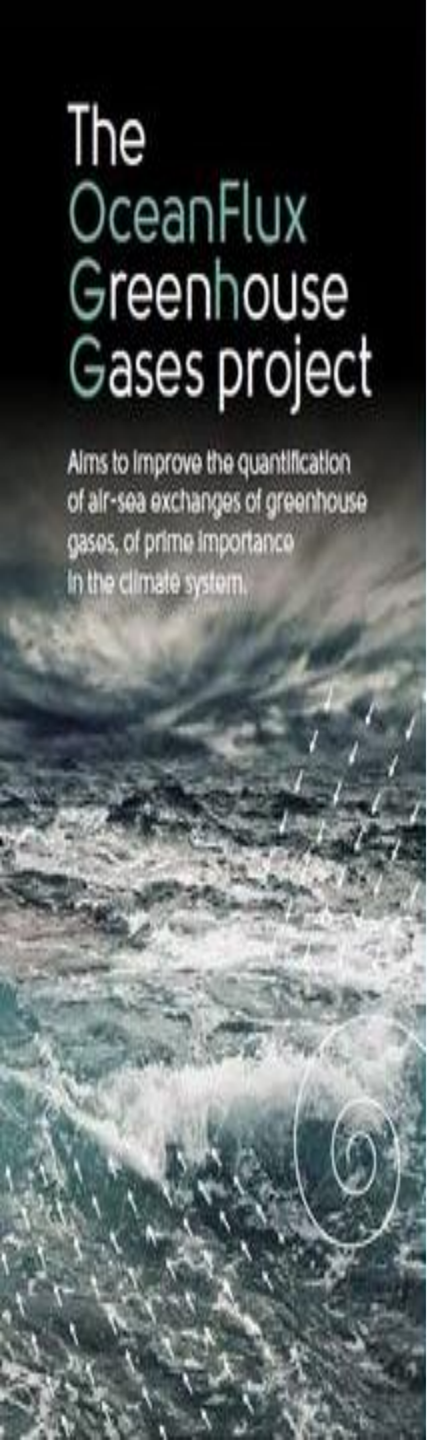


Relationship between bubble e-folding depth z_0 and wind speed u_{10}. (Black dots: observations by *Vagle et al.* [2010]; Blue circles: bubbly flow solutions assuming waves in equilibrium with local winds.



This model

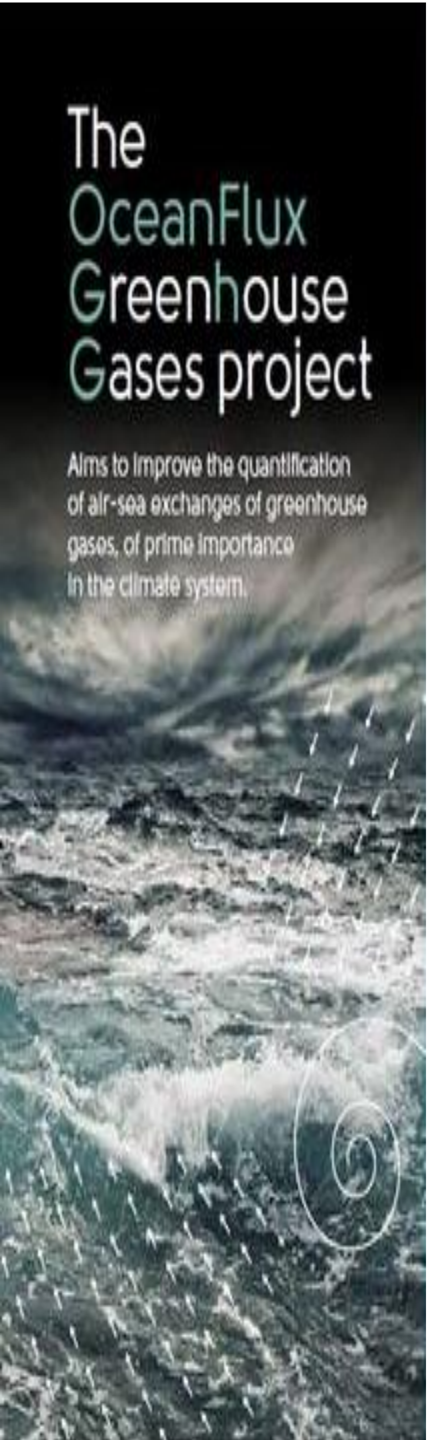
- bubbles of sizes **>35 microns** are included
- **fraction** of different gases change with time
- considers the effect of ambient **pressure change** on bubble size change
- readily **coupled** to upper ocean dynamic model
- Bubble injection is **constrained** by laboratory and *in situ* observations



Total Gas Flux

$$F = F_{sfc} + F_p + F_c + SP\frac{C_{mix}}{C_w}\int \frac{d\Phi}{dt}\,dz$$

- F_{sfc} is the gas flux through the ocean surface
- F_p is the gas flux through large bubbles that partially dissolve
- F_c the gas flux through small bubbles that completely dissolve
- the last term is an effective gas flux due to the change of bubble surface area assuming a proportionate fraction of molecules attach

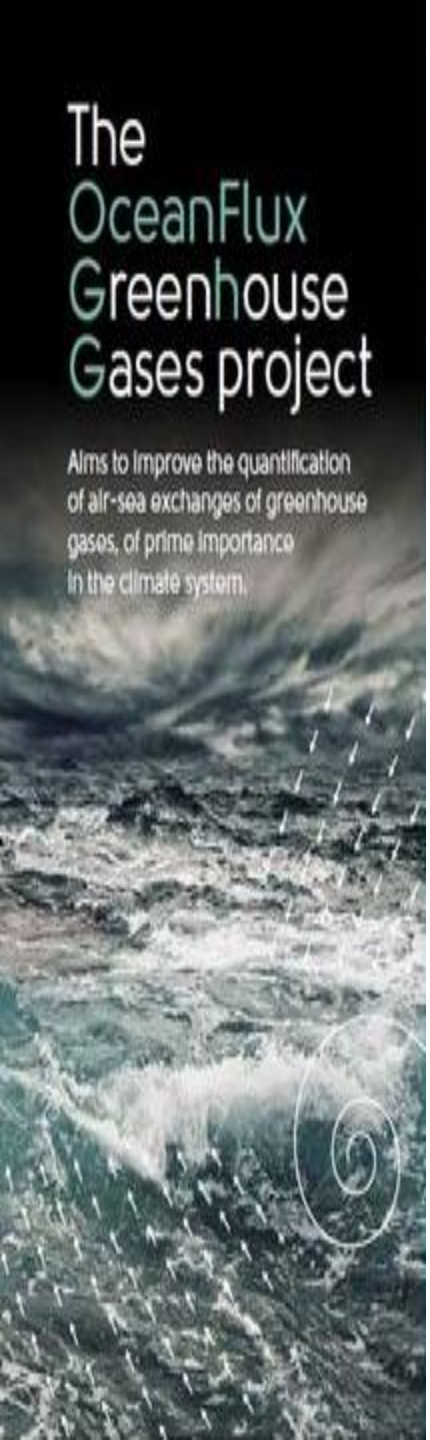


Estimated from Liang Model

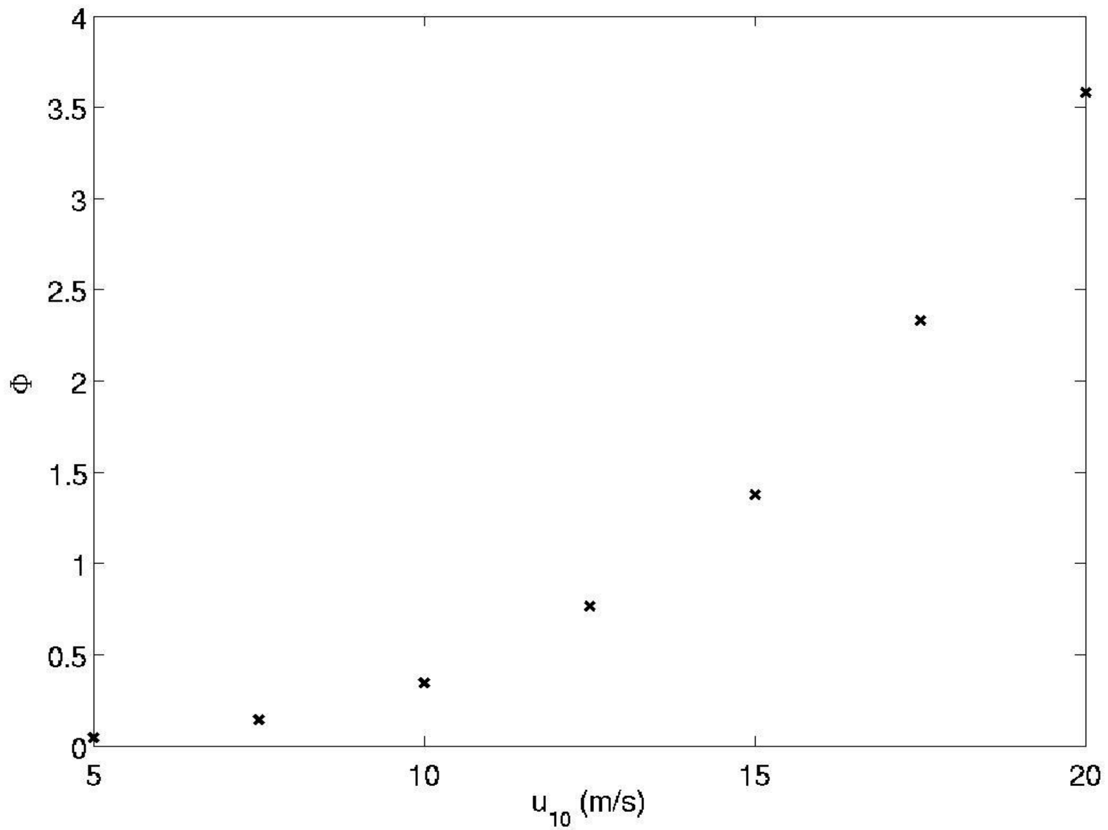
$$F = k_{sfc}(S_{eff}P - C) + k_b\left[S_{eff}P(1 + \Delta_{overpressure}) - C\right] + F_c + SP\frac{C_{mix}}{C_w}\int\frac{d\Phi}{dt}dz$$

$$F = k_{tot}\left[S_{eff}P(1 + \Delta) - C\right]$$

$$\Delta = \frac{k_b}{k_T}\Delta_{overpressure} + \frac{F_c + SP\frac{C_{mix}}{C_w}\int\frac{d\Phi}{dt}dz}{k_T SP\left(1 + \frac{C_{mix}}{C_w}\Phi\right)}$$



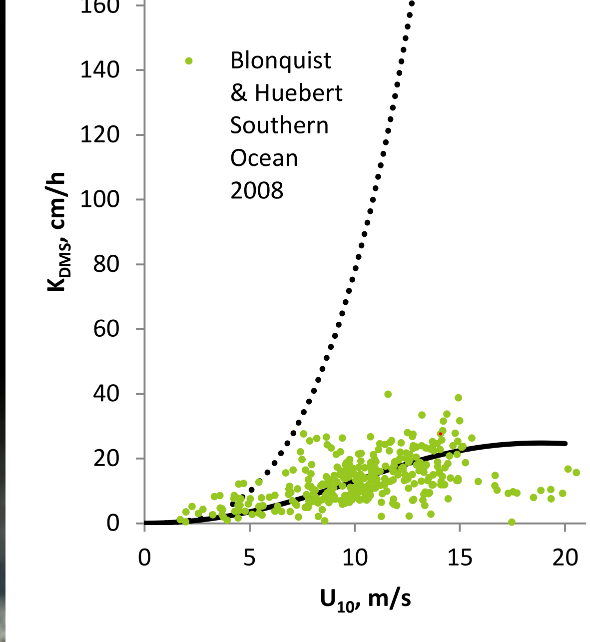
Relationship between Φ and wind speed

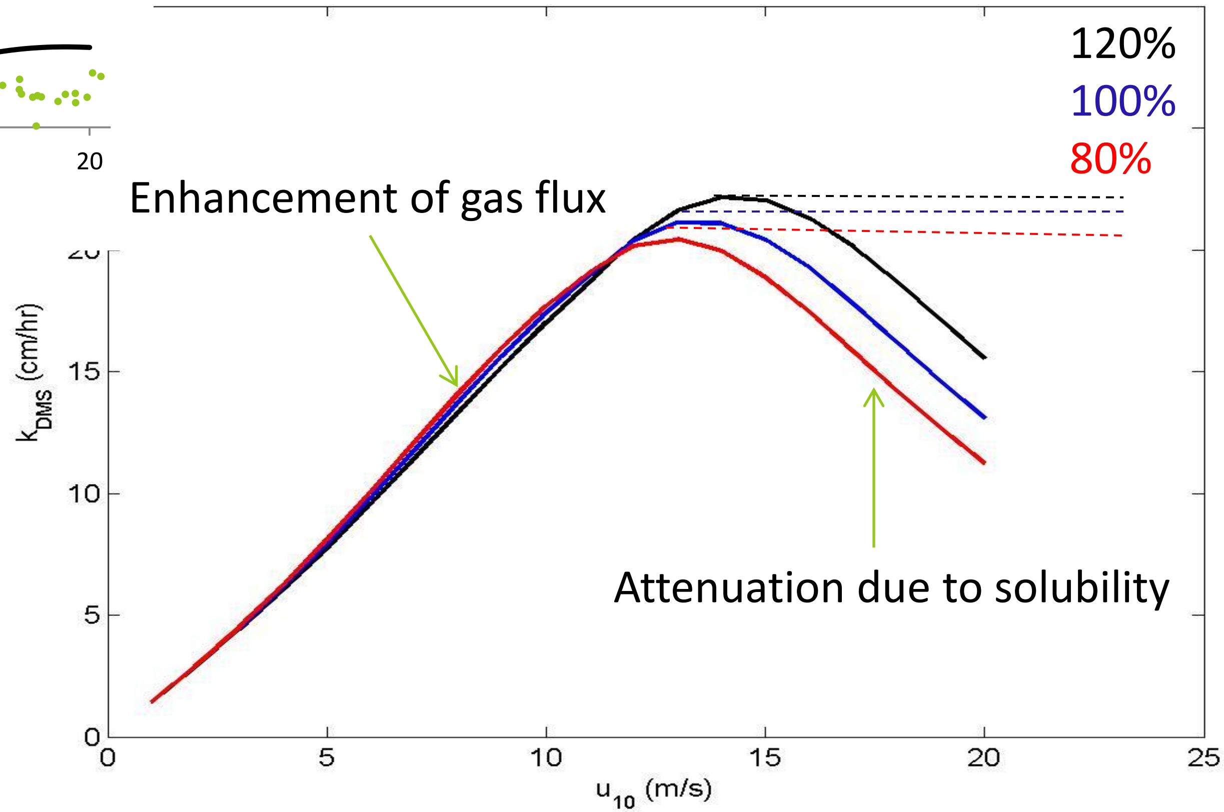


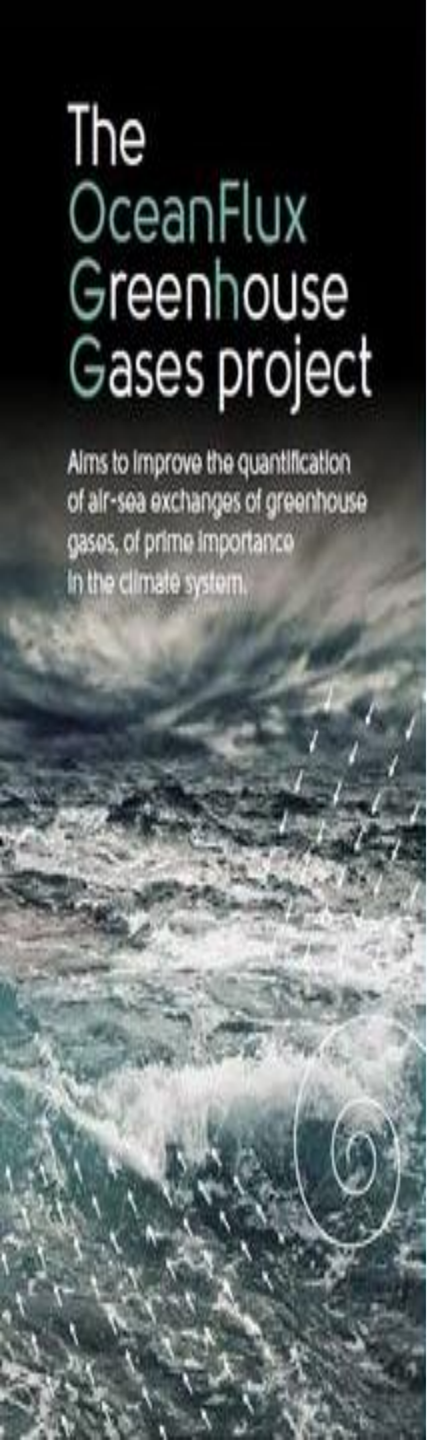
(1) the total injected bubble amount in the model is based on observations, which are limited, and a source of possible uncertainty; $\Phi_B = 0.40\ (U/10)^3$

(2) the formula for k_w in VM09 is at the lower end of observed values $\Phi_B = 0.090\ (U/10)^3$

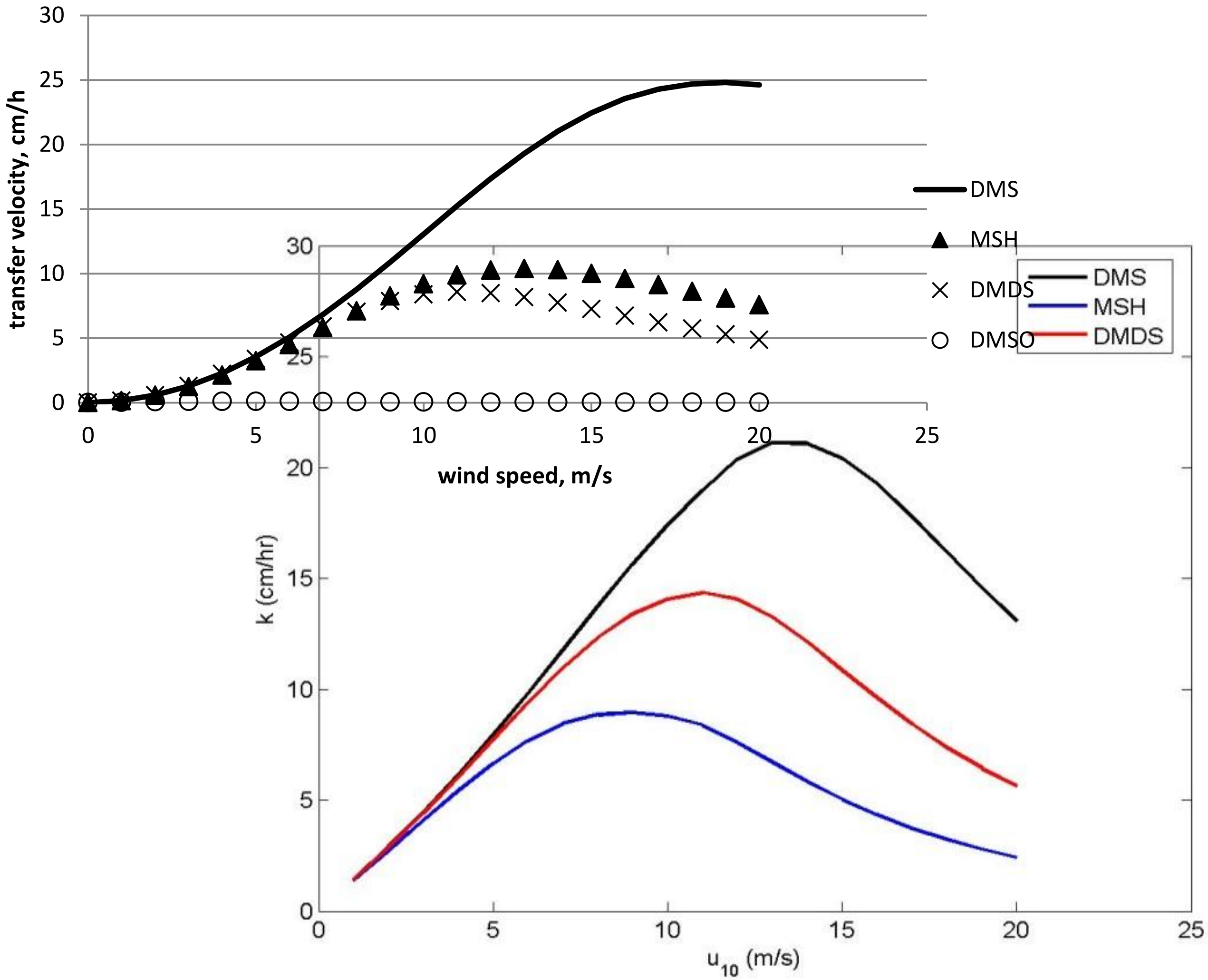
Sensitivity test on injected bubble amount

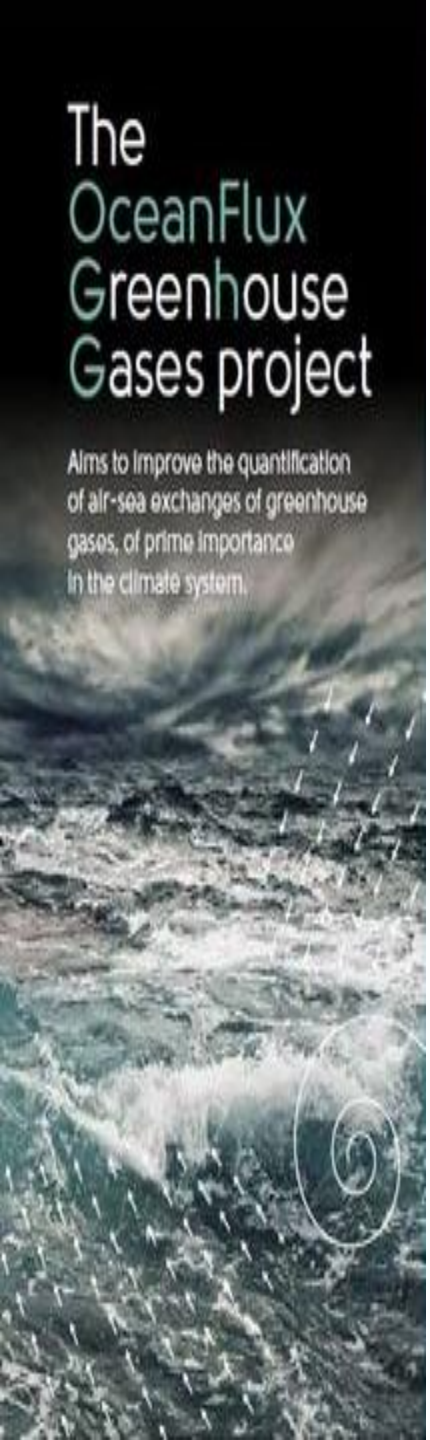




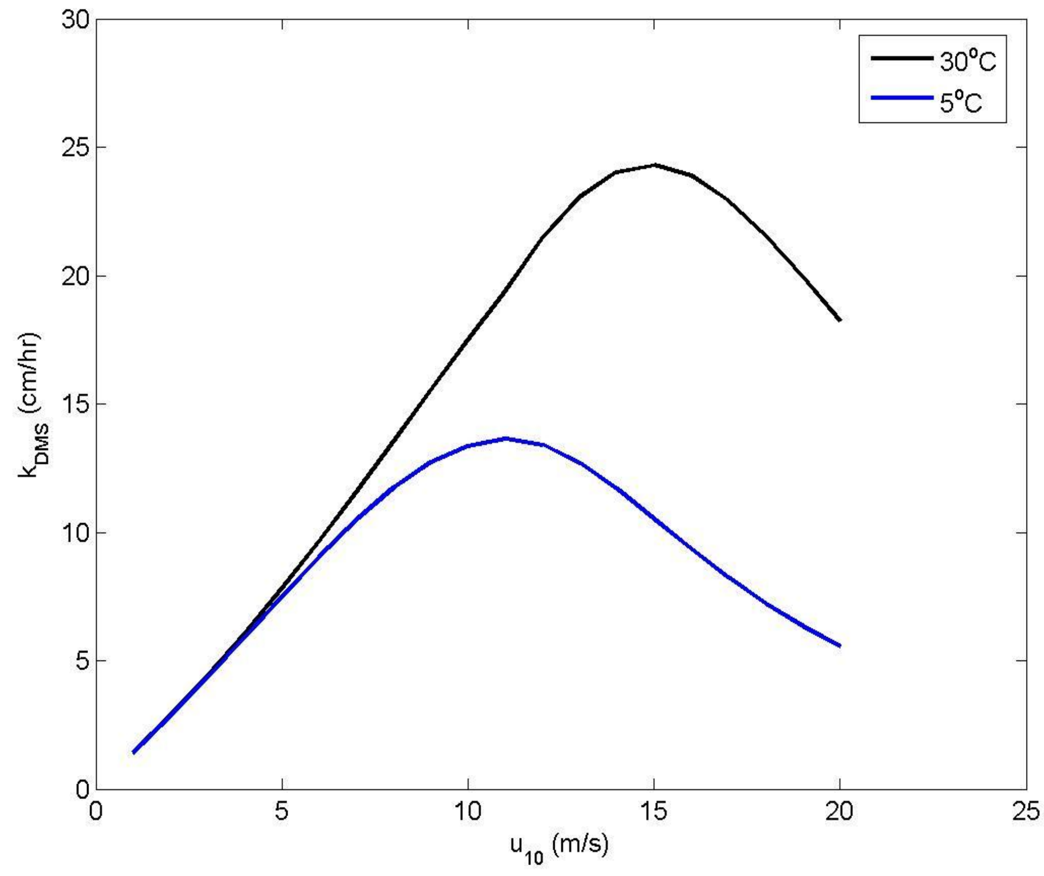


Gas flux profile for organic gases





Temperature effects



- DMS and derivatives expected to be moderately surface active

- At high winds (> 12 m/s) the surface ocean is significantly altered
  - the effective activity coefficient and therefore the fugacity of surface active compounds is expected to decrease
  - The result is higher relative water-side concentrations in the bubble influenced layer and lower transfer velocities

Current Results

Current Results

- Air-sea flux of DMS may be overestimated using traditional empirical models
- DMS air-sea flux reaches upper thresholds governed by a piston **velocity near 25 cm/h** and the corresponding concentration gradient.
- This sets upper DMS air-sea transfer rates at **120 $\mu Mm^{-2}d^{-1}$** based on observed field concentrations. (DMS C_w's range from <1 to 20 nM (Lee et al 2010; Zang et al, 2008))

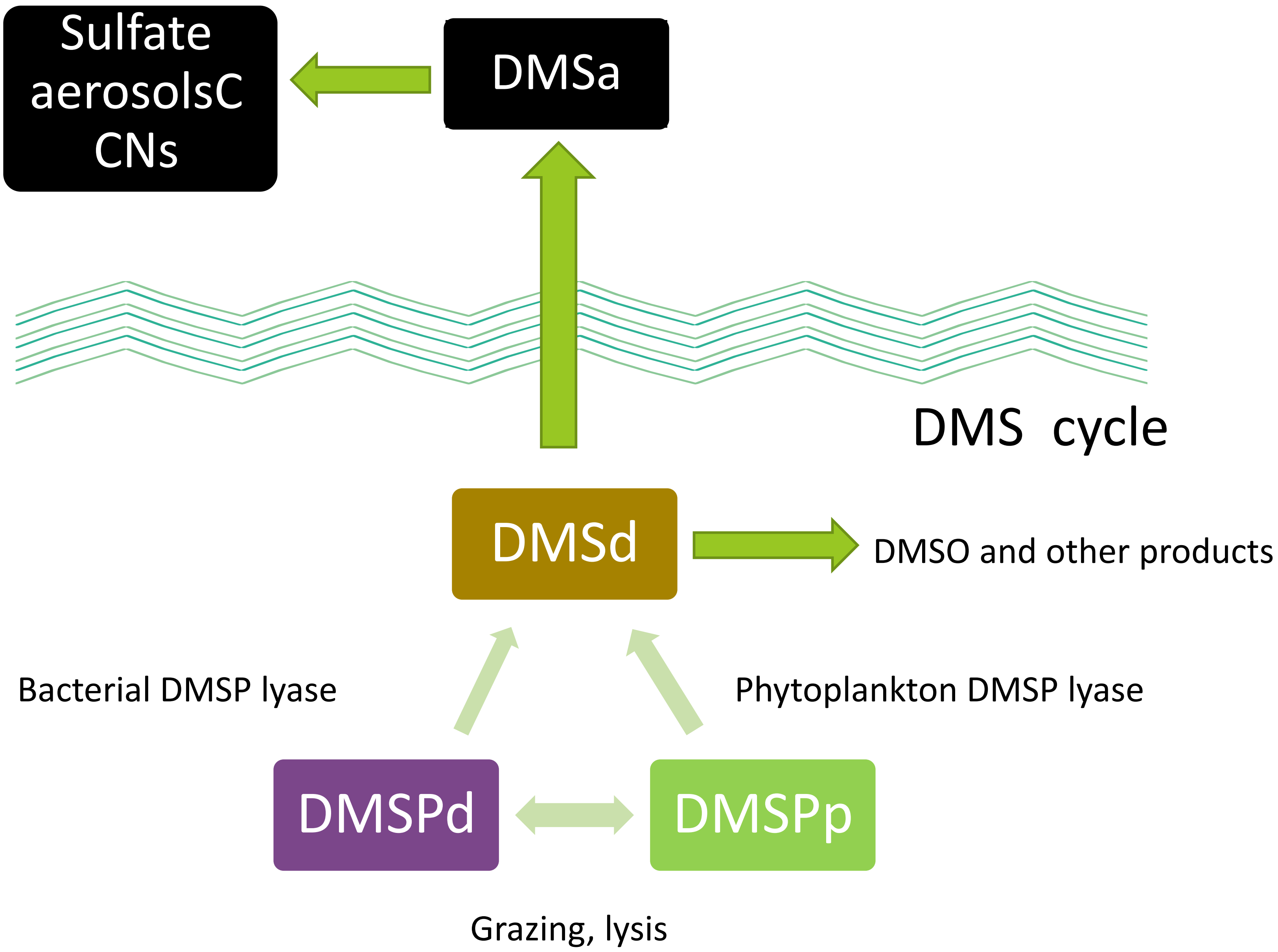
Next Steps…

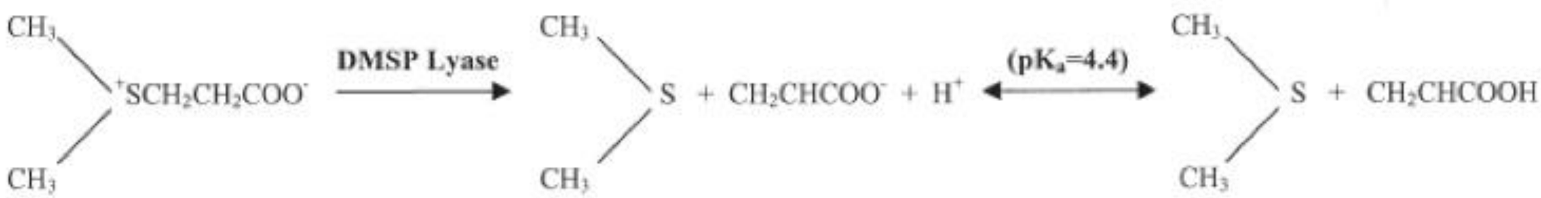
- Sensitivity analysis on nitrogen and oxygen
- Coupling to Lagrangian model
  - Equilibration of fast dissolving gases in partially dissolved bubbles will be explicitly resolved.
  - Bubble size distribution will be better resolved.
  - Add equilibration effect to the model Woolf [1993], Keeling [1993]
- Modeling of other of biogenic gases

That’s all for now…

What we know

- DMS C_w's range from <1 to 20 nM (Lee et al 2010; Zang et al, 2008)
- DMSP p + d, 9.22 (2.85-19.73) and 17.50 (4.33-36.09)nM (Zang et al, 2008)
- <u>Photodegradation rates</u> 0.006 to 0.028 nM/(Wm^{-2}) (Miles et al., 2009)
- <u>DMS degradation rates</u> 0.04 to 0.66 d^{-1}(Kieber et al., 1996)
- <u>DMS production rates</u> 0.7 to 0.9 nMd^{-1} (Bailey et al 2008)


Sulfate aerosolsC CNs
DMSa
DMS cycle
DMSd
DMSO and other products
Bacterial DMSP lyase
Phytoplankton DMSP lyase
DMSPd
DMSPp
Grazing, lysis

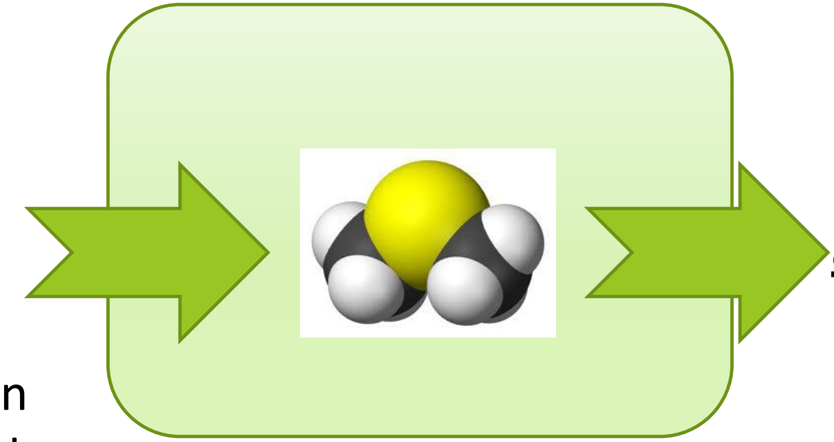


DMSP **DMS** **Acrylate** **DMS** **Acrylic Acid**

DMS box model

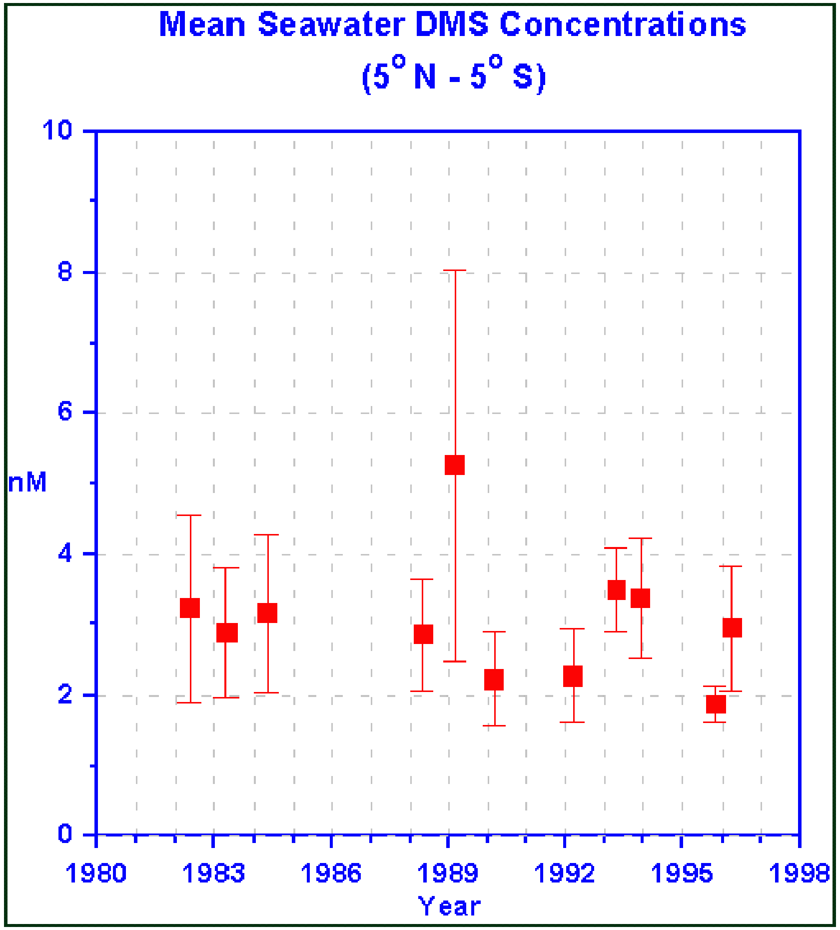
Sources:

- ✓ phytoplankton
- ✓ $DMSP_d$ breakdown
- ✓ advection



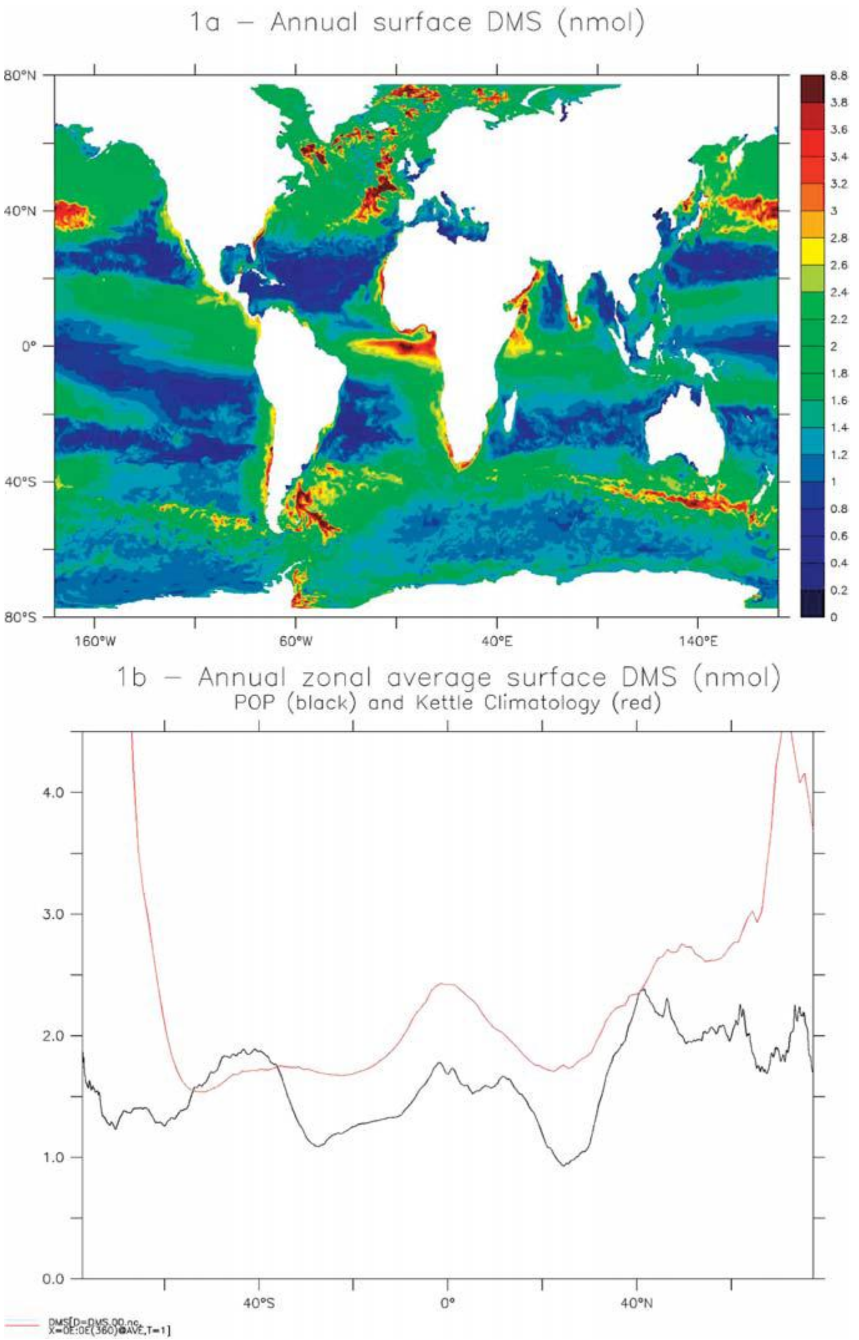
Sinks:

- ✓ Air-sea exchange
- ✓ Biodegradation
- ✓ Photodegradation
- ✓ advection



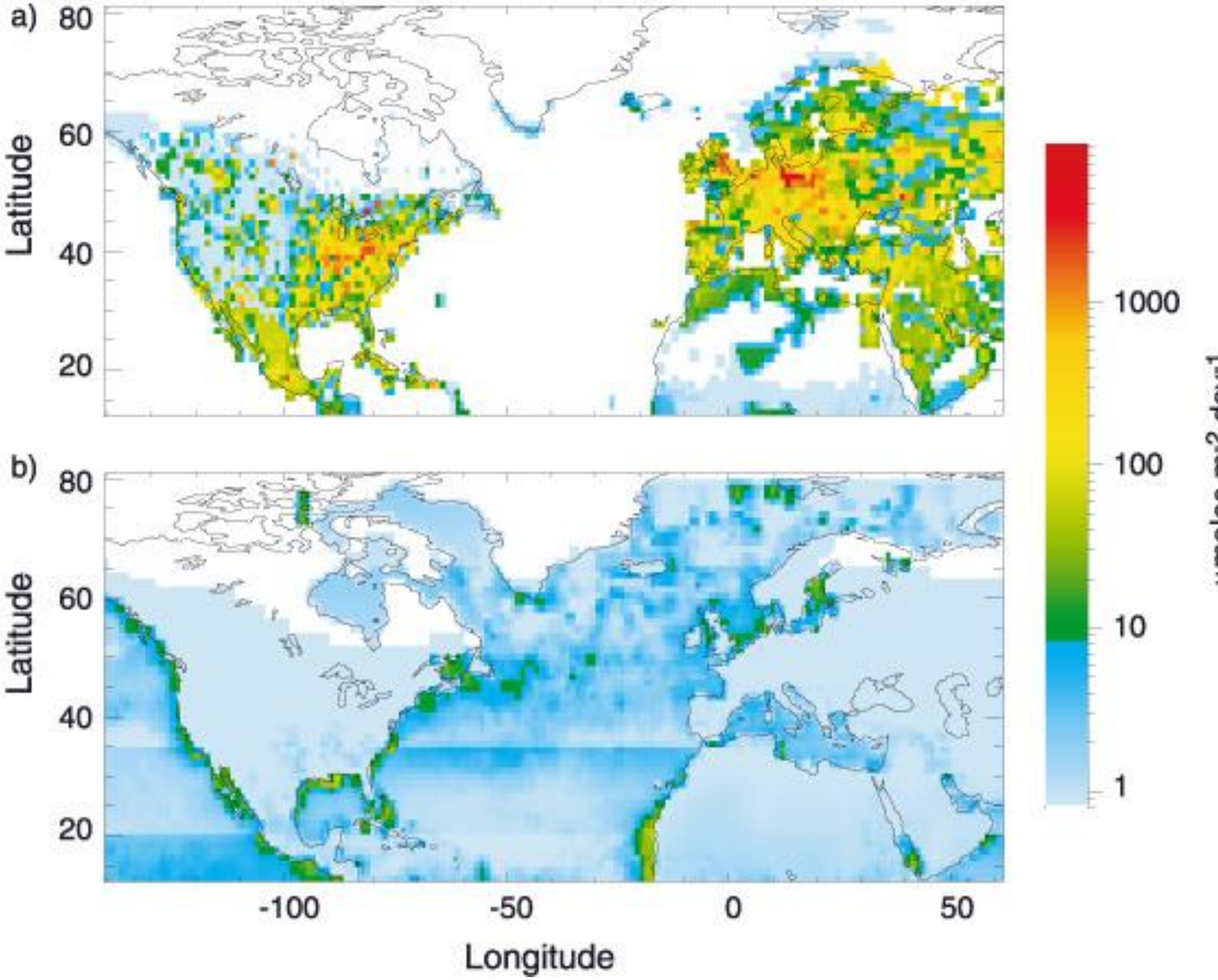
Equatorial Pacific (PMEL)- 15°N to 15°S DMS is relatively constant both seasonally and interannually (2.7 ± 0.7 nM (Bates and Quinn, *Geophys. Res. Lett.*, 24:861-864, 1997).

Observations



Surface ocean DMS

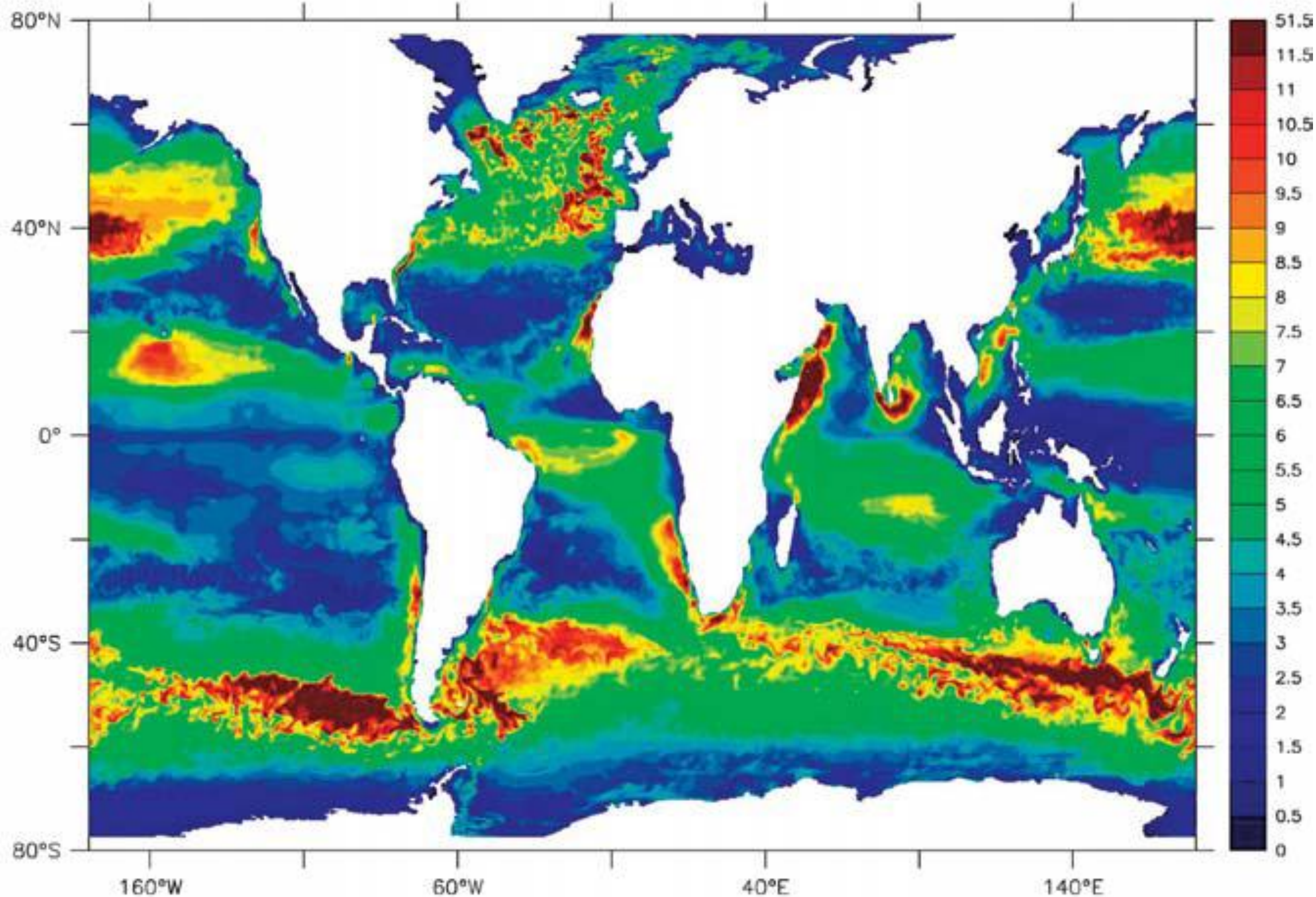
Earth Interactions Volume 8 (2004)



DMS fluxes

Bates et al. [1992]

7a – Annual DMS air–sea flux (mmol/m^2/day)



7b – Annual zonal average DMS air–sea flux (mmol/m^2/day)