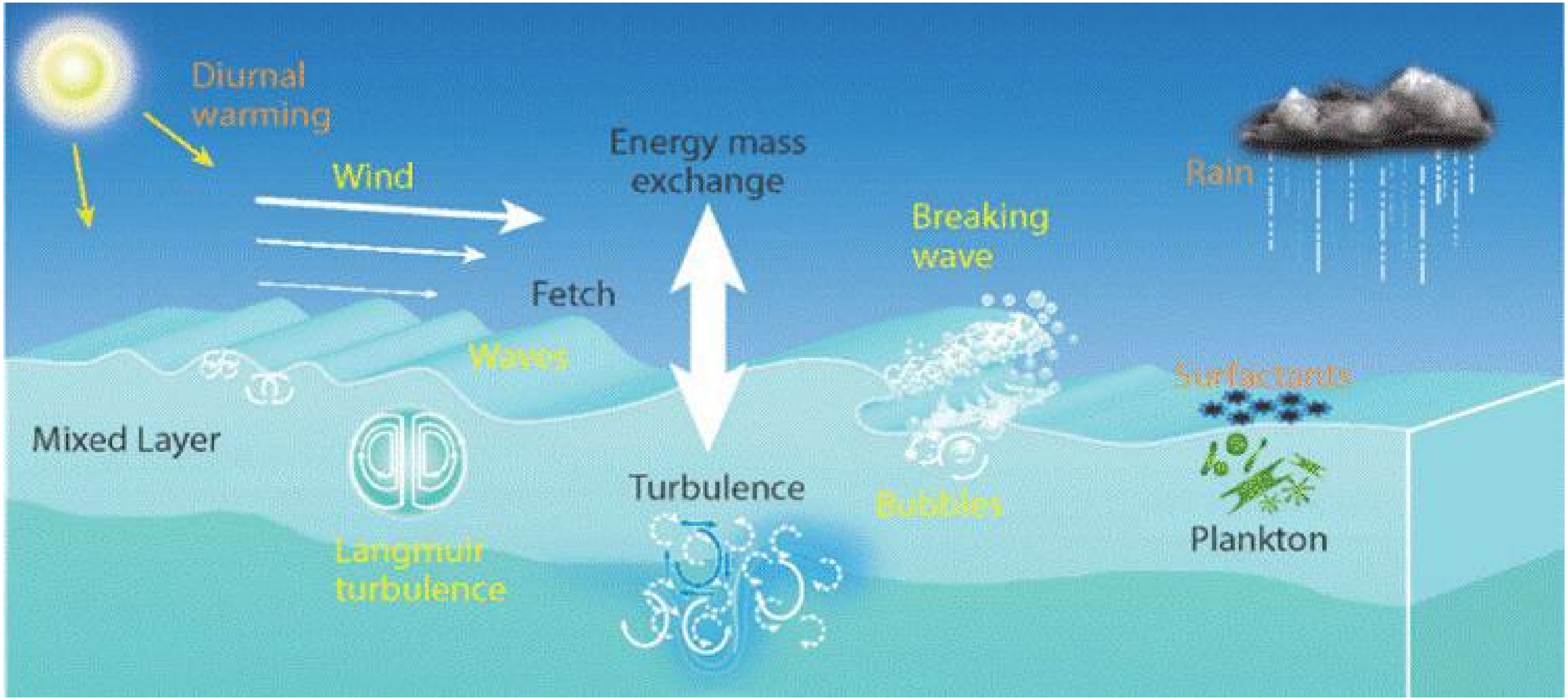
On the parameterisation of air-sea gas transfer of CO_2 via wave breaking energy dissipation rate

Andrew W. Smith[1], Adrian H. Callaghan[1] and Jean-Raymond Bidlot[2]
[1]Imperial College London [2]European Centre for Medium-Range Weather Forecasts

The 8th International Symposium on Gas Transfer at Water Surfaces | Plymouth, UK

Imperial College London | ECMWF European Centre for Medium-Range Weather Forecasts | PML Plymouth Marine Laboratory | UKRI Natural Environment Research Council

Air-Sea Fluxes



Momentum, heat, material and gas exchanged between atmosphere, waves, and ocean through dynamic and thermodynamic processes

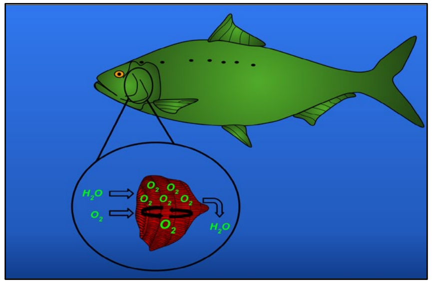
Diffusion • Wave growth and breaking

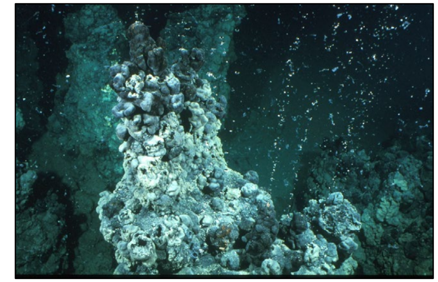
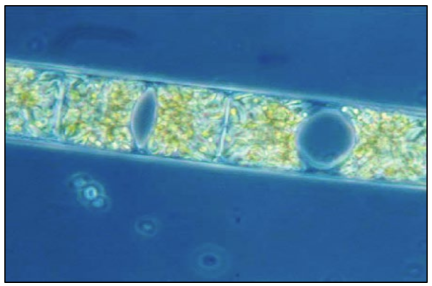
Bubbles, sea spray, spume facilitate exchange and impact up-scale budgets

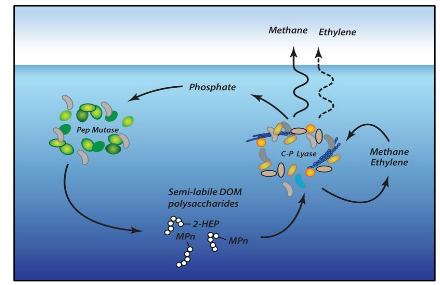
Air-sea gas fluxes on global climate

Notable Gases and their Importance

N_2 (62.6 %)	O_2 (34.3 %)	CO_2 (1.4 %)	CH_4 (0.0004 %)

N_2

1. Fixation by marine bacteria

NH_4^+

NO_2^{2-}

NO_3^- →

O_2

1. Aerobic respiration
2. Photosynthesis (byproduct)

CO_2

1. Aerobic respiration
2. Photosynthesis (reactant)
3. Carbon cycle/ loading

↓

$$CO_2 + H_20 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

(dissolved) 1 % | (carbonic acid) | (bicarbonate) 92 % | (carbonate) 7 %

CH_4

1. Benthic bacterial decomposition
2. Hydrothermal release
3. Methanogenesis

Scientific Objectives

1 Develop a hybrid gas transfer velocity parameterization with bubble-mediated gas exchange linked explicitly to breaking wave energy dissipation

Session 3 (Tues 17 May 14:30)
Energy dissipation-based estimates of whitecap coverage and air entrainment rates in whitecaps – Adrian Callaghan

2 Evaluate our parameterisation and existing wind-only and wind-wave parameterisations using outputs from a wind-forced spectral wave model, and compare with field measurements

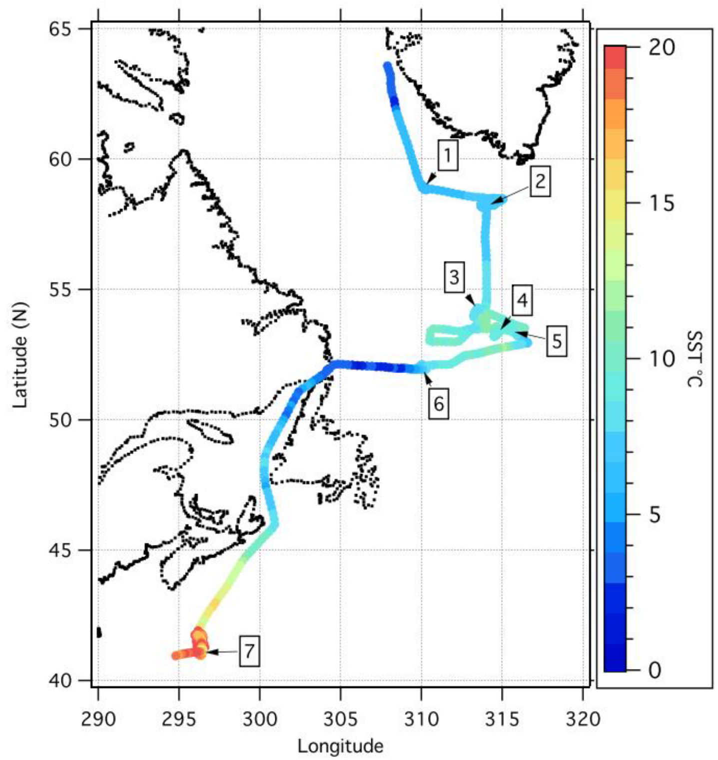
High **Win**d **G**as Exchange **S**tudy (HiWinGS, 2013)
Blomquist et al. (2017; **BL17**) : Wind-only
Deike and Melville (2018; **DM18**) : Wind-wave

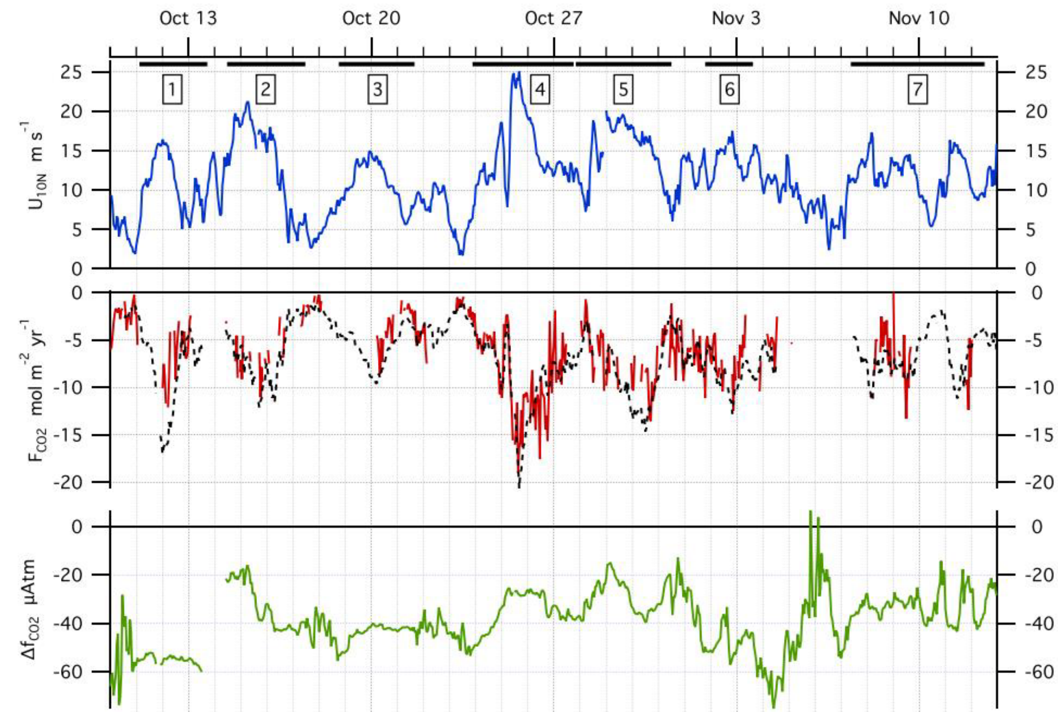
3 Investigate and identify sources of parameterisation success, uncertainty and error considering physical and chemical processes

- ☐
- ☐
- ☐
- ☐

4 Repeat 2-3 with a larger, more comprehensive data-set

Field Data: High Wind Gas Exchange Study



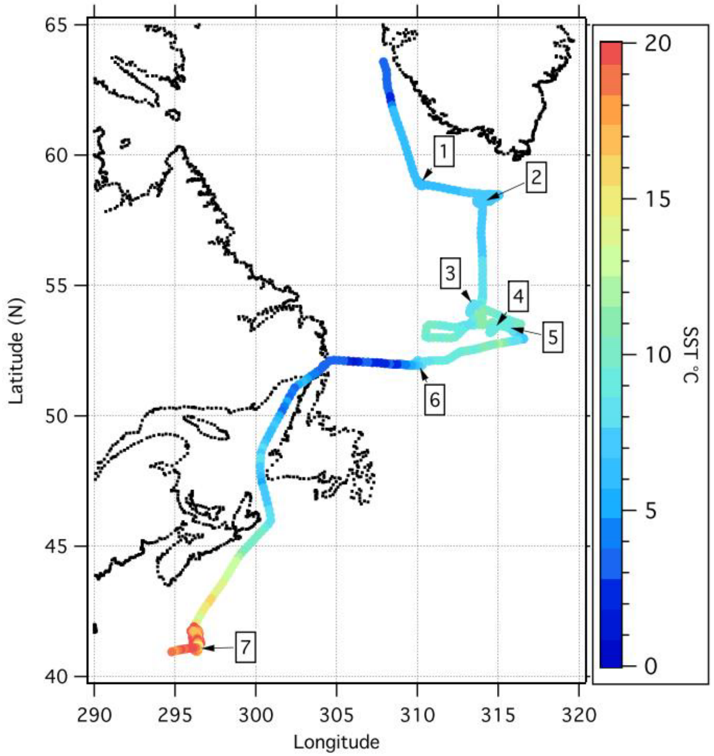


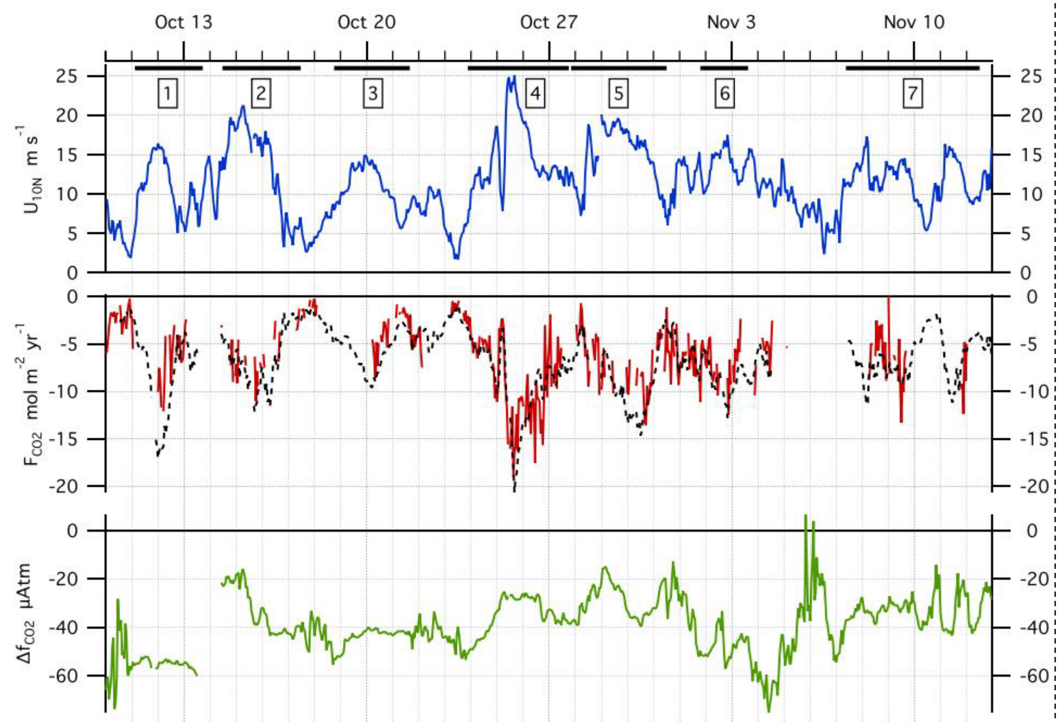
Measurements / Methods

1 — **9 October – 13 November 2013**: 7 intensive observation locations North Atlantic Ocean and Labrador Sea

2 — High-quality **eddy covariance fluxes**, buoy **wave measurements**, **CO_2** and **DMS flux** via cavity ring-down and atmospheric pressure ionization mass (Blomquist et al. 2010, 2014) spectrometers

Field Data: High Wind Gas Exchange Study





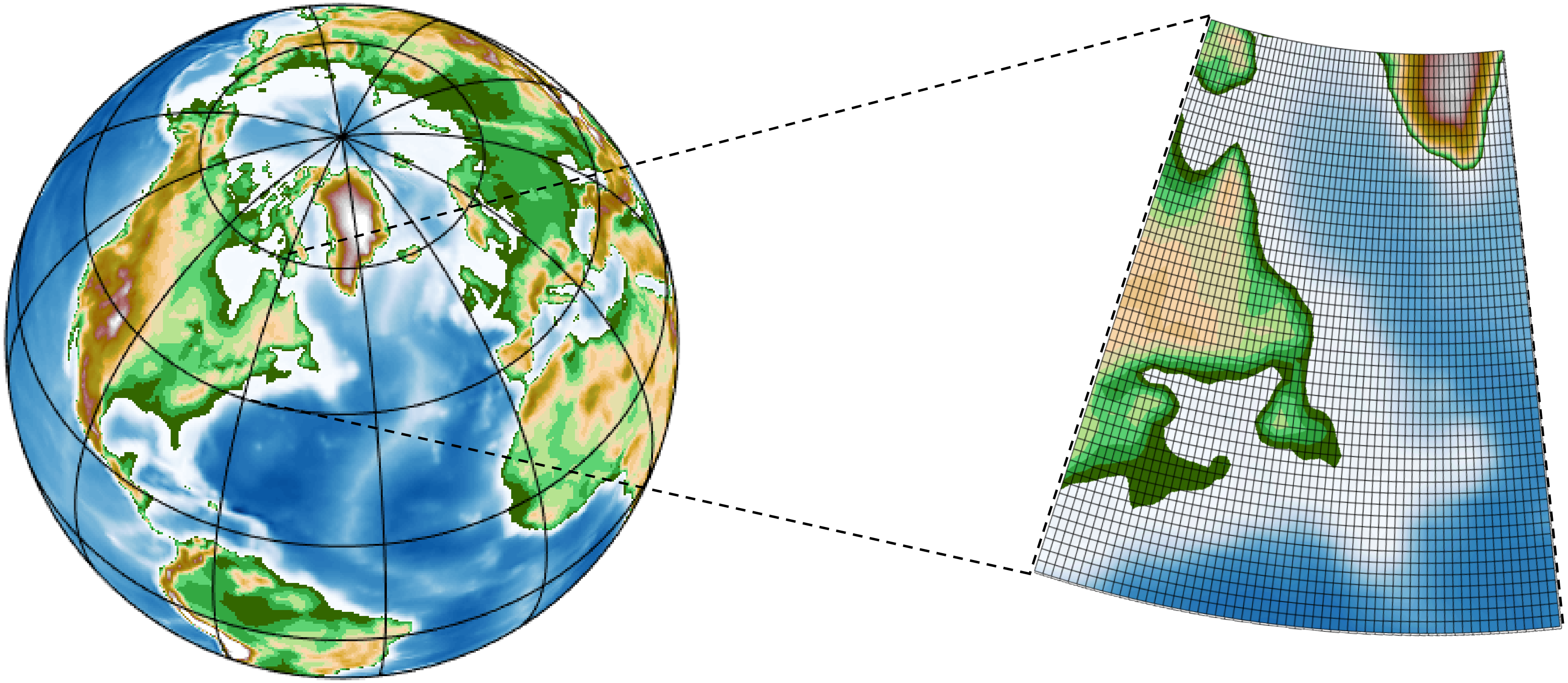
Measurements / Methods

3 **Gas transfer velocity of CO_2, DMS** measured over U_{10} = **1.8 - 25.2** m s^{-1}

Gas Transfer Velocity from Fluxes and Concentrations

$$k = \frac{F_{CO_2}}{\Delta C_{CO_2}} = \frac{F_{CO_2}}{S(\Delta p_{CO_2})} \rightarrow \frac{F_{CO_2}}{S(\Delta f_{CO_2})}$$

Spectral Wave Model: ECMWF ERA-5H

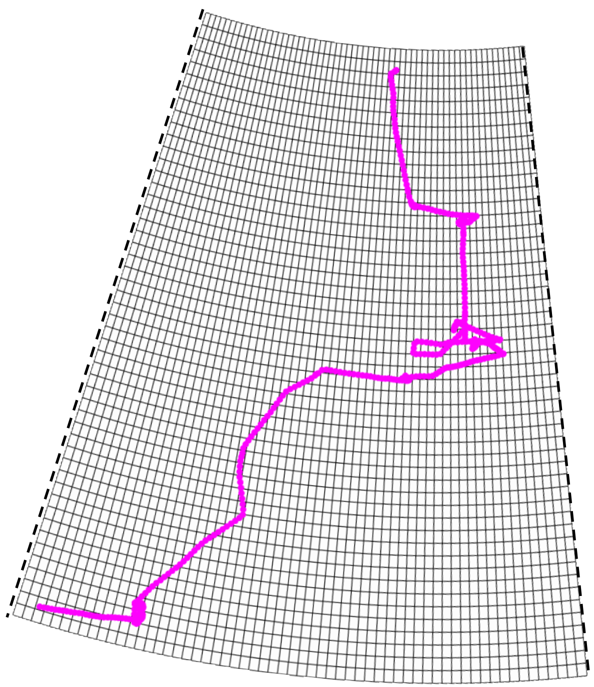


Model Details

1 Global uncoupled wave model forced by hourly **ERA-5** wind (U_{10N}), surface air density, gustiness, and sea ice cover

2 **14** km × **14** km (**0.125**° x **0.125**°) spatial resolution
36 frequencies (f_{min} = 0.035 Hz) x **36** directions

Spectral Wave Model: ECMWF ERA-5H



At each grid point

$F(f, \theta)$ → Wave spectrum partitioned

$1.2 \times 28(u_*/c)\cos(\theta - \phi)$

if ≥ 1 → Wind-sea

if < 1 → Swell

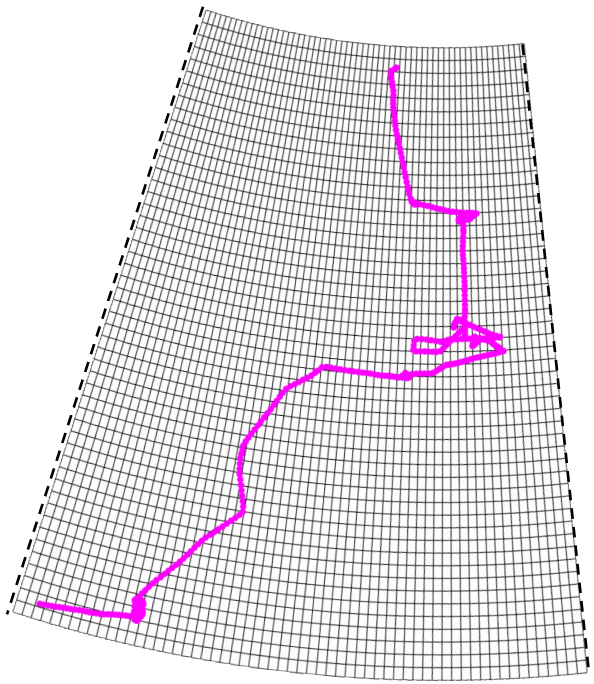
τ_a → u_*, U_{10N}

Model Details

3 — **9 October – 13 November 2013**: 1-hour outputs
Interpolated in space and time to cruise coordinates

4 — **2-D wave spectrum** $F(f, \theta)$ and **total atmospheric stress** τ_a calculated at each model grid-point

Spectral Wave Model: ECMWF ERA-5H



Wind-sea	Swell	Total
$H_{s,ww}$	$H_{s,sw}$	$H_{s,tot}$
$\overline{T}_{ww}$	$\overline{T}_{sw}$	$\overline{T}_{tot}$
		T_p
$\overline{\theta}_{ww}$	$\overline{\theta}_{sw}$	$\overline{\theta}_{tot}$
$\sigma_{\theta,ww}$	$\sigma_{\theta,sw}$	$\sigma_{\theta,tot}$
$\phi_{in,ww}$	$\phi_{in,sw}$	ϕ_{in}
$\phi_{diss,ww}$	$\phi_{diss,sw}$	ϕ_{diss}
		MSS

Model Details

3 — **9 October – 13 November 2013**: 1-hour outputs
Interpolated in space and time to cruise coordinates

4 — **2-D wave spectrum** $F(f,\theta)$ and **total atmospheric stress** τ_a calculated at each model grid-point

Results: Hybrid Gas Transfer Velocity Parameterisation

$$k = \frac{F_{CO_2}}{S(\Delta f_{CO_2})} = k_0 + k_b$$

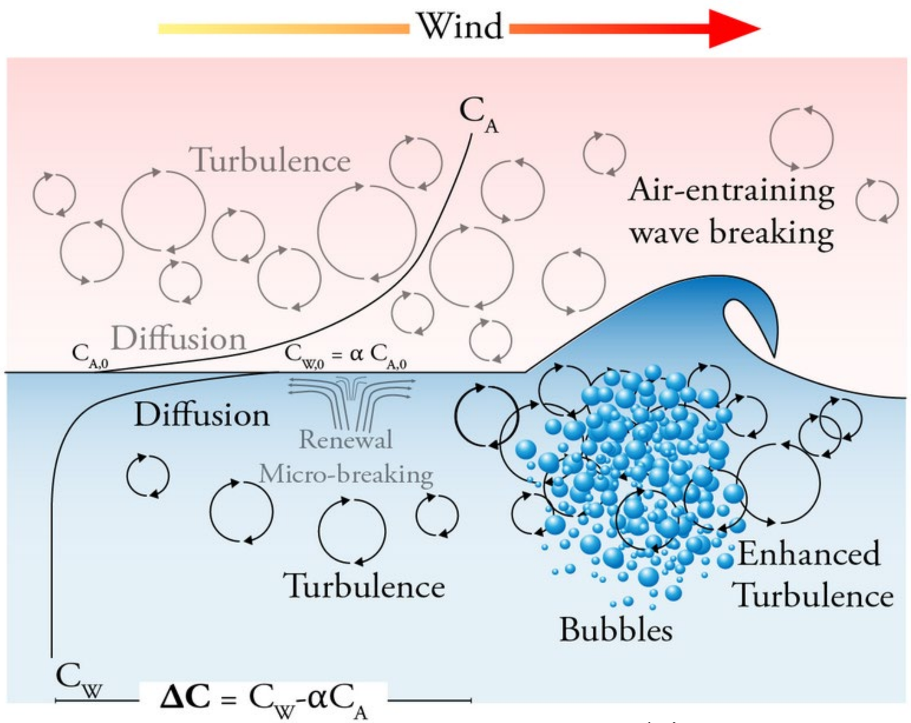
Full-form — Hybrid

Diffusive Gas Transfer Velocity

$$k_0 \propto (D/\nu)^n = (\nu/D)^{-n} = Sc^{-n}$$

Bubble-Mediated Gas Transfer Velocity

$$k_b \propto \frac{V_b}{\alpha} = \frac{\int_0^\infty (4/3)\pi r^3 Q(r)dr}{\alpha}$$



Source: Sophia E. Brumer

Evaluated Parameterisations

1. $k_{BL17} = 0.958U_{10N}^{1.675}$ — Source: Blomquist et al. (2017)
2. $k_{DM18} = A_{NB}u_* + \frac{A_B}{\alpha}u_*^{5/3}\sqrt{gH_{s,tot}}^{4/3}$ — Source: Deike and Melville (2018)
3. $k_{SC22} = 47U_{10N}Sc^{-1/2} + \frac{1}{\alpha}a_{eff}\overline{w}_{ent}W_{growth}$ — Current work

Results: Hybrid Gas Transfer Velocity Parameterisation

Our Parameterisation

$$k_{SC22} = 47 U_{10N} Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$$

Wind Speed | Diffusivity | Solubility | Air Entrainment | Wave Energy Dissipation

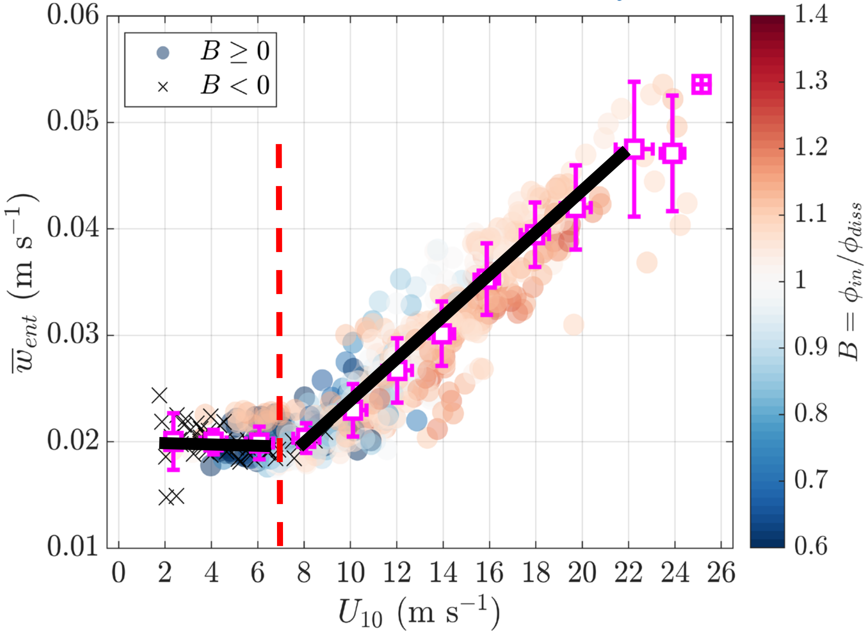
$$\overline{w}_{ent} = \hat{z}_p^*(\mathrm{H}_{s,ww})/\mathrm{T}_{ww}$$

$$\hat{z}_p^* = 0.06(H_{s,ww} - H_{s,crit}) + 0.03 \propto \tau_{degas}$$

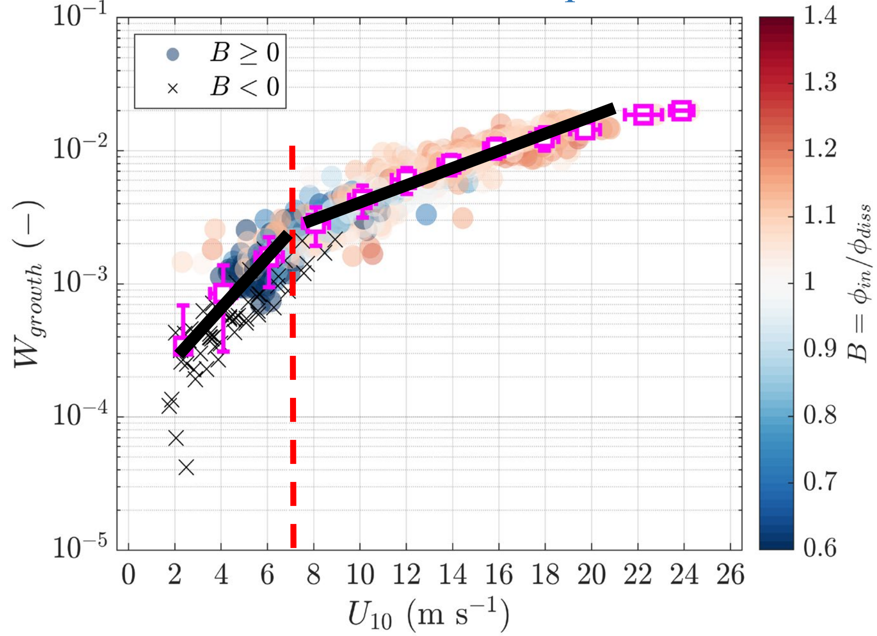
$$W_{growth} = \frac{S_{wcap}}{\rho_w \Omega \hat{z}_p^*}$$

$$S_{wcap} \approx \phi_{diss} = \rho_w g \int_0^{2\pi} \int_0^{\infty} S_{diss}(\omega, \theta)\, d\omega d\theta$$

Entrainment Velocity



Growth-Phase Whitecap Fraction

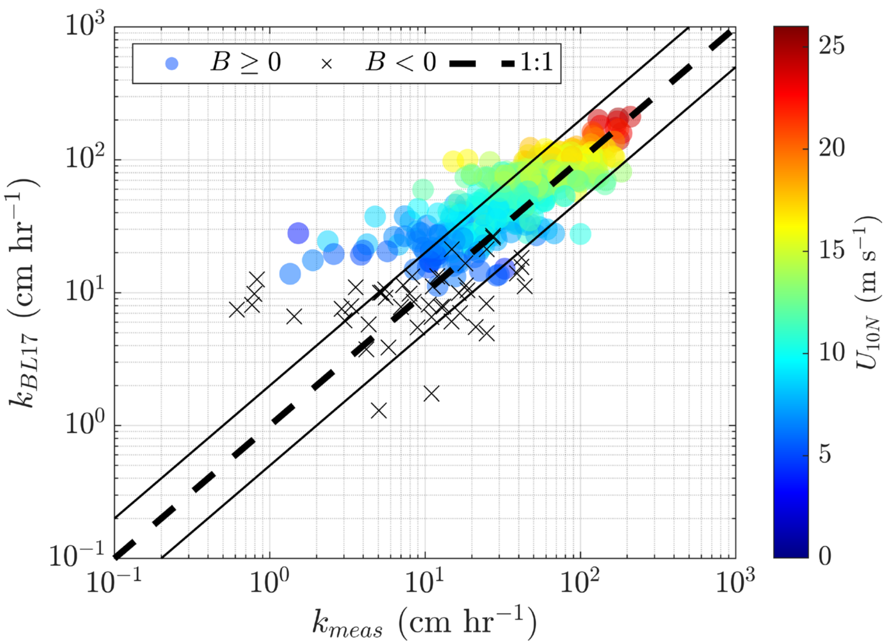


Results: Evaluating Gas Transfer Velocity Parameterisations

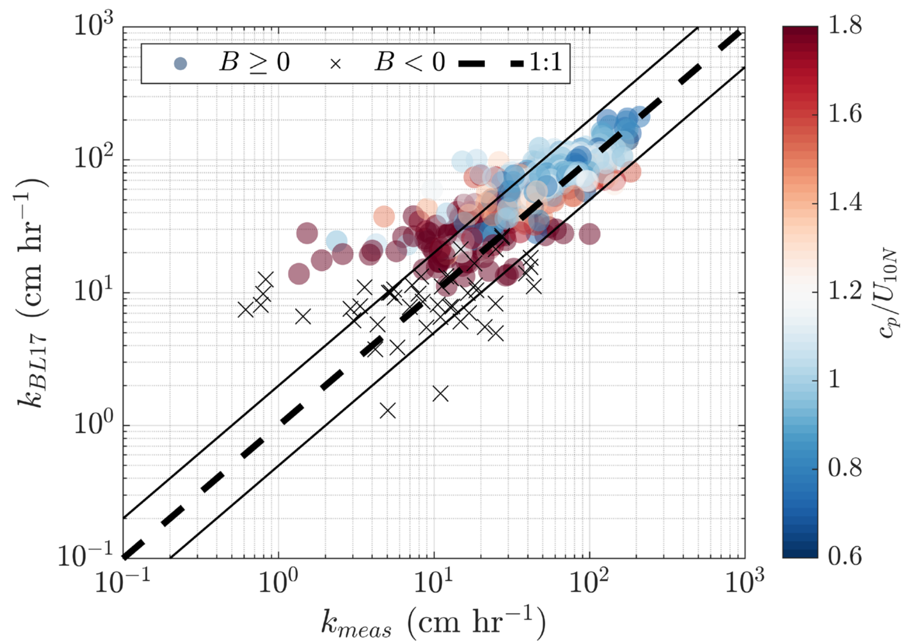
Evaluated Parameterisations

	Parameterisation	Source
1	$k_{BL17} = 0.958 U_{10N}^{1.675}$	Source: Blomquist et al. (2017)
2	$k_{DM18} = A_{NB} u_* + \frac{A_B}{\alpha} u_*^{5/3} \sqrt{g H_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47 U_{10N} Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$	Current work

Wind Speed



Wave Age

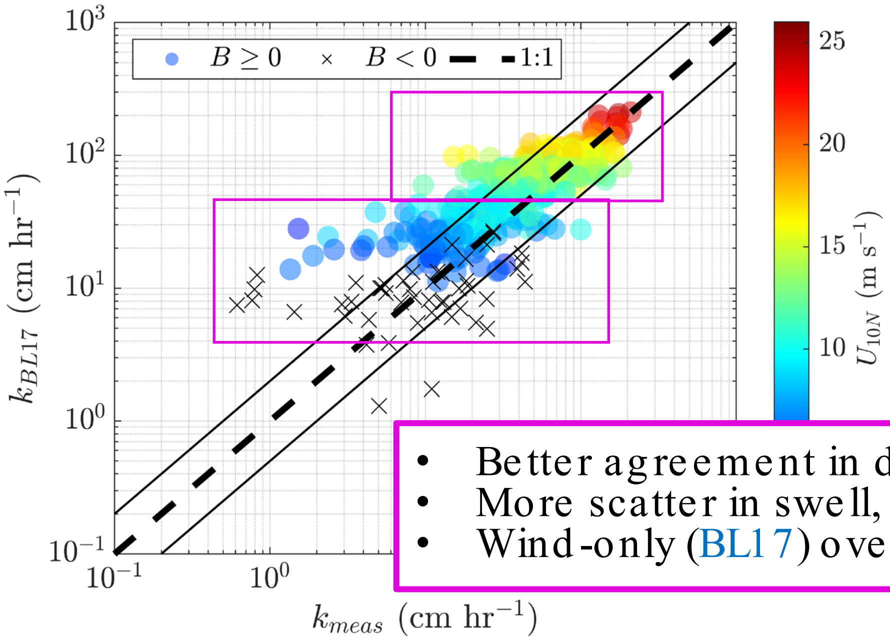


Results: Evaluating Gas Transfer Velocity Parameterisations

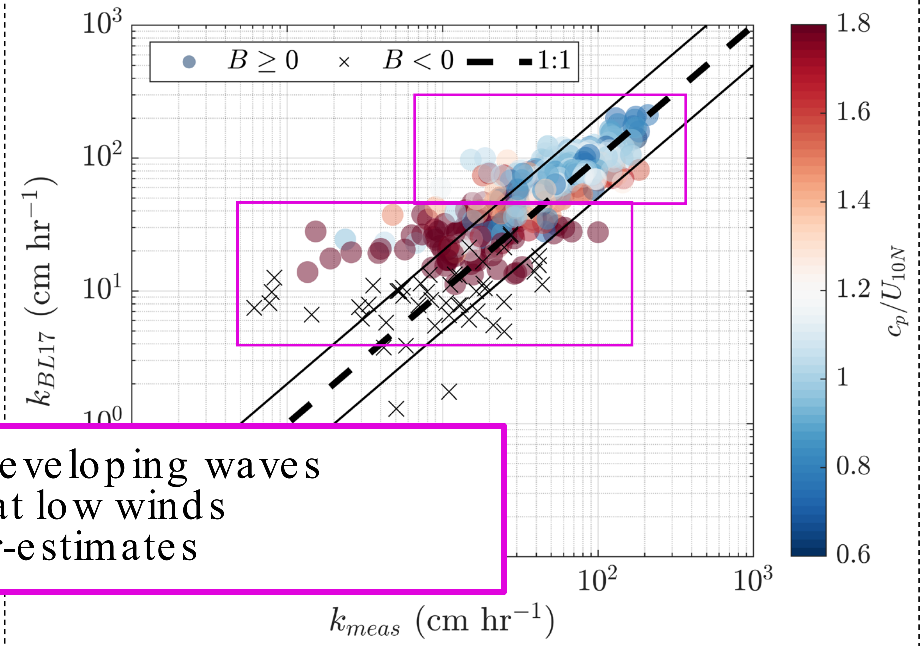
Evaluated Parameterisations

1. $k_{BL17} = 0.958 U_{10N}^{1.675}$ — Source: Blomquist et al. (2017)
2. $k_{DM18} = A_{NB} u_* + \frac{A_B}{\alpha} u_*^{5/3} \sqrt{g H_{s,tot}}^{4/3}$ — Source: Deike and Melville (2018)
3. $k_{SC22} = 47 U_{10N} Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$ — Current work

Wind Speed



Wave Age



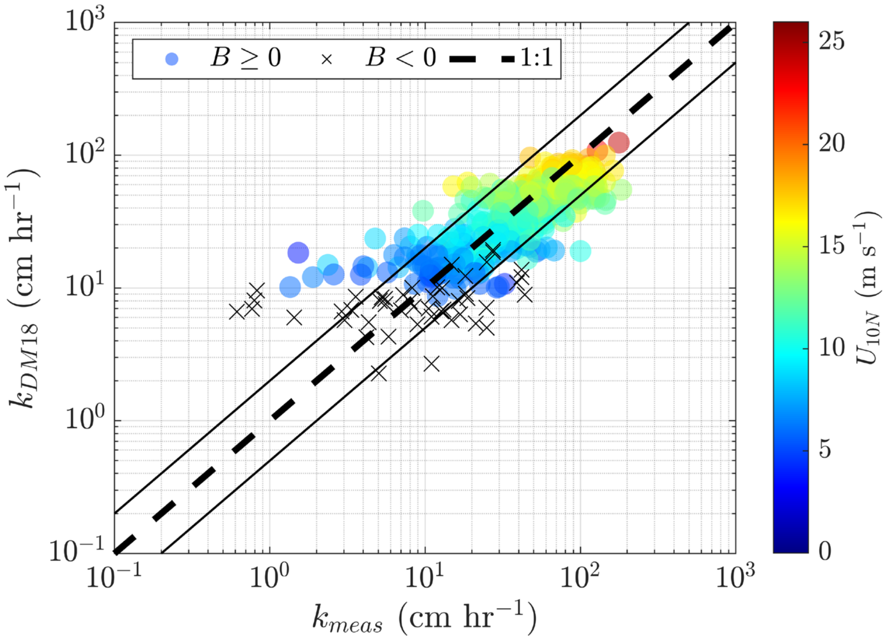
- Better agreement in developing waves
- More scatter in swell, at low winds
- Wind-only (BL17) over-estimates

Results: Evaluating Gas Transfer Velocity Parameterisations

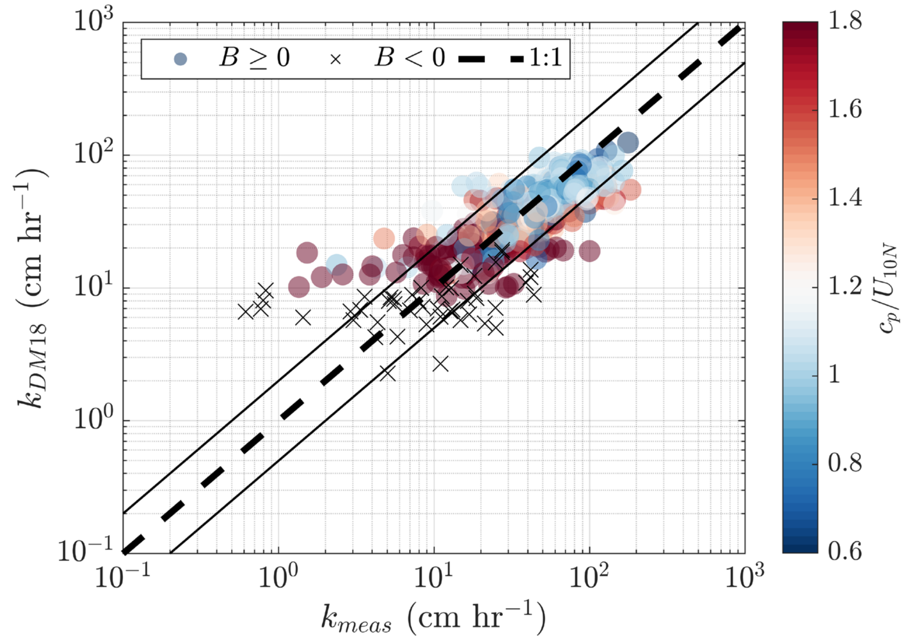
Evaluated Parameterisations

	Parameterisation	Source
1	$k_{BL17} = 0.958 U_{10N}^{1.675}$	Source: Blomquist et al. (2017)
2	$k_{DM18} = A_{NB} u_* + \frac{A_B}{\alpha} u_*^{5/3} \sqrt{g H_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47 U_{10N} Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$	Current work

Wind Speed



Wave Age

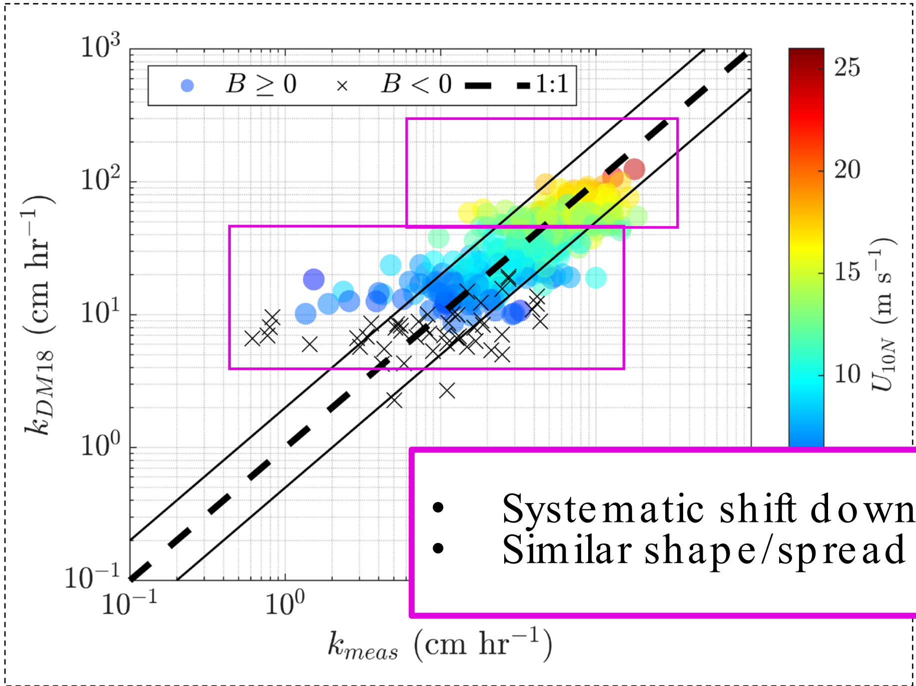


Results: Evaluating Gas Transfer Velocity Parameterisations

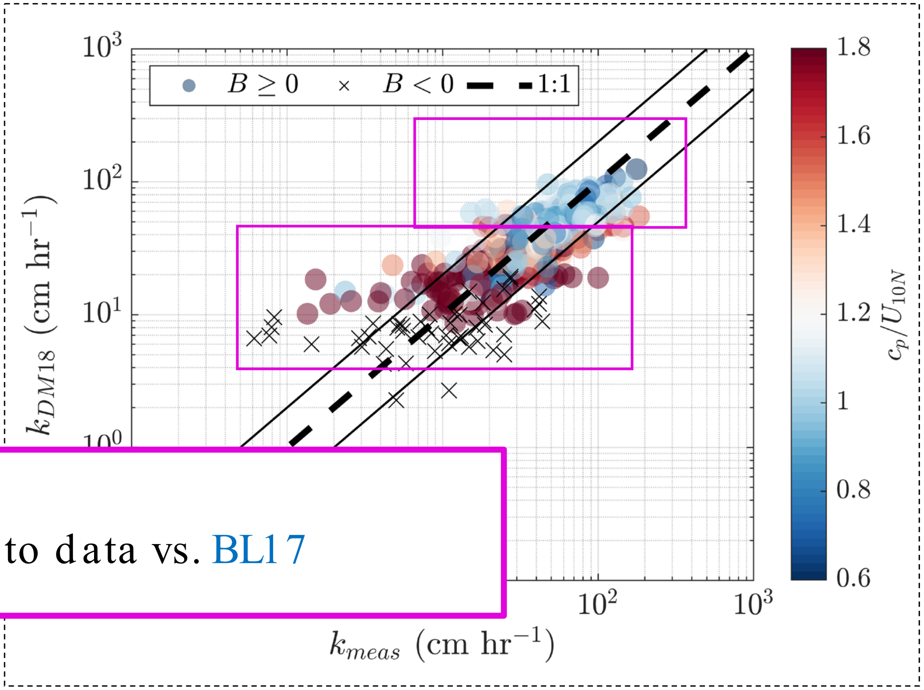
Evaluated Parameterisations

	Parameterisation	Source
1	$k_{BL17} = 0.958 U_{10N}^{1.675}$	Source: Blomquist et al. (2017)
2	$k_{DM18} = A_{NB} u_* + \frac{A_B}{\alpha} u_*^{5/3} \sqrt{g H_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47 U_{10N} Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$	Current work

Wind Speed



Wave Age



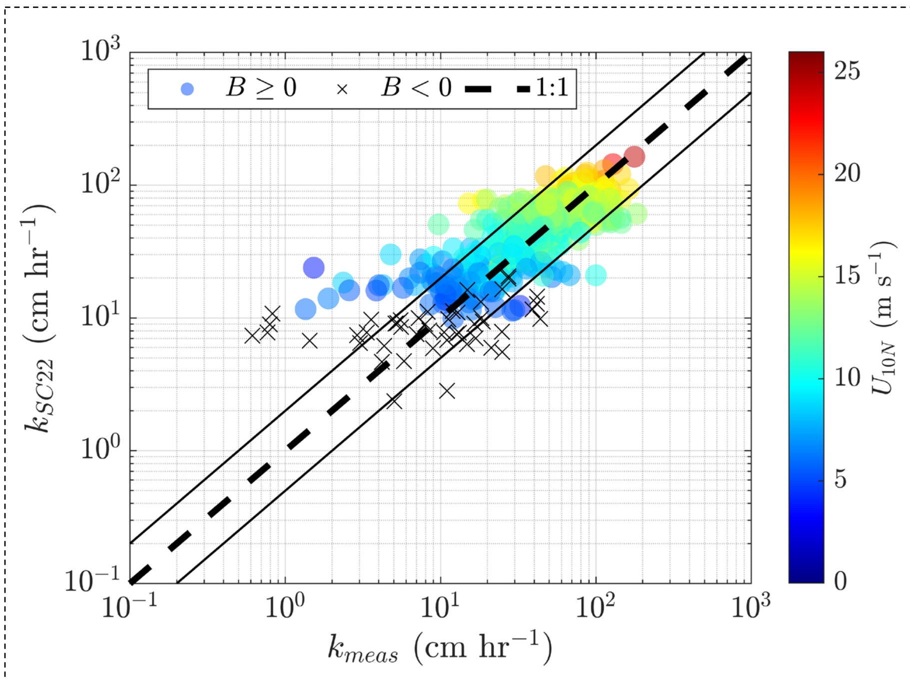
- Systematic shift down
- Similar shape/spread to data vs. BL17

Results: Evaluating Gas Transfer Velocity Parameterisations

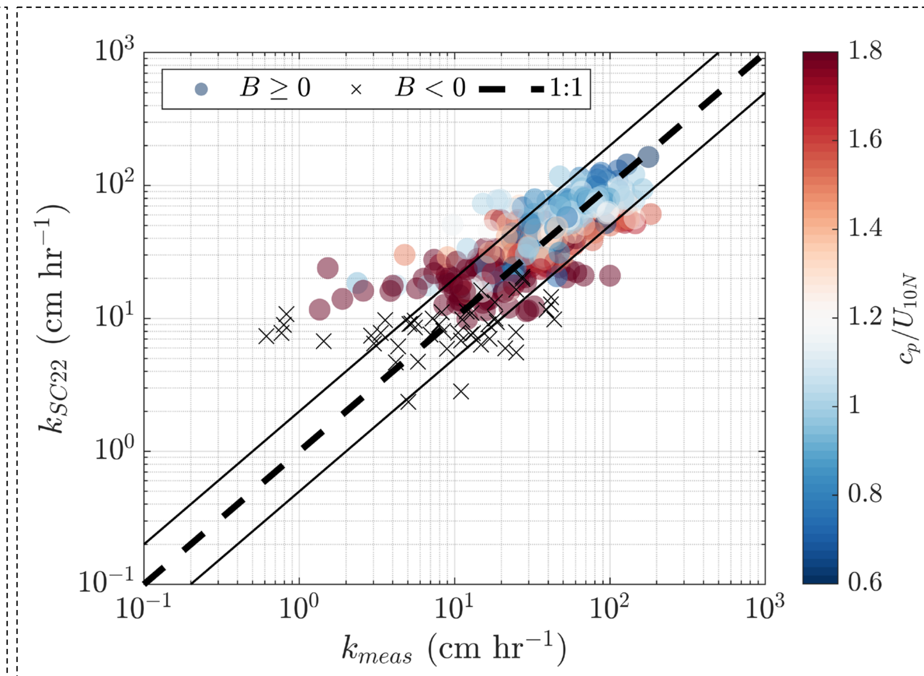
Evaluated Parameterisations

1	$k_{BL17} = 0.958U_{10N}^{1.675}$	Source: Blomquist et al. (2017)
2	$k_{DM18} = A_{NB}u_* + \frac{A_B}{\alpha}u_*^{5/3}\sqrt{gH_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47U_{10N}Sc^{-1/2} + \frac{1}{\alpha}a_{eff}\overline{w}_{ent}W_{growth}$	Current work

Wind Speed



Wave Age

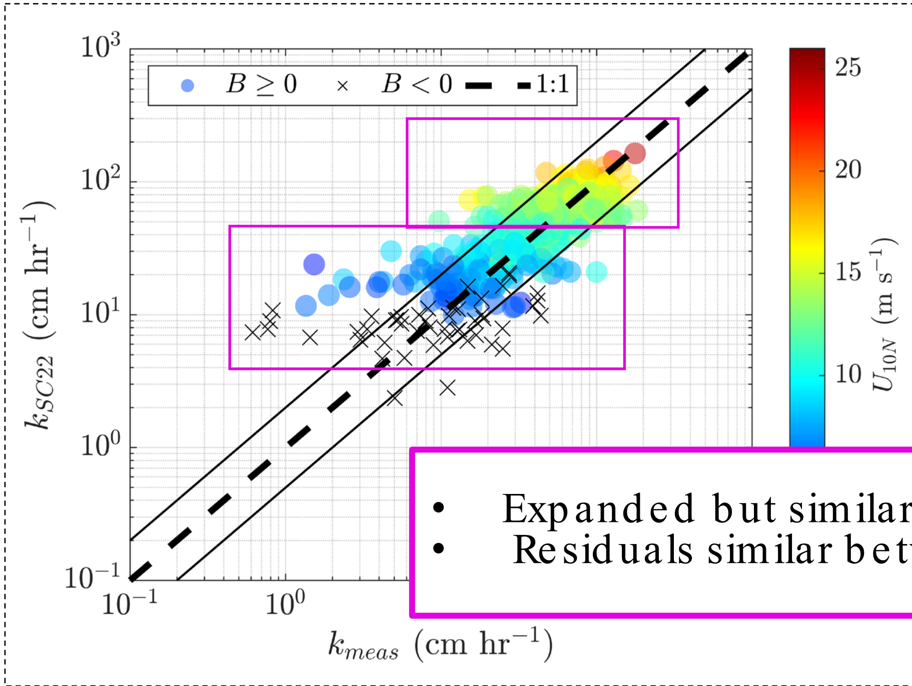


Results: Evaluating Gas Transfer Velocity Parameterisations

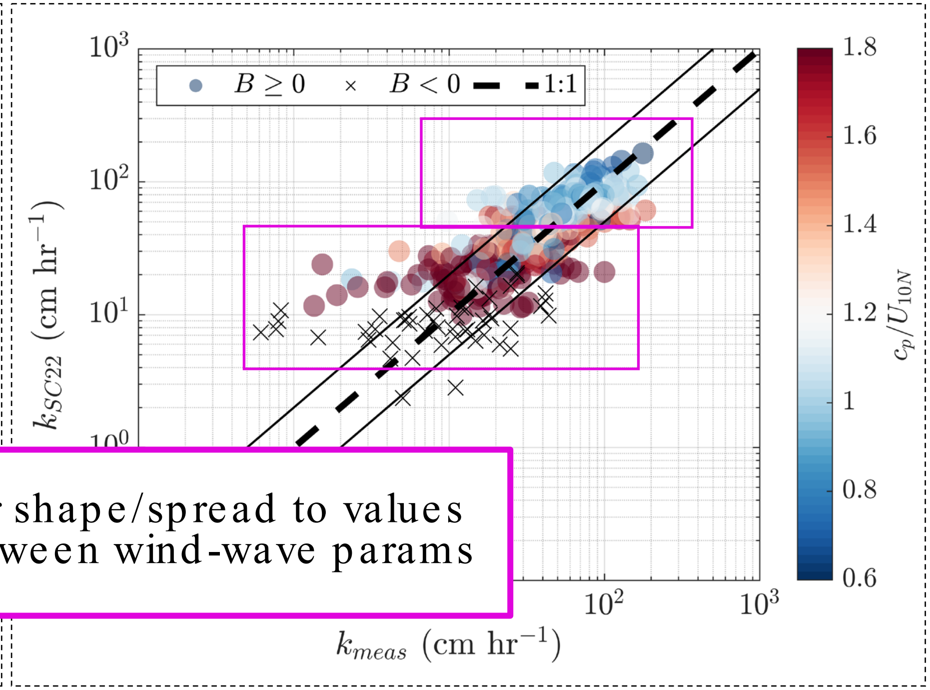
Evaluated Parameterisations

1. $k_{BL17} = 0.958U_{10N}^{1.675}$ — Source: Blomquist et al. (2017)
2. $k_{DM18} = A_{NB}u_* + \frac{A_B}{\alpha}u_*^{5/3}\sqrt{gH_{s,tot}}^{4/3}$ — Source: Deike and Melville (2018)
3. $k_{SC22} = 47U_{10N}Sc^{-1/2} + \frac{1}{\alpha}a_{eff}\overline{w}_{ent}W_{growth}$ — Current work

Wind Speed



Wave Age



- Expanded but similar shape/spread to values
- Residuals similar between wind-wave params

Results: Evaluating Gas Transfer Velocity Parameterisations

Evaluated Parameterisations

1	$k_{BL17} = 0.958U_{10N}^{1.675}$	Source: Blomquist et al. (2017)
2	$k_{DM18} = A_{NB}u_* + \frac{A_B}{\alpha}u_*^{5/3}\sqrt{gH_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47U_{10N}Sc^{-1/2} + \frac{1}{\alpha}a_{eff}\overline{w}_{ent}W_{growth}$	Current work

Performance Summary

Sea State		BL17	DM18	SC22
Developing / Developed ($c_p/U10_N < 1.2$)	R^2:	0.81	0.73	0.72
	RMSE:	28.8	22.5	22.9
Swell ($c_p/U10_N \geq 1.2$)	R^2:	0.73	0.75	0.73
	RMSE:	21.6	23.2	21.4
Total (all)	R^2:	0.82	0.77	0.75
	RMSE:	24.8	22.6	22.0

Results: Parameterisation Success, Uncertainty, and Error

Wind-Wave Parameterisations

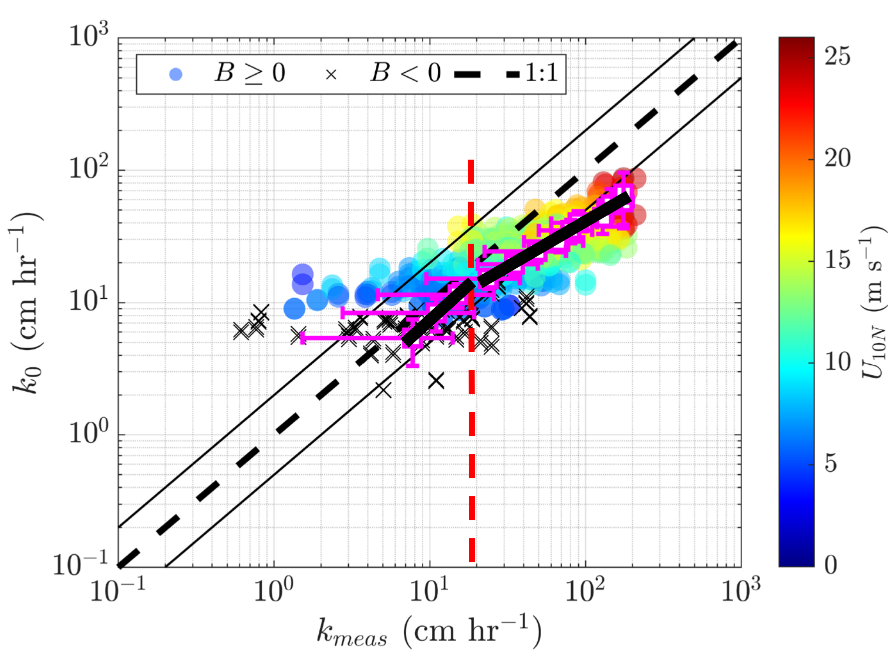
(2) $k_{DM18} = A_{NB}u_* + \frac{A_B}{\alpha}u_*^{5/3}\sqrt{gH_{s,tot}}^{4/3}$ Source: Deike and Melville (2018)

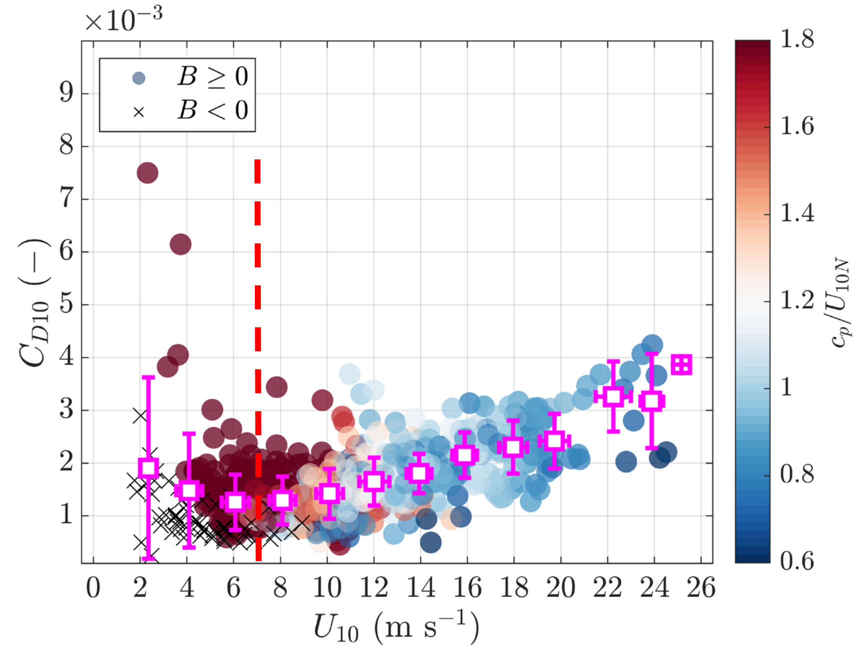
(3) $k_{SC22} = 47U_{10N}Sc^{-1/2} + \frac{1}{\alpha}a_{eff}\overline{w}_{ent}W_{growth}$ Current work

Diffusive Gas Transfer Velocity

$A_{NB}u_*$ COARE 3.1; Fairall, et al. (2011)

$47U_{10N}Sc^{-1/2}$ Asher and Wanninkhof (1998); Blomquist, et al. (2017)





Results: Parameterisation Success, Uncertainty, and Error

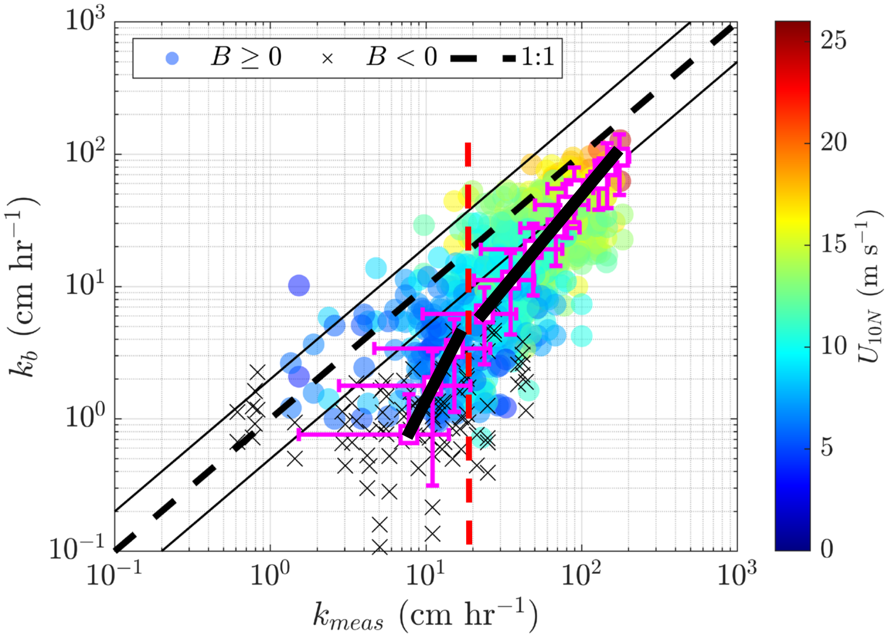
Wind-Wave Parameterisations

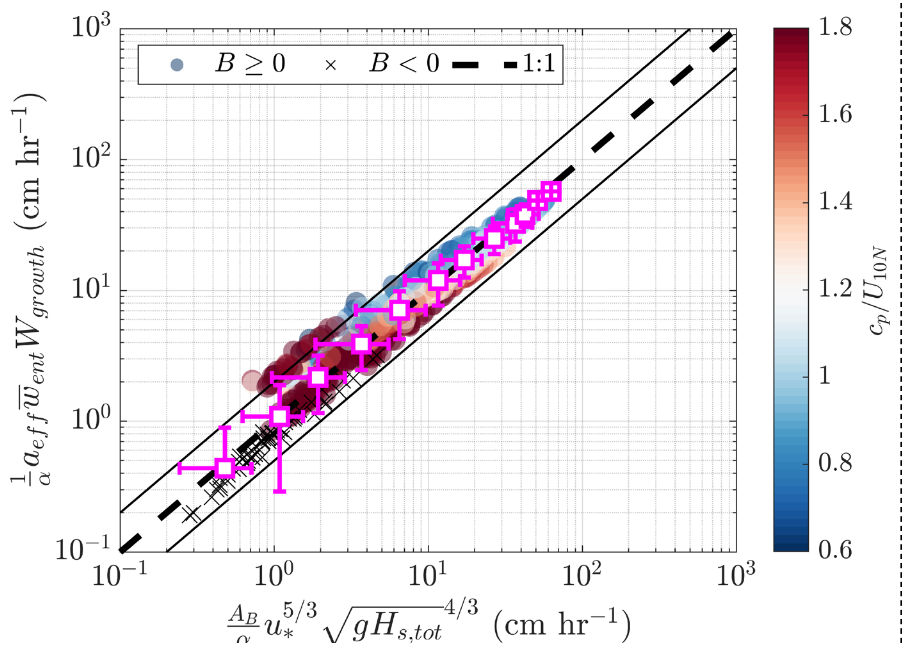
2	$k_{DM18} = A_{NB} u_* + \frac{A_B}{\alpha} u_*^{5/3} \sqrt{g H_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47 U_{10N} Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$	Current work

Bubble-Mediated Gas Transfer Velocity

$\frac{A_B}{\alpha} u_*^{5/3} \sqrt{g H_{s,tot}}^{4/3}$ — Deike and Melville (2018) and refs. therein

$\frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$ — Callaghan et al. (in. prep.)





Results: Parameterisation Success, Uncertainty, and Error

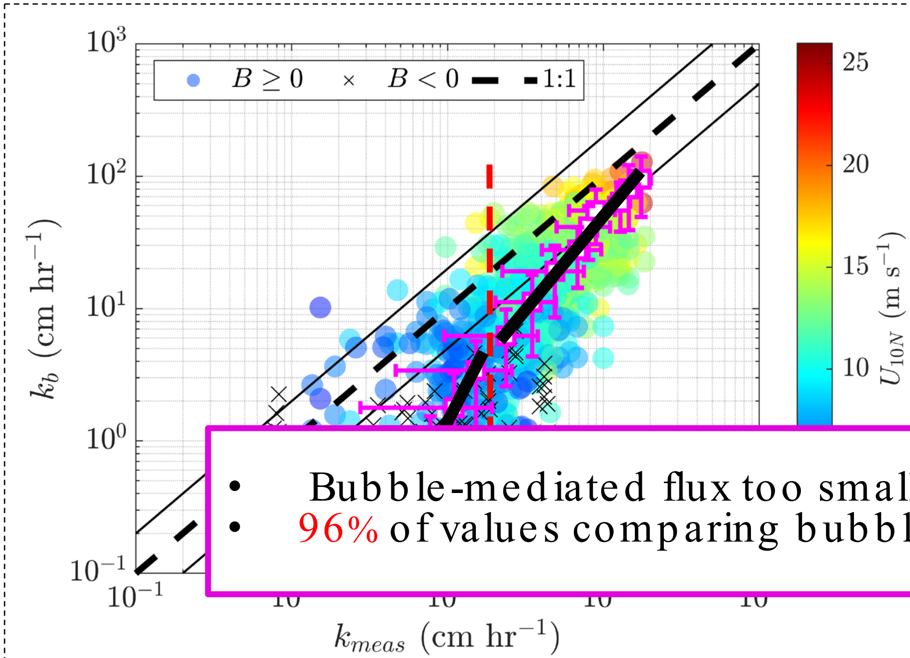
Wind-Wave Parameterisations

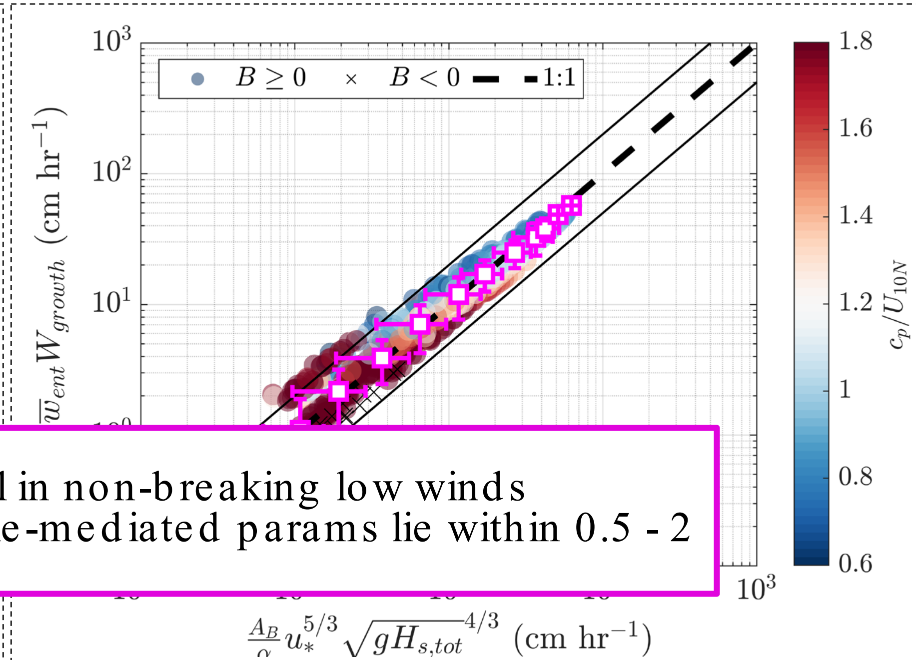
2	$k_{DM18} = A_{NB}u_* + \frac{A_B}{\alpha} u_*^{5/3} \sqrt{gH_{s,tot}}^{4/3}$	Source: Deike and Melville (2018)
3	$k_{SC22} = 47U_{10N}Sc^{-1/2} + \frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$	Current work

Bubble-Mediated Gas Transfer Velocity

$\frac{A_B}{\alpha} u_*^{5/3} \sqrt{gH_{s,tot}}^{4/3}$ — Deike and Melville (2018) and refs. therein

$\frac{1}{\alpha} a_{eff} \overline{w}_{ent} W_{growth}$ — Callaghan et al. (in. prep.)





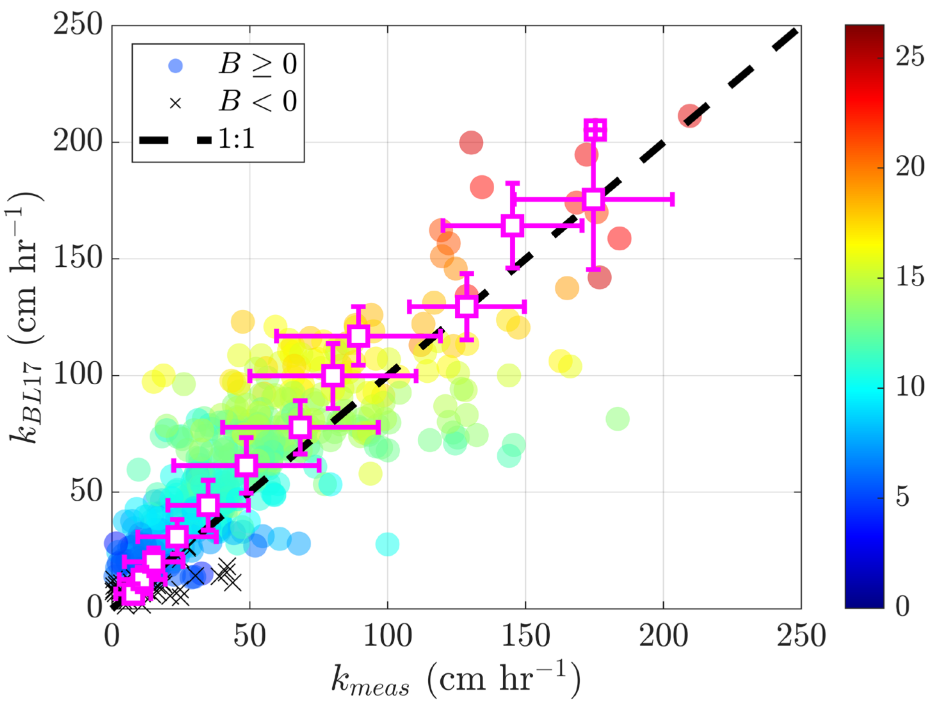
- Bubble-mediated flux too small in non-breaking low winds
- 96% of values comparing bubble-mediated params lie within 0.5 - 2

Conclusions

1

Wind-speed based parameterisations are inadequate

- Scatter too large
- Missing wave breaking as the dominant air entrainment mechanism at intermediate and high winds
- Missing low-wind swell influence, sheltering effects, chemistry



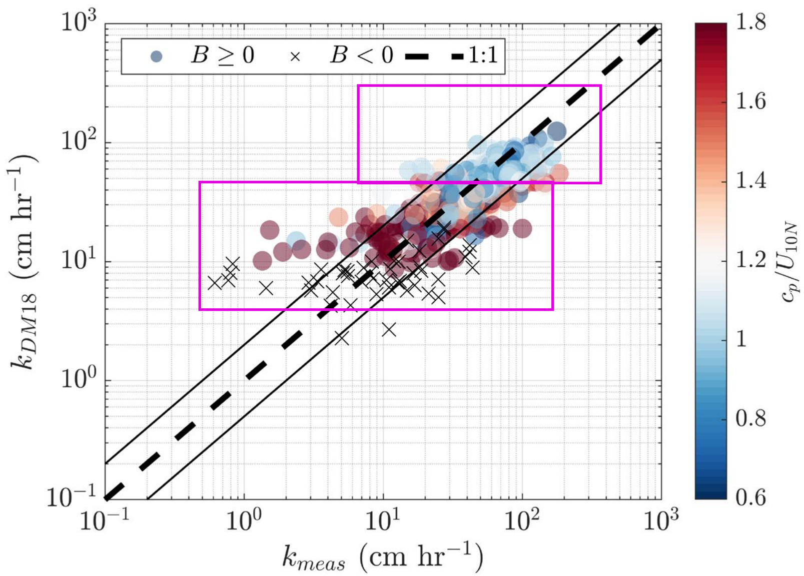
Conclusions

2

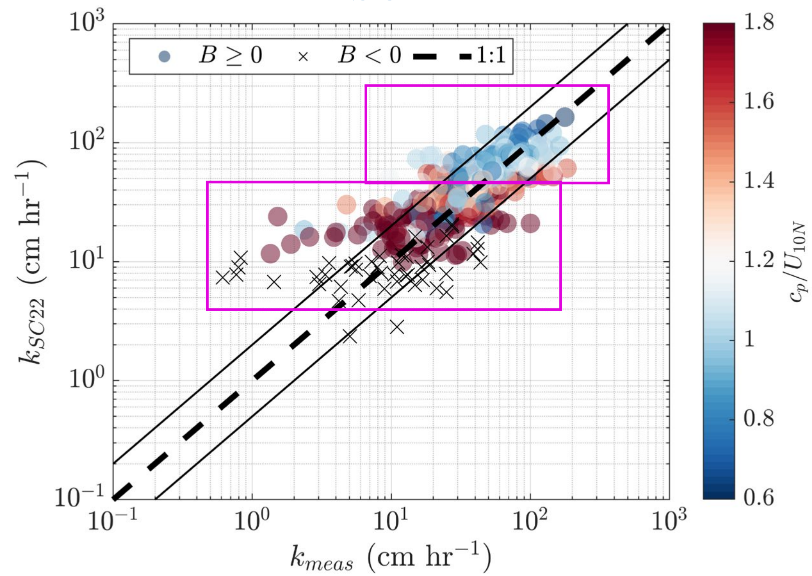
Wind-wave parameterisations of DM18 and SC22 perform similarly across developing, developed, and swell sea states

- Correlation coefficients in the mid 70s, similar RMSE
- Similar description of air entrainment, solubility effects
- Both perform more poorly at low winds, with more scatter in swell seas

DM18



SC22



Conclusions

1 Wind-speed based parameterisations are inadequate

- Scatter too large
- Missing wave breaking as the dominant air entrainment mechanism at intermediate and high winds
- Missing low-wind swell influence, sheltering effects, chemistry

2 Wind-wave parameterisations of DM18 and SC22 perform similarly across developing, developed, and swell sea states

- Correlation coefficients in the mid 70s, similar RMSE
- Similar description of air entrainment, solubility effects
- Both perform more poorly at low winds, with more scatter in swell seas

3 Both DM18 and SC22 are improvements on wind-only parameterisation but there is still room for further improvement

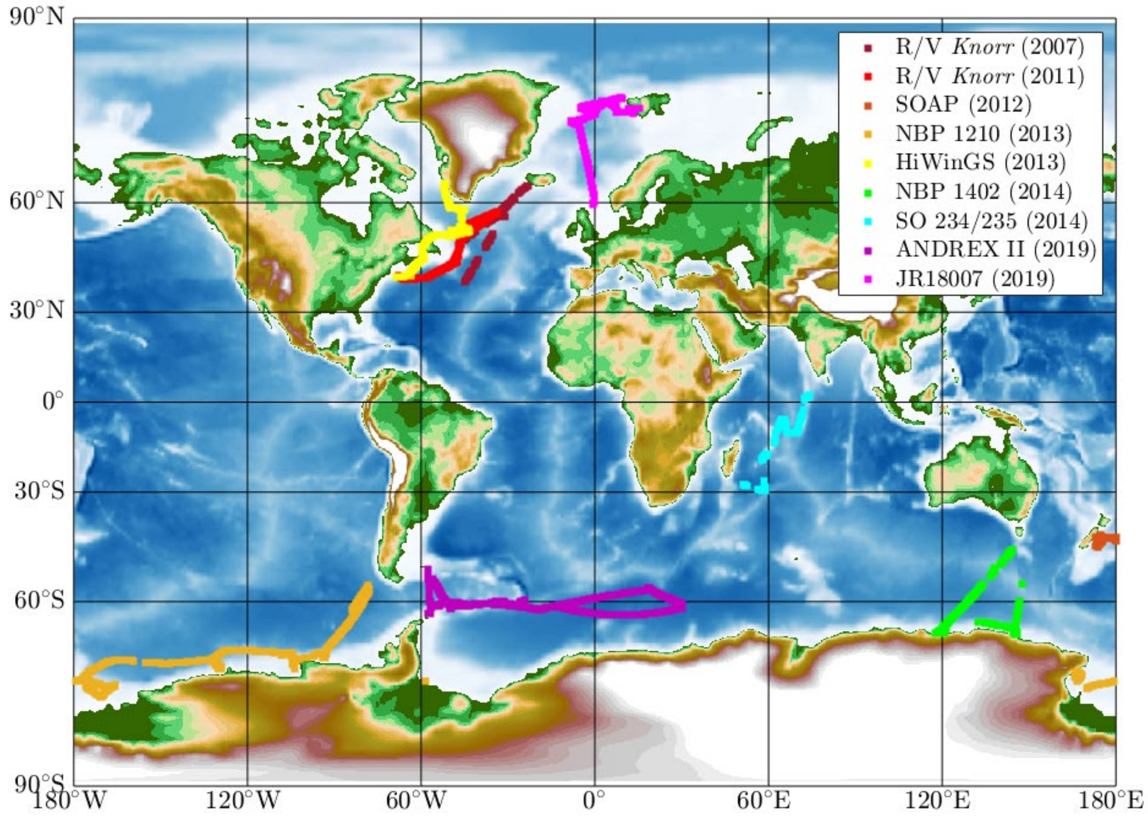
- Physics: Wave sheltering, directional spread, wind-wave alignment, choice of wave height for entrainment/ballistic velocity, is effective air fraction constant?
- Chemistry: Radius-dependence of bubbles/lifetime/efficiency
- Dataset: Location? Fetch? Instrument choices/error? … Need more data!

Future Work

1

Evaluate parameterisations across more datasets

- 9 cruise datasets (> 7000 gas transfer velocity measurements)
- Spans 12 years, 2007-2019
- Different wind speeds, wave conditions, fetch, water temperature (solubility)



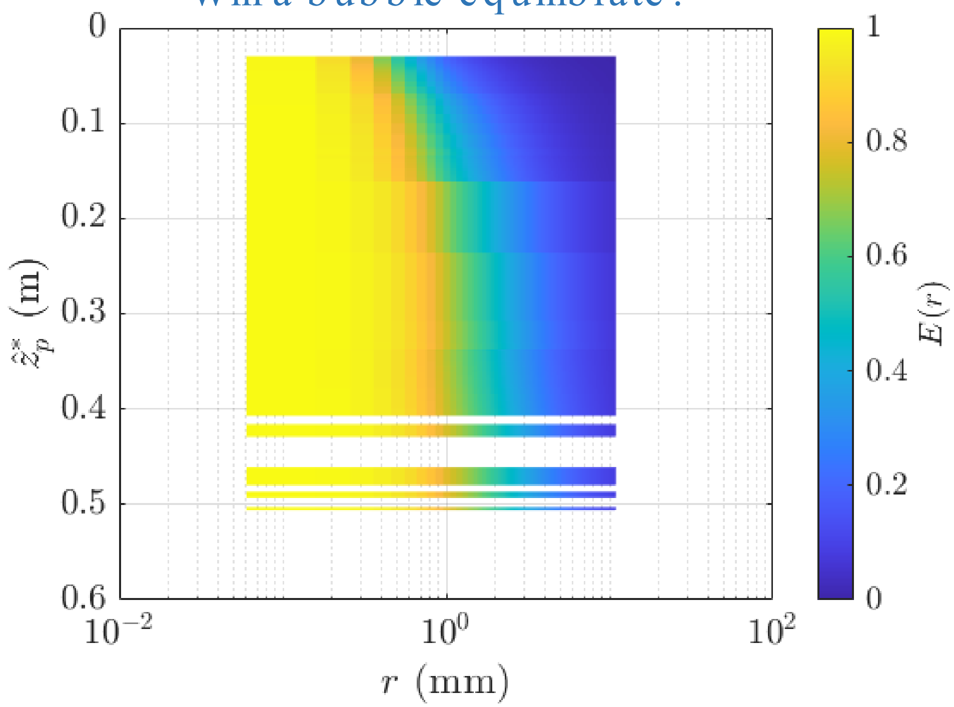
Future Work

2

Incorporate missing equilibration chemistry through efficiency factor

- Based on parameterisations for radius-dependent bubble equilibration, rise velocity, plume penetration depth, solubility
- Account for contributions of bubbles of different sizes

Will a bubble equilibrate?



Efficiency factor

$$E(r) = \frac{z_0}{z_0 + H_{eq}}$$

Characteristic bubble depth

$$z_0 \approx \hat{z}_p^*$$

Equilibration distance

$$H_{eq}(r) = \frac{4\pi}{3\alpha} \frac{rU(r)}{k(r)}$$

Diffusional flow rate or gas transfer coefficient

$$k(r) = 8\sqrt{\frac{\pi D U(r)}{2r}}$$

$$k_b \propto \frac{V_b}{\alpha} = \frac{\int_0^\infty (4/3)\pi r^3 Q(r) E(r) dr}{\alpha}$$

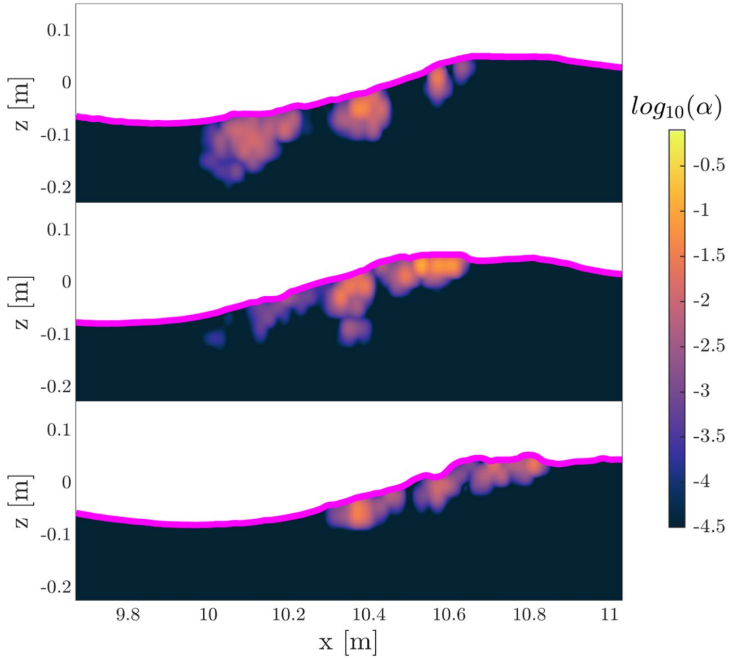
Future Work

3

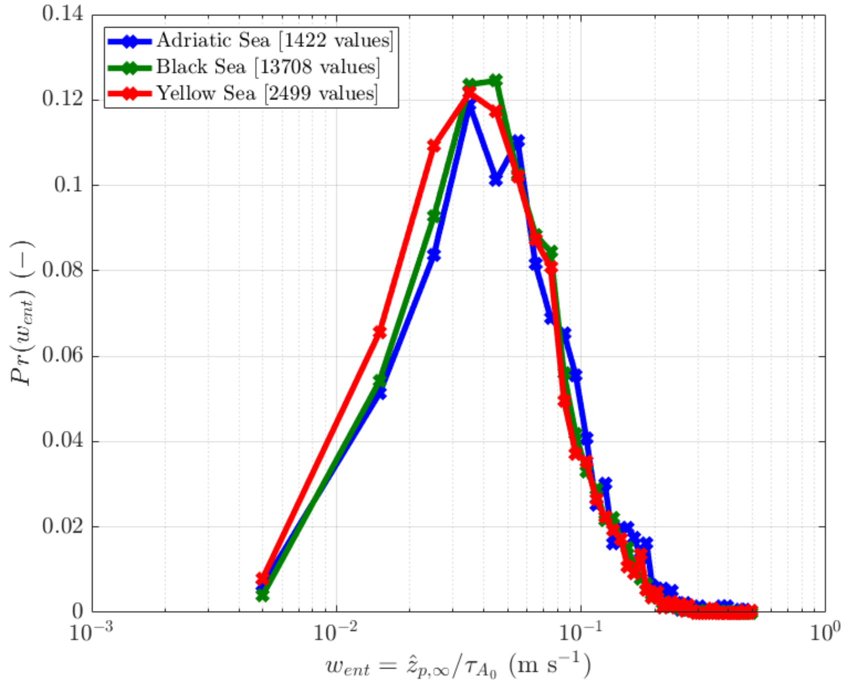
Laboratory testing & field data of breaking waves to constrain α_{eff} and $\overline{w}_{ent}$

- Various air fraction estimates from literature (0.2-0.6; Lamarre and Melville, 1991; Deane and Stokes, 2002; Deane 1999)
- Optimize entrainment velocity against field estimates from Adriatic Sea, Black Sea, Yellow Sea

Source: Rui Cao



Source: Joe Peach



Acknowledgements

Dr. Adrian Callaghan
Senior Lecturer
Imperial College London

Principal investigator
Laboratory and field studies in support of parameterisation physics

Dr. Ming-Xi Yang
Chemical Oceanographer
Plymouth Marine Laboratory

Gas transfer velocity data from cruises
Eddy covariance flux analysis

Dr. Jean-Raymond Bidlot
Senior Scientist
European Centre for Medium-Range Weather Forecasts

Spectral wave model execution and outputs

Further Work at GTWS22

Earlier this week

Dr. Adrian Callaghan
Senior Lecturer, Imperial College London

Session 3 (Tues 17 May 14:30)
Energy dissipation-based estimates of whitecap coverage and air entrainment rates in whitecaps

Rui Cao
Ph.D. Student, Imperial College London

Poster Session (Tues 17 May 17:30 - 19:00)
Observations of breaking wave air entrainment and bubbles in varying wind and wave conditions

Upcoming at 10:30

Joe Peach
Ph.D. Student, Imperial College London

Statistical distributions of whitecap variables using a novel remote sensing technique to detect and track individual whitecaps in digital sea surface images