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Global synthesis of air-sea CO_2 transfer velocity estimates from ship-based eddy covariance measurements

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A short history of gas exchange studies

1973 *Liss*
Two layer model
flux = $K\ \Delta C$

1986 *Liss & Merlivat*
Different K v. U slopes and Sc exponents in different regimes

1986 *Broecker et al.*
Eddy covariance (EC) with open path IR give CO_2 flux an order of magnitude too large

1987 *Jaehne et al.*
Small scale waves matter: $K \propto u_* Sc^n$, n from -2/3 to -1/2

1992 *Wanninkhof*
Global ^{14}C disequilibrium
K_{CO2} assumed to $\propto U^2$

1997 *Woolf*
Bubble-mediated gas exchange more important for less soluble gas

1999 *Wanninkhof & McGilllis*
EC (closed-path IR, not dried) $K_{CO2} \propto U^3$

2000 *Nightingale et al.*
Dual tracer $^3He/SF_6$
Quadratic relationship between K and U; n ≅ -1/2

A short history of gas exchange studies (continued)

2003 *Zhao & Toba.*
Parametrize K with wave Reynolds number

2004 *Frew et al.*
Active thermography:
Small waves a better proxy of K than U as they account for surfactants

2004 *Huebert et al.*
EC K_{DMS} vs. U power ~1
K >0 at low U

2010 *Miller et al.*
EC CO_2 flux measurements markedly improved by using closed path, dried IR analyzer

2014 *Landwehr/Blomquist et al.*
Confirm benefits of drying the air in EC CO_2 flux measurements

2016 *Butterworth & Miller*
First autonomous EC CO_2 flux measurements on ship

2017 *Bell/Blomquist et al.*
$K_{CO2} > K_{DMS}$ at high U due to bubbles

2021 *Yang et al.*
Strong evidence that natural surfactants modulate K_{CO2} over open ocean

This work

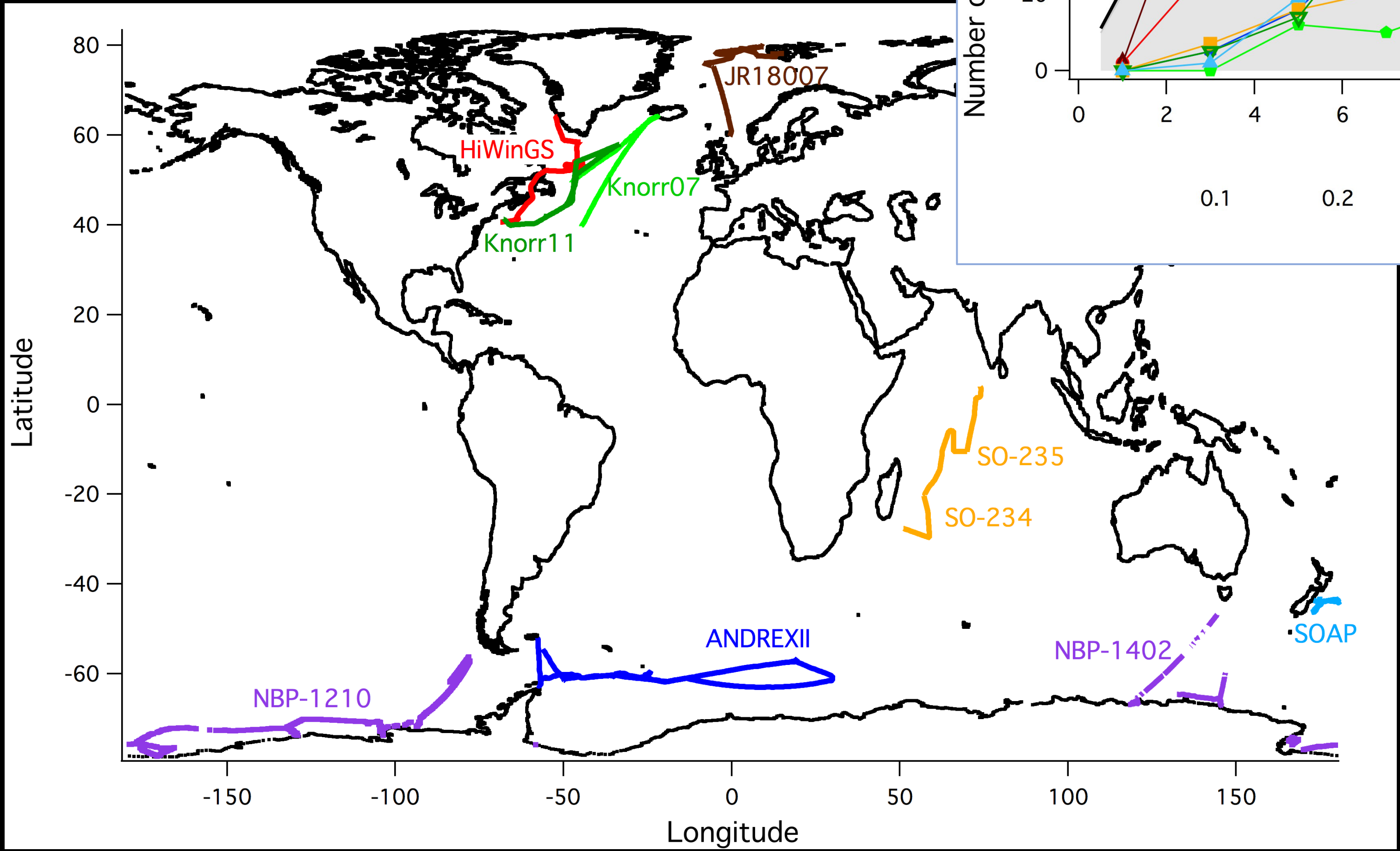
- Synthesis of the state-of-the-art shipboard CO_2 gas transfer velocity (K_{CO2}) measurements since 2007
  - Consistent flux averaging time interval (hourly)
  - Updated solubility and Schmidt number parametrization (Wanninkhof 2014)
  - Inclusion of cool skin effect on ΔC (Woolf et al. 2016)
- Assessment of measurement uncertainty
- Physical processes
  - Moderate wind
  - Low wind
  - Large and small waves
- Conclusion and outlook

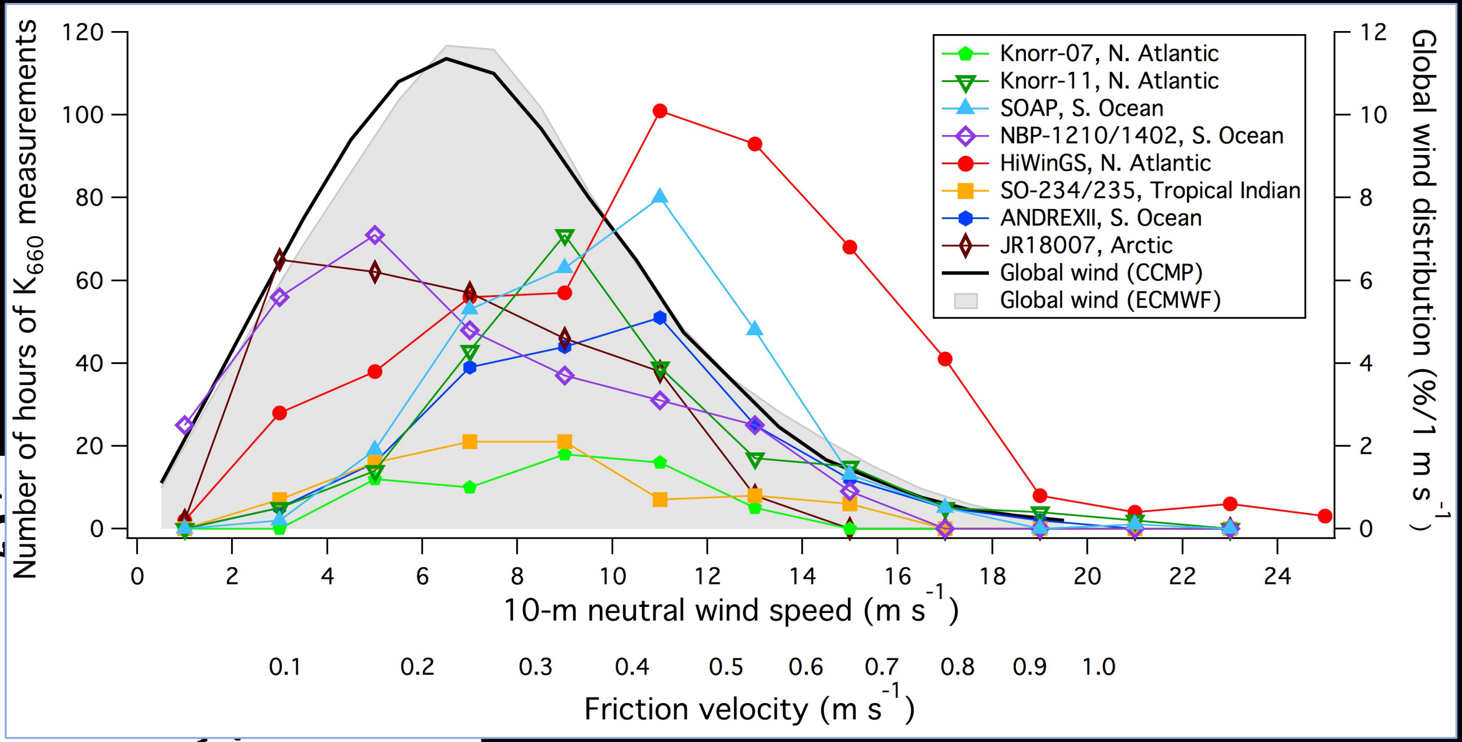
Datasets

11 cruises from the last decade+

All used closed-path, dried CO_2 Analyzer (2000 h of data)

$$K_{660,CO2} = \text{flux} / \Delta C \, (660/Sc)^{-0.5}$$





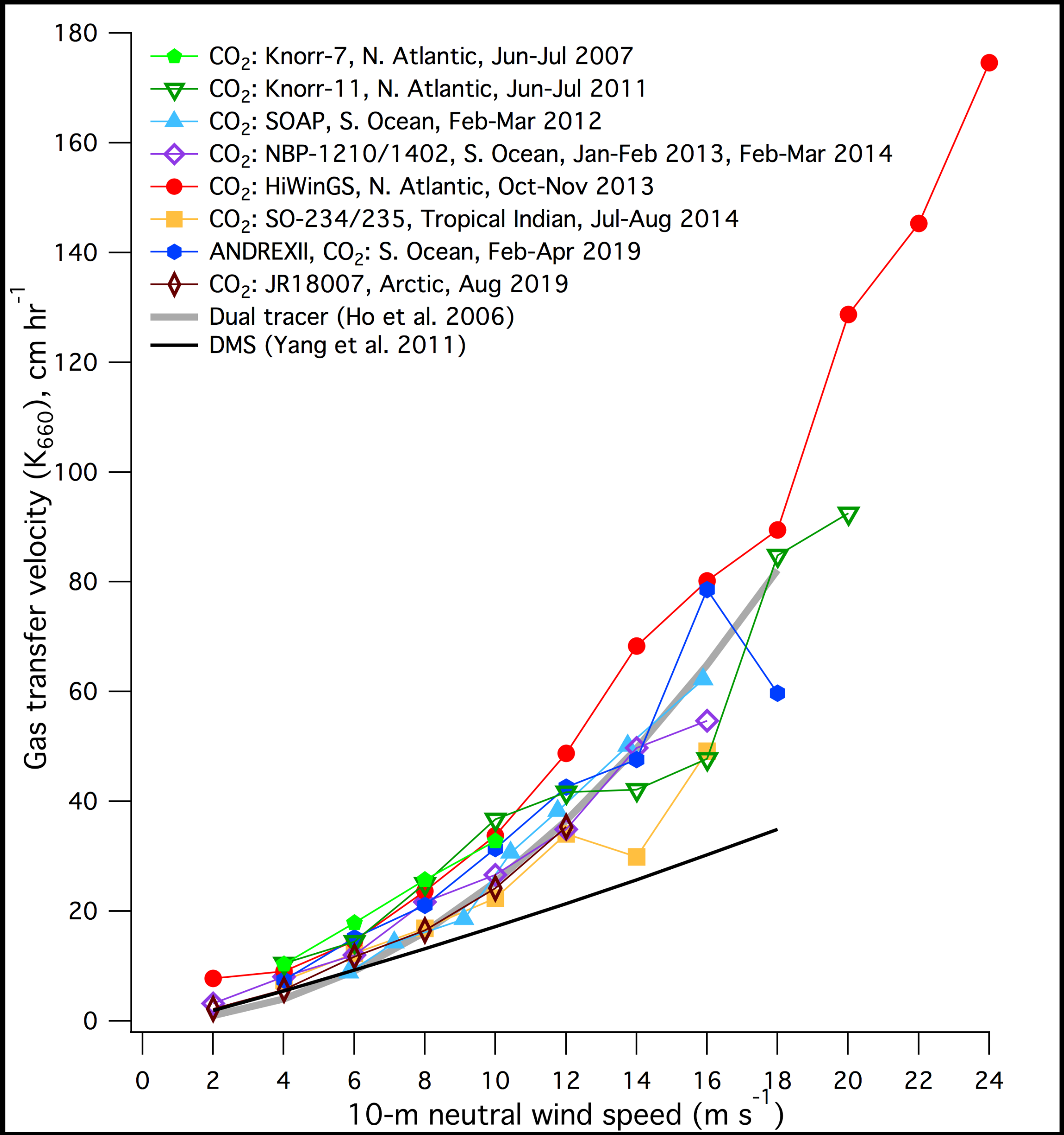
Most data at moderate wind speeds

Measurements in very low/high winds still limited (but >> other methods)

Results

- $K_{660,CO2}$ vs. wind speed (U_{10N})

- Ballpark agreement in $K_{660,CO2}$ among 8 datasets (11 cruises)
- At moderate to high wind speeds, CO_2 and dual tracer transfer similar, much higher than $K_{660,DMS}$
- $K_{660,CO2}$ vs. wind speed relationship non-linear (but less than U^2), and no obvious sign of 'leveling off' at high wind speeds



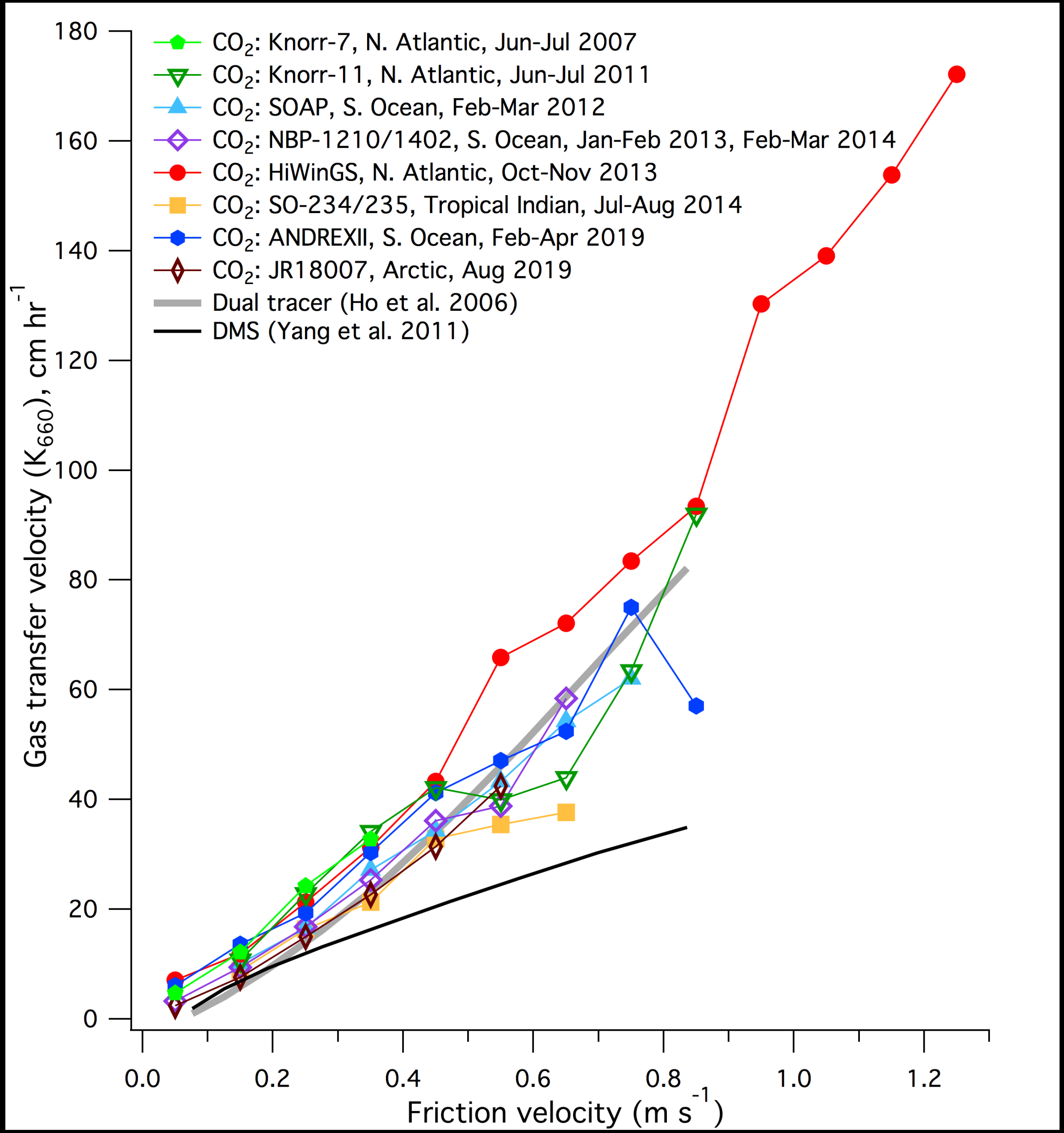
Results

- $K_{660,CO2}$ *vs. friction velocity* (u_*)

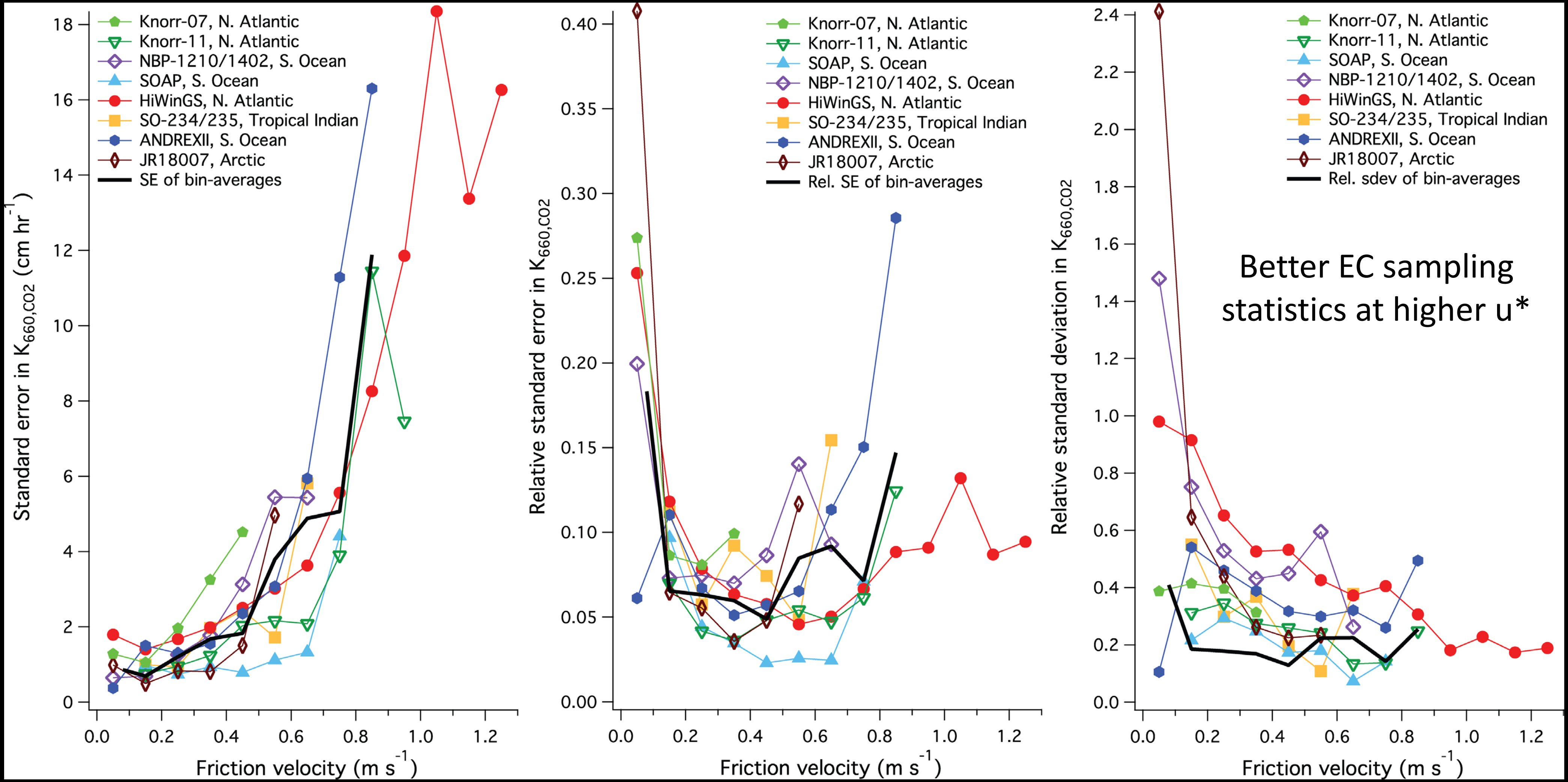
- Approximately **linear** relationship between $K_{660,CO2}$ and u_* (between u_* of 0.1 and 0.5 m s^{-1})

- At given u_*, $K_{660,CO2}$ tends to be higher in N. Atlantic/Southern Ocean than in Arctic/tropics

- What causes regional variation in $K_{660,CO2}$ among different cruises?



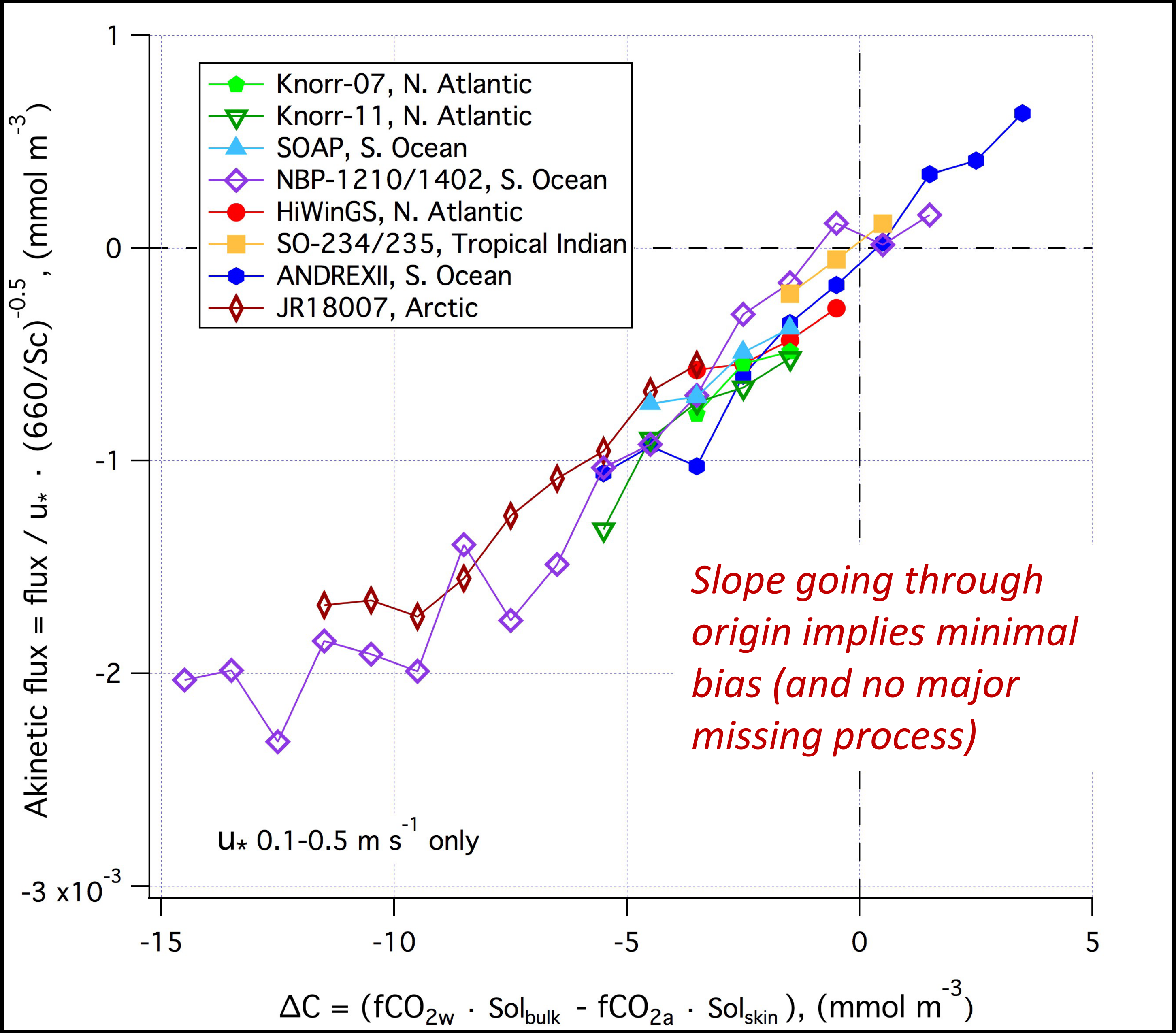
Variability and representativeness of sampling



Standard error (SE) within u_* bins increase with u_*

Rel. SE (SE/ K_{660bin}) highest at low/high u_* due to limited sampling

Rel. sdev (sdev / K_{660bin}) decreases with u_*



Assessment of uncertainty

- 'Akinetic flux'

K_{660} = flux /ΔC $(660/Sc)^{-0.5}$

- Bias in well-processed EC flux should be small (<10%; Dong et al. 2021)
- Bias in ΔC generally thought to be <10% at sufficient|ΔC|
- *Low |ΔC| data usually discarded in K_{660} calculation, a waste!*

Akinetic flux = flux $(660/Sc)^{-0.5}$ $/u_*$

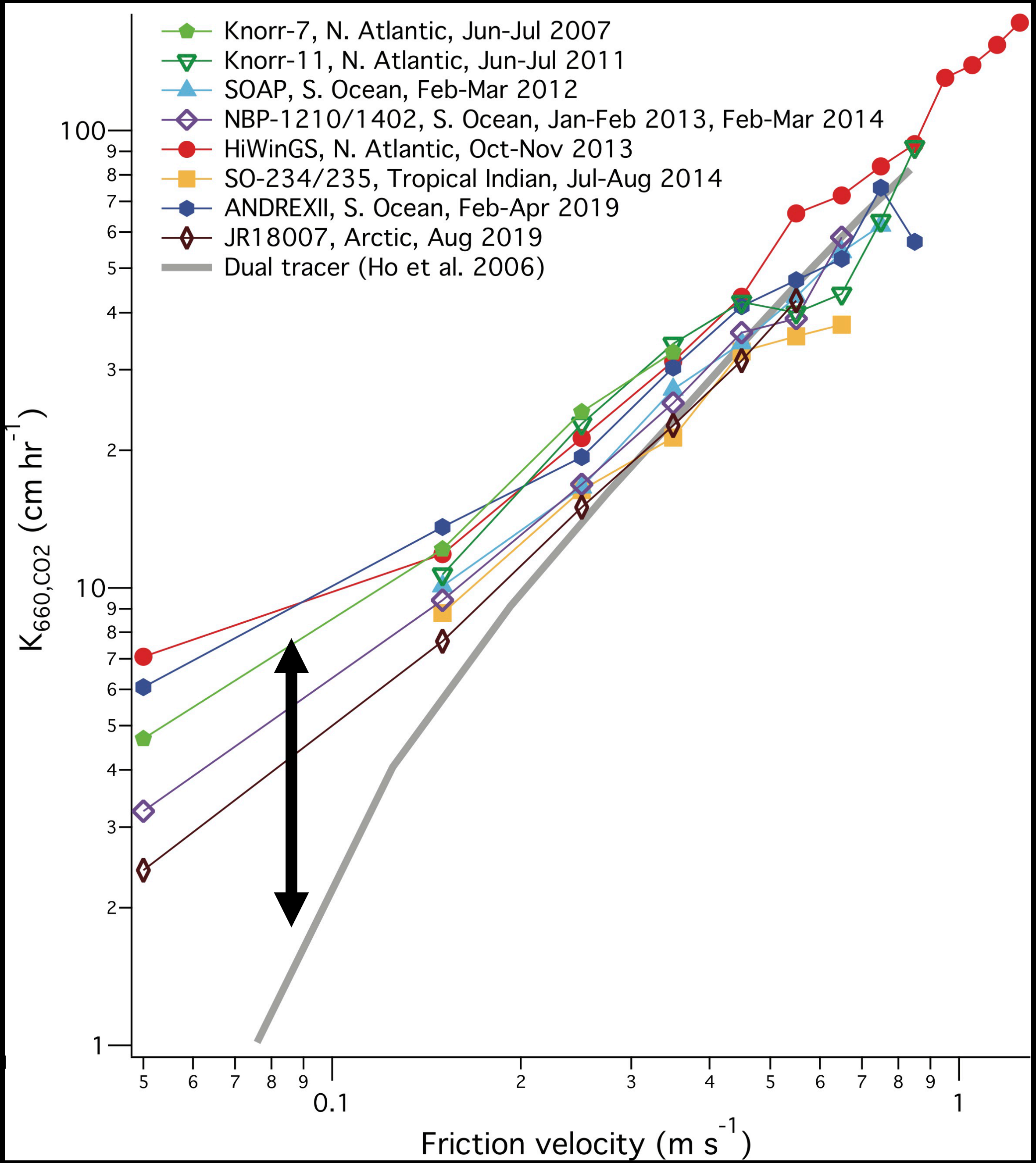
= ΔC K_{660} $/u_*$

where the **slope is ~transfer coefficient (K_{660}/u_*)**

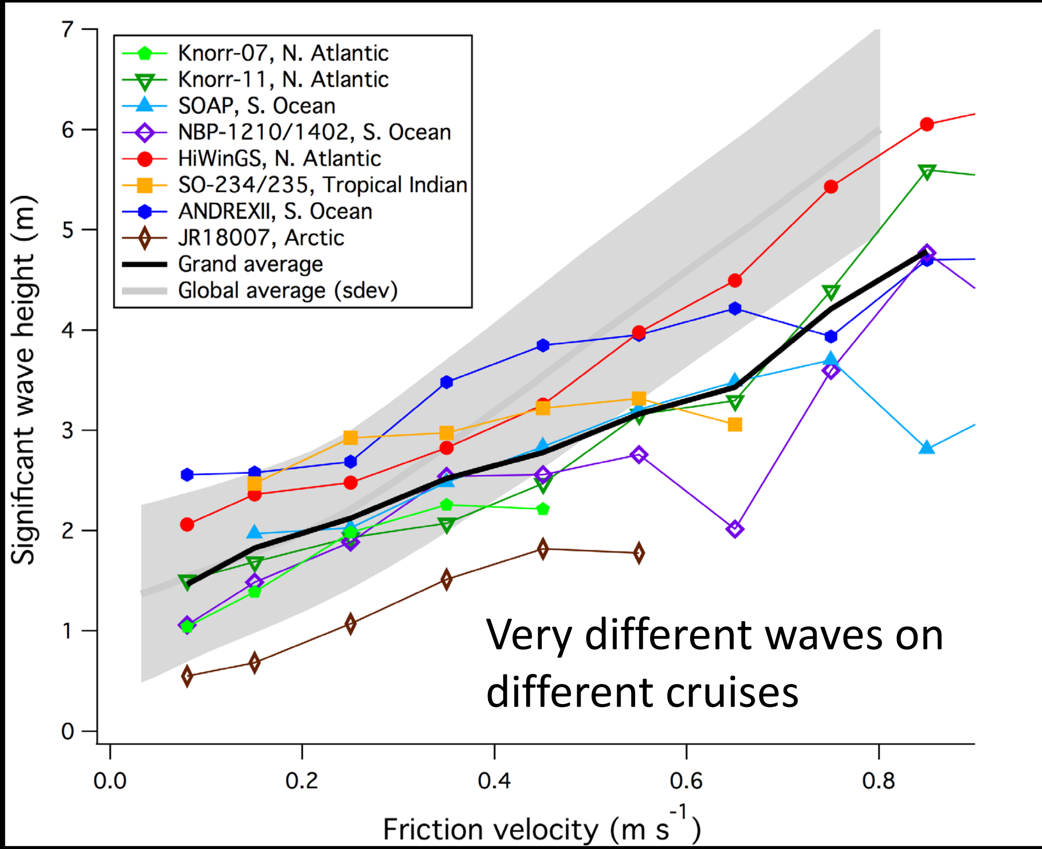
Low wind speed regime

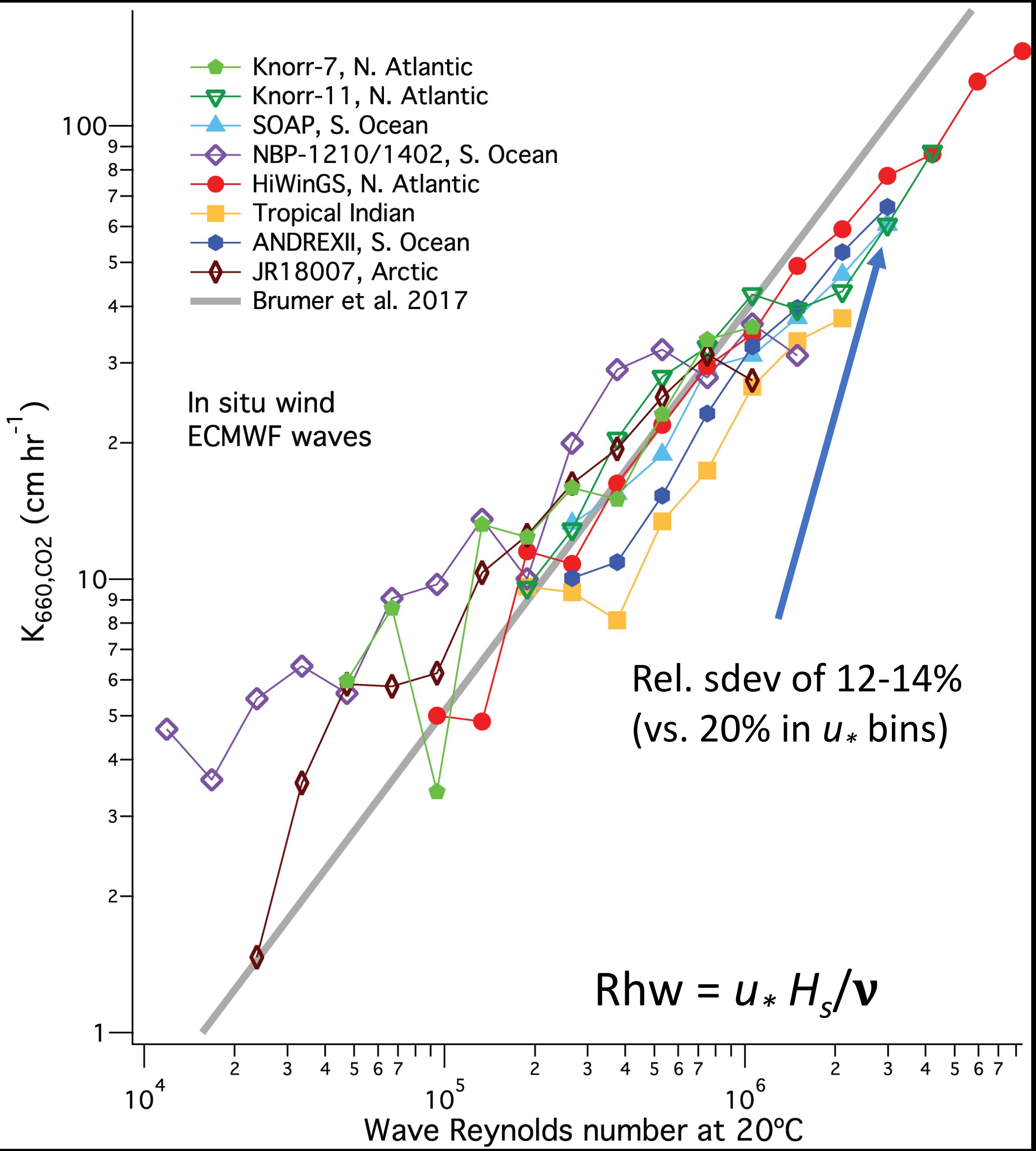
$K_{660,CO2} > K_{660,dualtracer}$ at low u_* by ~4 cm hr^{-1}, possibly because of

- Chemical enhancement in CO_2 (ca. 1-2 cm hr^{-1}, Wanninkhof 1992)
- Assumption of K = 0 in dual tracer fit, when convective driven turbulence may result in ca. 1-2 cm hr^{-1} at U=0 (COARE model)
- Uncertainty in Schmidt number exponent as f(U, surfactants, e.g. Esters et al 2017)



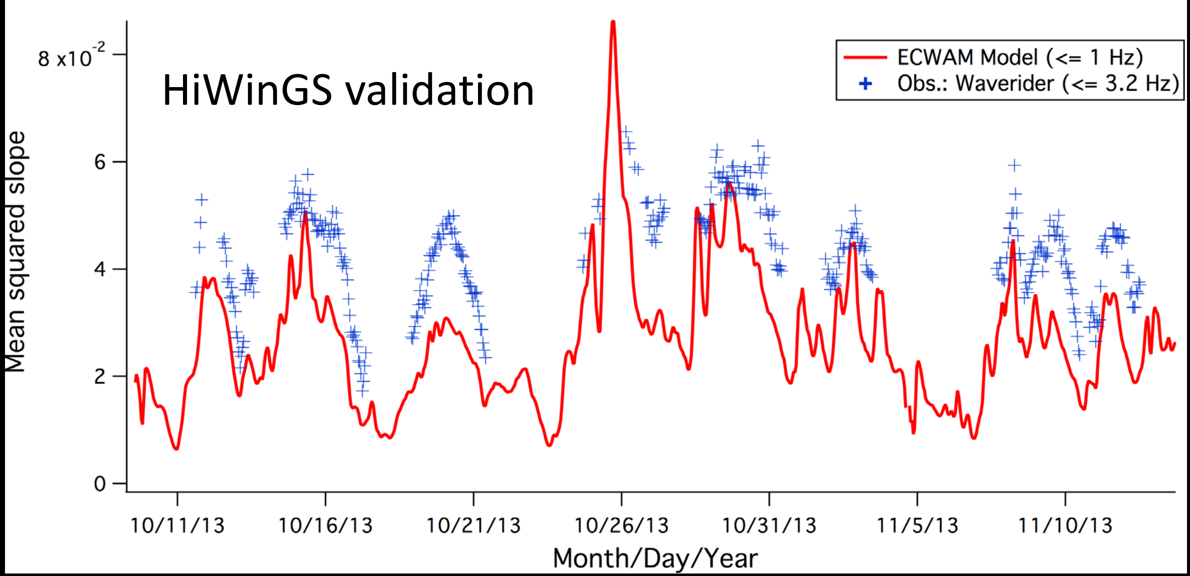
High wind speed regime



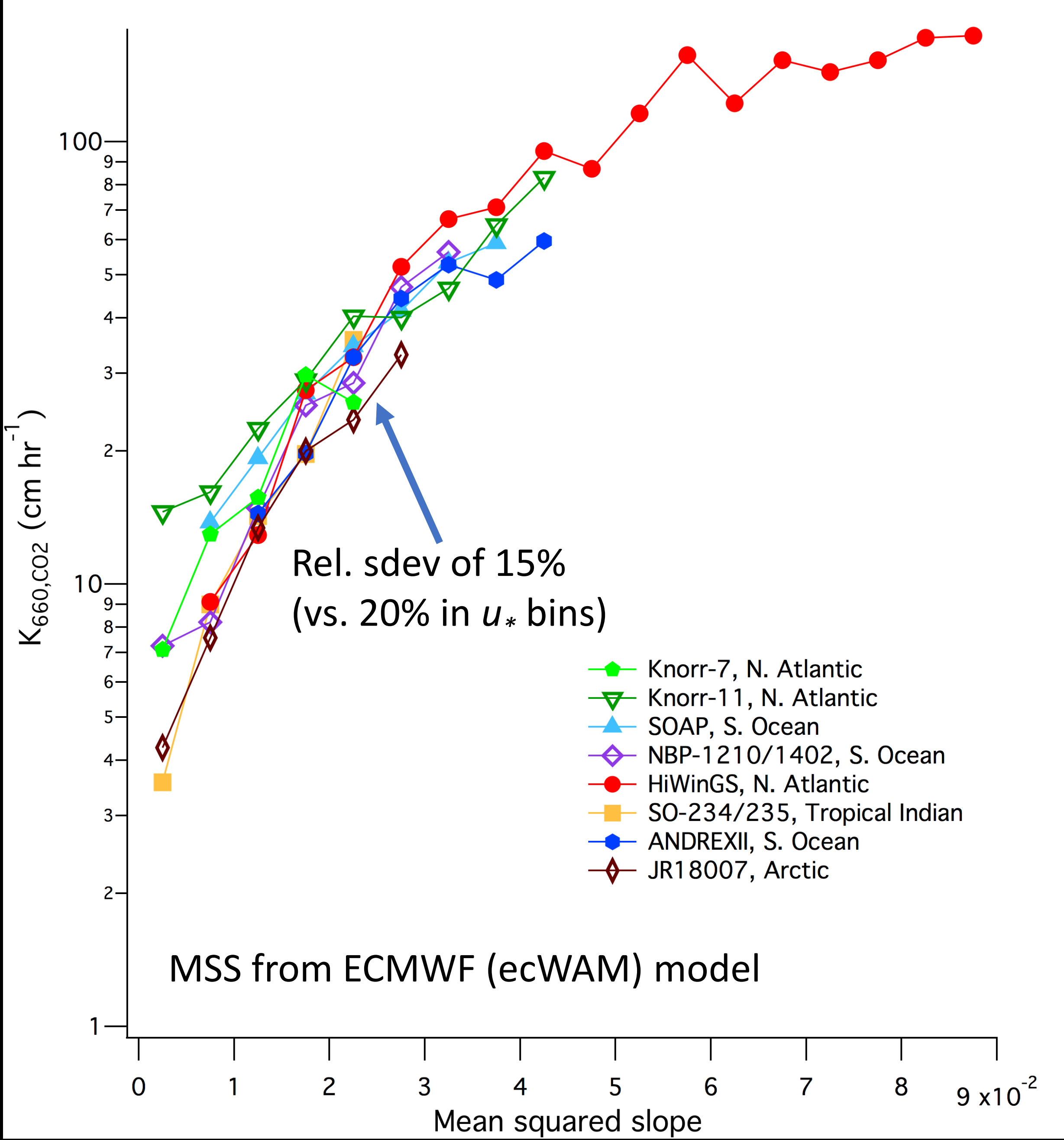


Wave Reynolds number helps to collapse some of the scatter and regional variability at high wind speeds

Importance of small waves
- Mean squared slope

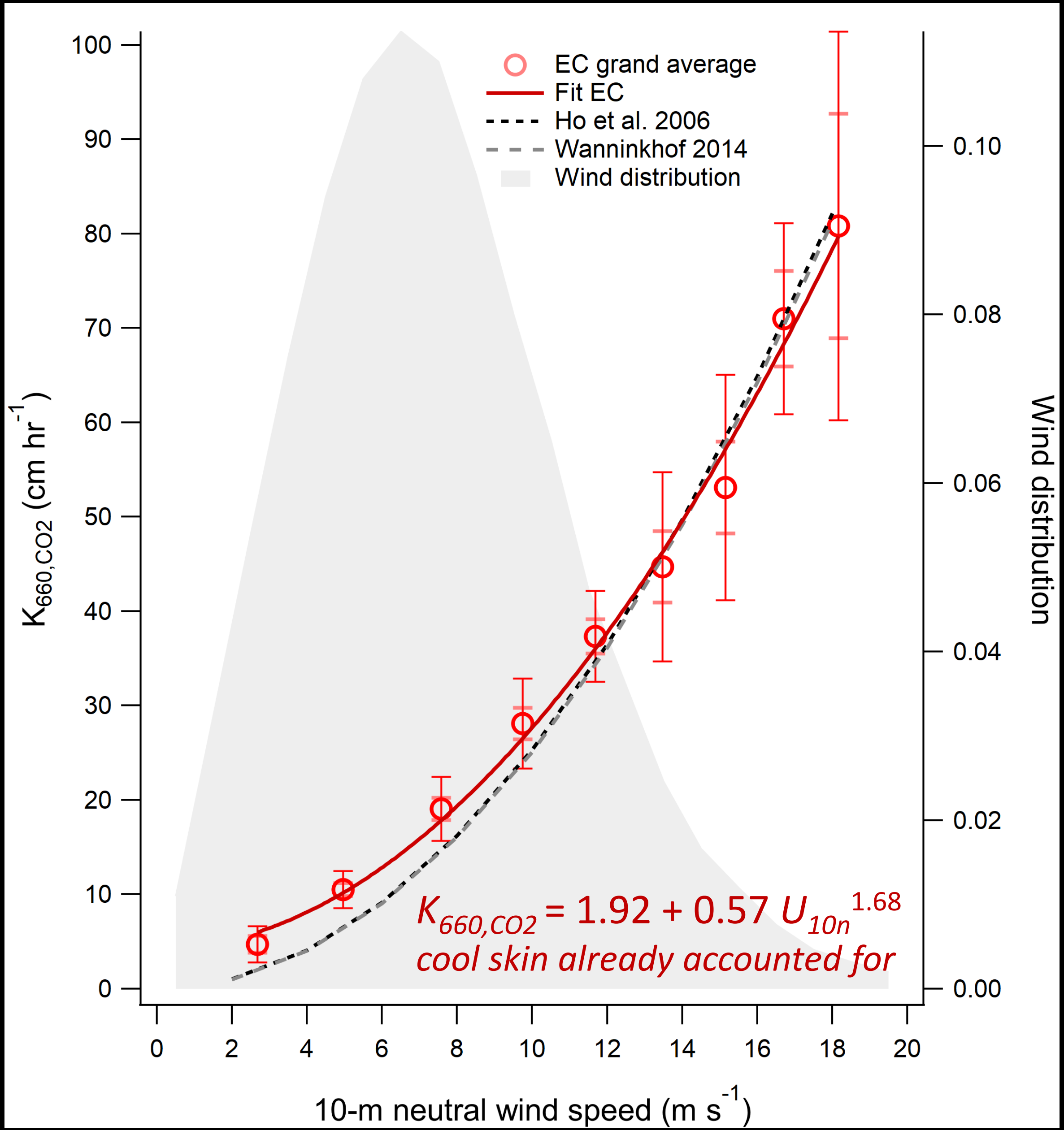


Mean squared slope of small waves helps to collapse some of the scatter at low to moderate wind speeds
(consistent with Frew et al. 2004)

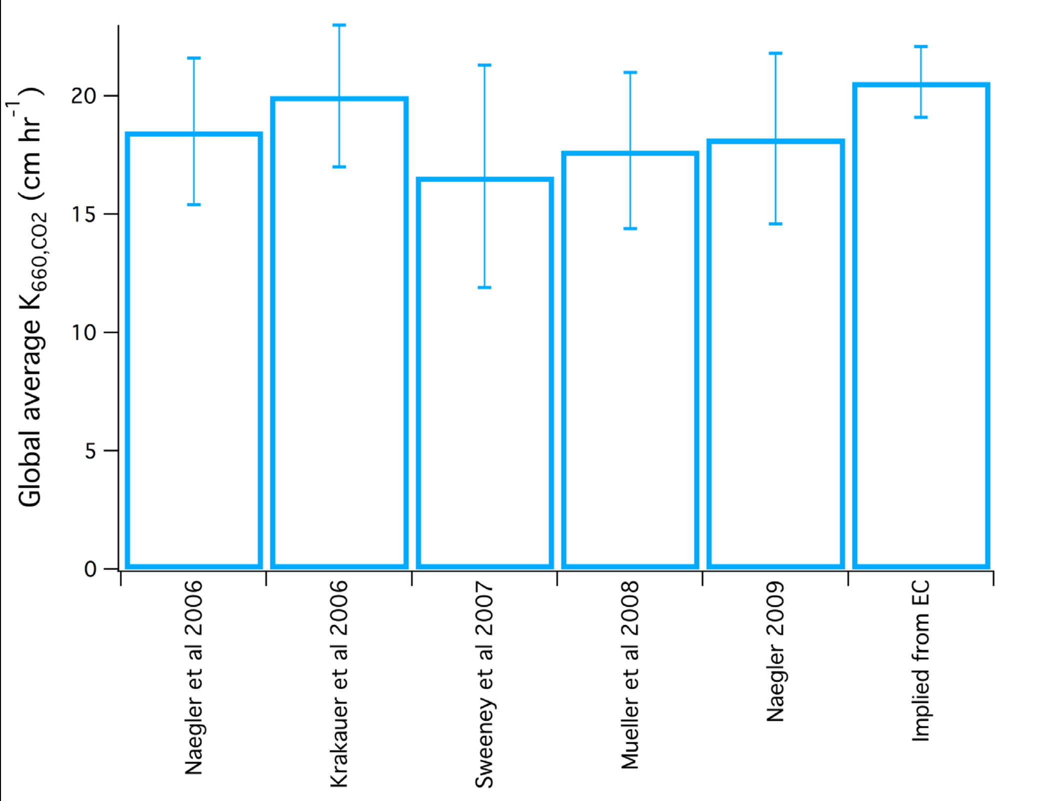


Grand average of EC $K_{660,CO2}$ x global wind distribution gives a global mean $K_{660,CO2}$ of ~ 20 cm hr^{-1}

- in agreement with latest ^{14}C-based estimates
- ~20% higher than implied by dual tracer



Yang et al. Frontiers, in review



Naegler 2009

Key take home messages

from first synthesis of $K_{660,CO2}$ from EC flux measurements

What we know:

- Uncertainty/variabil
  - Rsdev (RSE) 20% (7
  - Absolute uncertain while relative unce
- *U* dependence & m
  - $K_{660,CO2}$ scales ~line winds and <U^2 ove
  - $K_{660,CO2}$ >>0 in low w
  - < $K_{660,CO2}$ > *consiste*
- Waves matter
  - Wave Reynolds number and mean squared slope help to collapse variability in $K_{660,CO2}$ in high and moderate winds, respectively

What remains unclear:

- ubbles
  - bubbles towards $K_{660,CO2}$ *inant (COARE model) to* *e & Melville 2018) to* *et al.2019)*
  - 1) shows that surfactants ${}_{60,CO2}$ by 30% at *U* of 7 m s^{-1} bility among cruises?
- er descriptor of $K_{660,CO2}$?
  - small waves/surfactants/bubbles all in one go, with satellite scalability?

See **Yang** et al. poster on

- Surfactants

See **Dong** et al. posters on

- EC flux uncertainty
- Southern Ocean EC CO_2 flux and *K*

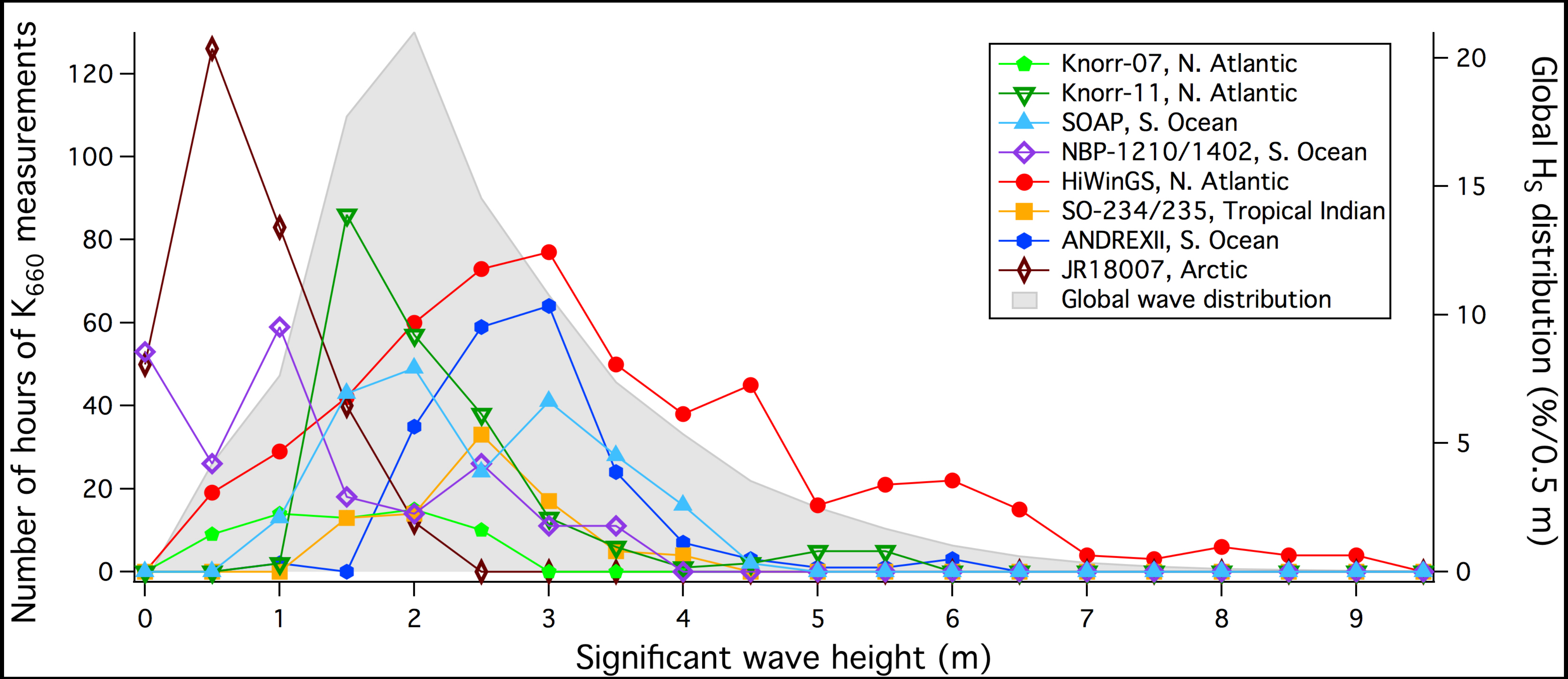
See **Bell** et al. talk on

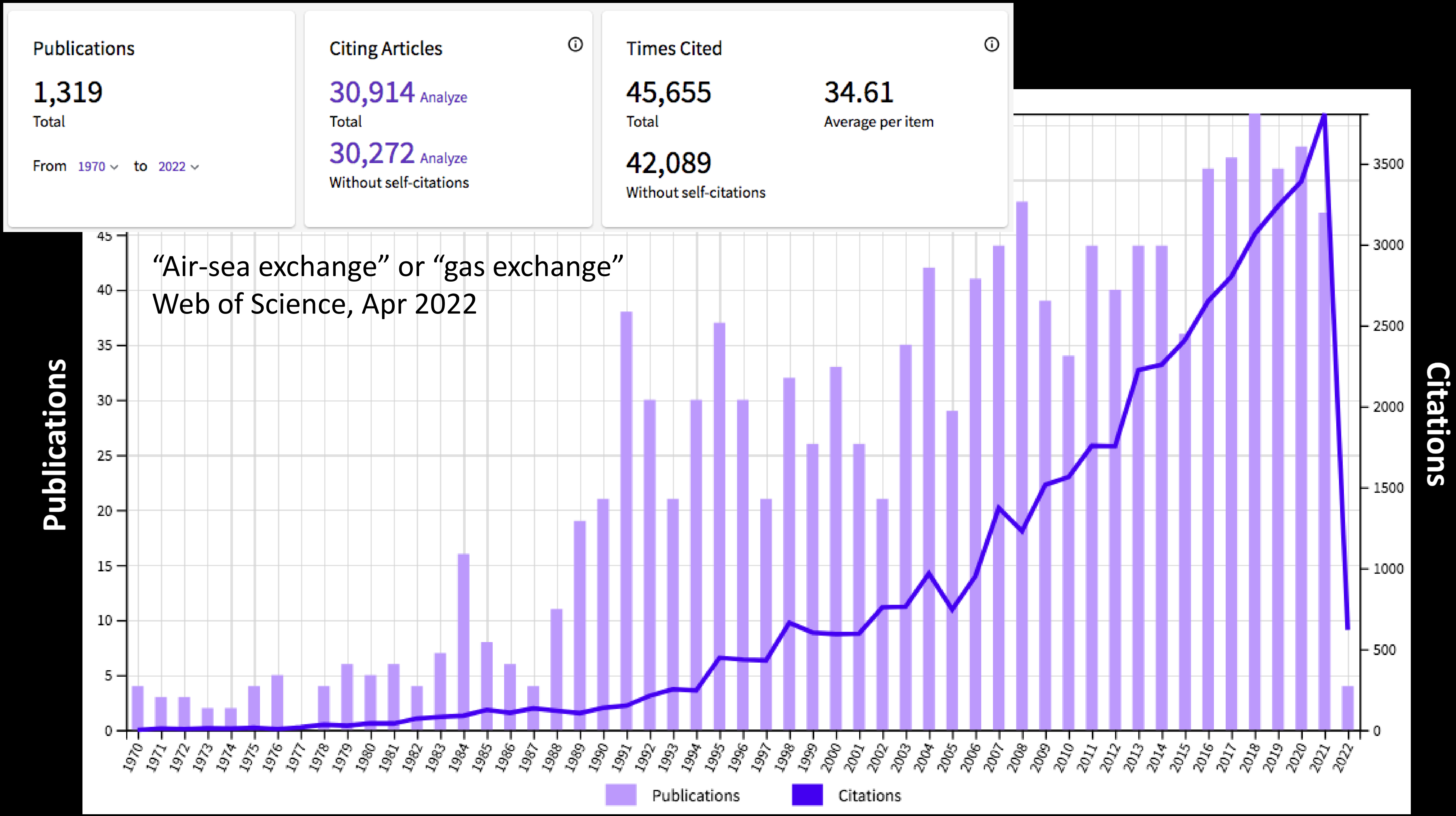
- Parametrization of *K* with scattering

CRUISE ID	TIME	SHIP	REGION	CO_2 ANALYZER	N > 20 (30) µATM	MEAN SST	ORIGINAL REFERENCE
Knorr-07(a/b)	Jun-Jul 2007	*Knorr*	North Atlantic	Modified LI-COR Li-7500	61 (61)	13	Miller et al. 2009
Knorr-11	Jun-Jul 2011	*Knorr*	North Atlantic	Modified LI-COR Li-7500	215 (215)	10	Bell et al. 2017
SOAP	Feb-Mar 2012	*Tangaroa*	Southern Ocean (temperate)	Modified LI-COR Li-7500	220 (220)	15	Landwehr et al. 2018
NBP-1210/1402	Jan-Feb 2013; Feb-Mar 2014	*Palmer*	Southern Ocean (polar)	LI-COR Li-7200	302 (302)	0	Butterworth & Miller 2016
HiWinGS	Oct-Nov 2013	*Knorr*	North Atlantic	Picarro G1301-f (LI-COR Li-7200)	530 (467)	10	Blomquist et al. 2017
SO-234/235	Jul-Aug 2014	*Sonne*	Tropical Indian	LI-COR Li-7200	86 (44)	25	Zavarsky et al. 2018
ANDREXII	Feb-Apr 2019	*James Clark Ross*	Southern Ocean (subpolar)	Picarro G2311-f	289 (199)	1	Yang et al. 2021
JR18007	Aug 2019	*James Clark Ross*	Arctic	Picarro G2311-f	278 (278)	6	Dong et al. 2021

Cruise ID	K_{660} fit to u_* (bin-averages)	K_{660} fit to u_* (hourly data)	r^2 of hourly fit	Min/median/max in ΔfCO_2	In-situ U_{10n} vs. ECMWF U_{10n}
Knorr-07(a/b)	$-2.7 + 103.1u_*$	$-0.2 + 91.1u_*$	0.48	-122/-51/-36	$0.46 + 0.97\ U_{10n}$_ECMWF
Knorr-11	$-4.3 + 105.8u_*$	$-5.7 + 112.2u_*$	0.58	-110/-50/-35	$0.96 + 0.96\ U_{10n}$_ECMWF
SOAP	$-2.9 + 83.2u_*$	$-7.7 + 96.2u_*$	0.72	-130/-54/-36	$1.91 + 0.88\ U_{10n}$_ECMWF
NBP-1210/1402	$-4.7 + 88.8u_*$	$-3.2 + 85.3u_*$	0.51	-250/-55/24	$0.43 + 0.99\ U_{10n}$_ECMWF
HiWinGS	$-2.7 + 94.6u_*$ ($-4.4 + 104.3u_*$)	$-4.3 + 99.8u_*$ ($-6.8 + 111.9u_*$)	0.40 (0.37)	-63/-41/-11	$0.33 + 0.96\ U_{10n}$_ECMWF
SO-234/235	$-0.3 + 58.2u_*$ ($-3.3 + 77.1u_*$)	$-2.0 + 66.9u_*$ ($-1.9 + 72.0u_*$)	0.54 (0.67)	-49/9/40	$-0.45 + 1.13\ U_{10n}$_ECMWF
ANDREXII	$-2.0 + 94.0u_*$	$-4.8 + 100.0u_*$	0.46	-87/-12/76	$0.16 + 1.01\ U_{10n}$_ECMWF
JR18007	$-4.5 + 79.0u_*$	$-3.8 + 78.1u_*$	0.72	-183/-122/-64	$0.50 + 0.97\ U_{10n}$_ECMWF

Distributions of waves

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