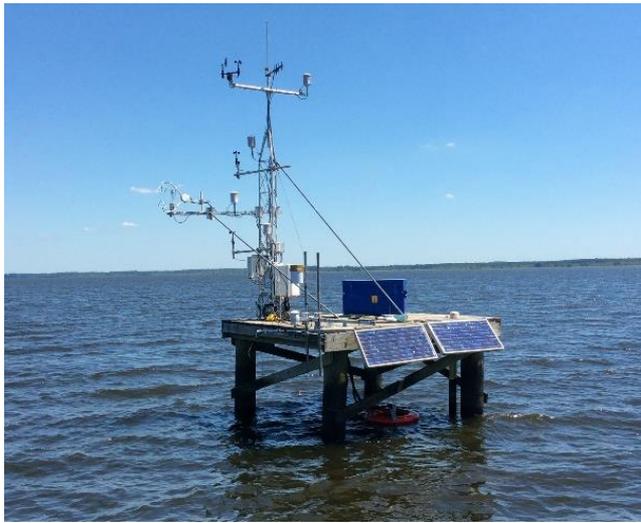


# Gas transfer velocities at water and rough-surface interfaces

Gabriel Katul<sup>1,2,3</sup> & Heping Liu<sup>4</sup>



Ross Barnett Reservoir, Mississippi, USA.

Photo credit: Heping Liu

A view of the large 20-foot-diameter lysimeter at Davis planted to beans in 1968.



University of California, Davis, CA

weighing lysimeter. From *Pruitt et al. (1972)*

## Presentation for the TERENO Workshop, Garmisch, Germany (26.9.2017)

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<sup>3</sup> MICMoR Visiting Scientist, KIT/IMK-IFU, Garmisch-Partenkirchen, Germany

<sup>4</sup>Department of Civil and Environmental Engineering, Washington State University, Pullman, Washington State, USA

# Introduction

- The significance of air-water gas exchange on ecosystem and climate-related processes (e.g. CO<sub>2</sub> exchange with open water surfaces) is not in dispute. Likewise for gas exchange between a turbulent atmosphere and a rough surface (e.g. evaporation from soil to atmosphere, nitrous oxide emissions,..).
- However, the mechanisms describing the *efficiency* of gas transport by turbulence at such **interfaces** remains multifaceted and subject to active research.

# Introduction

There is a '***renaissance***' in mass transfer studies across *interfaces* because of rapid advancements in measurements (e.g. remote sensing using high resolution IR cameras<sup>1,2</sup>, fiber optic cables<sup>3</sup>, stable isotopic techniques<sup>4</sup>), and simulations (LES and DNS<sup>5</sup>):

## Examples:

<sup>1</sup>**Bare soil evaporation**: Haghghi, E., and D. Or (2013, 2015).

<sup>2</sup>**Air-sea exchange of CO<sub>2</sub> and sparingly soluble gases**: Garbe et al. (2004).

<sup>3</sup>**Crop evapotranspiration by Bowen ratio**: Euser et al. (2014).

<sup>4</sup>**Sediment-water interface**: Merlivat, L., and M. Coantic (1975).

<sup>5</sup>**Ocean-atmosphere gas exchange**: Fredriksson et al. (2016).

# Introduction

- Instead of dealing with **fluxes** and **concentration differences**, it is preferable to deal with '*gas transfer velocity*' when quantifying turbulent transport efficiency.
- Flux:  $F = k \Delta C$ ;  $\Delta C = C_s - C_b$

$$k = \frac{F}{\Delta C}.$$

- The *efficiency* of gas transport by turbulence at such interfaces must account for eddies.

# Review of k-Formulations

- Common  $k$  formulations *that account for turbulent eddies* are based on **surface renewal** schemes subject to assumptions about contact durations at the interface.

- For an air-water interface, the water-side gas transfer velocity (*Lamont and Scott, 1970*)

$$k = \alpha Sc^{-n} (\epsilon \nu)^{1/4}$$

- For gas transfer from rough surfaces into a turbulent atmosphere (*Brutsaert, 1965*)

$$k = A \sqrt{D_m} u_*^{3/4} (\kappa \nu z_o)^{-1/4}$$

# Objective

- Show that these formulations inherit their *universal character* from Kolmogorov's 1941 inertial subrange scaling adjusted by viscous cutoff.

The proposed derivation explains why

- (i) gas transfer models are insensitive to renewal time distributions, and
- (ii) the similarity constants ( $\alpha$  or  $A$ ) are independent from the specifics of the interfacial system.

# Definitions and review of air-water gas transfer theories



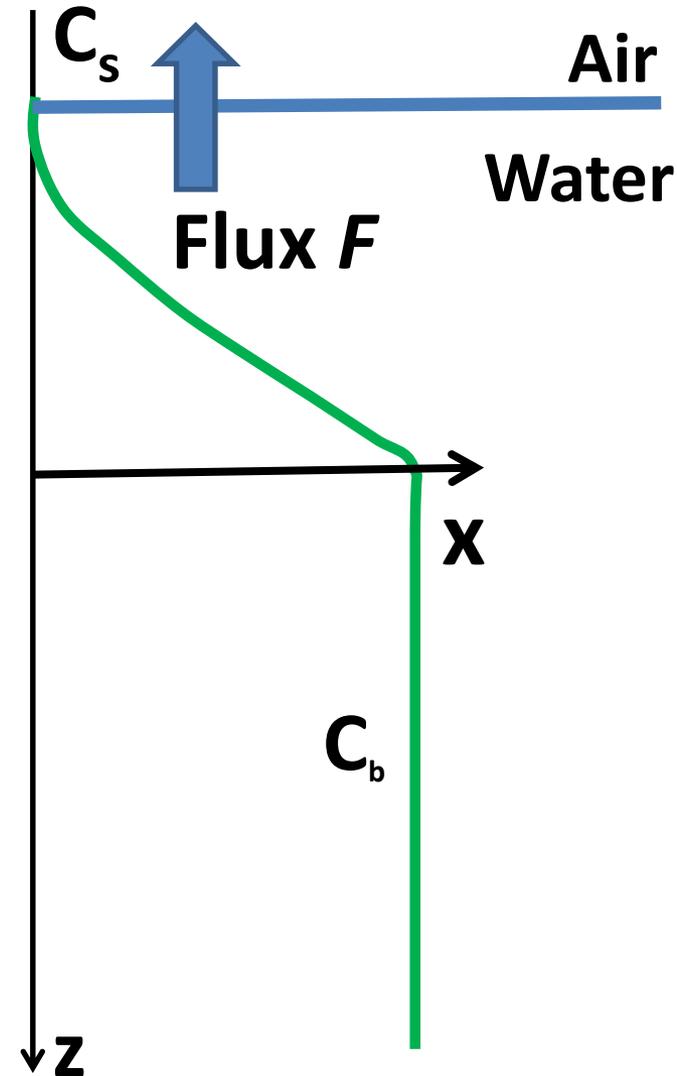
**Eibsee Lake**, Bavaria, Germany: Photo Credit - Alessandra Trompeo

# Gas Transfer Velocity at an Air-Water Interface

## Transfer Velocity

## Velocity

- Flux:  $F = k \Delta C$ ;
- Concentration Difference:  
$$\Delta C = C_s - C_b$$
;
- $C_s$  surface concentration determined from gas phase measurements and *Henry's Law* (or the *Ostwald solubility coefficient*).



# Gas transfer velocity models: What is done in practice

- Early formulations for  $k$  - **still in use in climate models** - are based on mean velocity  $U$ .

Based on Cole and Caraco's (1998) review:

$$k = a + bU^c$$

- $a$ : 0 – 2.07
- $b$ : 0.2 - 0.75
- $c$ : 1-2

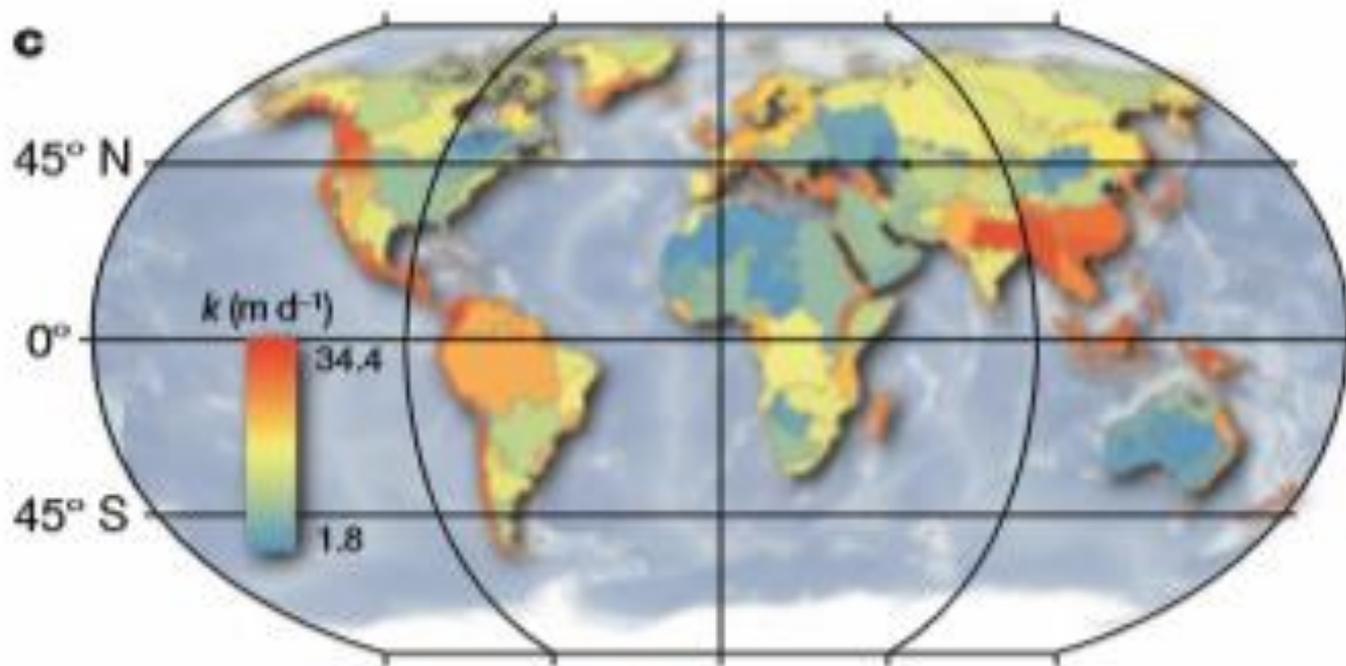


Mean wind speed at  
a reference height  
(often 10 m)

# Global maps of $k$ for inland water

- From Raymond et al. (2013) – based on

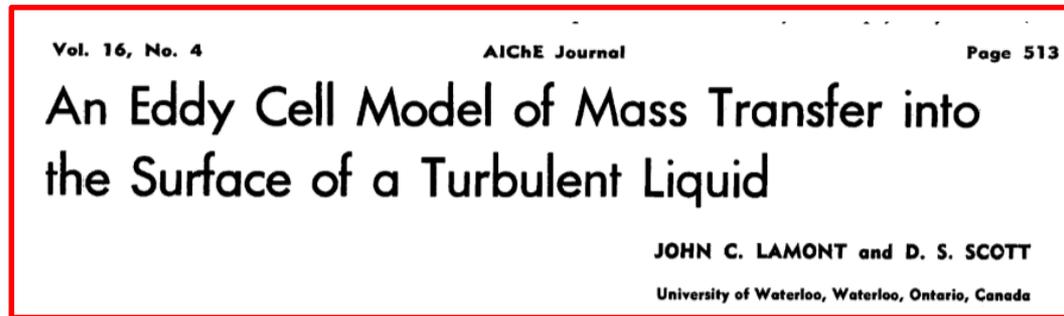
$$k = a + bU^c$$



# Formulation of gas transfer velocity at air-water interface

- A detailed formulation for  $k$  is based on surface renewal/*micro-eddy* theory (**Lamont and Scott, 1970**).

- $k = \alpha Sc^{-n} (\epsilon \nu)^{1/4};$



$\alpha = 0.4$  (but 0.2-0.6 reported range)

$Sc$  = Molecular Schmidt Number =  $\nu / D_m$  ( $\gg 1$  for water)

$\nu$  = Kinematic viscosity of water,  $D_m$  = molecular diffusion of C

$\epsilon$  = Water-side mean turbulent kinetic energy (TKE) dissipation rate

$n = 1/2$  (but  $2/3$  is for smooth wall).

# The meaning of $(\epsilon \nu)^{1/4}$

## Kolmogorov scales for small eddies

$\eta = \left(\frac{\nu^3}{\epsilon}\right)^{1/4}$  is the Kolmogorov length scale, *smallest* scale of turbulence where turbulent kinetic energy is dissipated by the action of viscosity.

$\tau_k = \sqrt{\left(\frac{\nu}{\epsilon}\right)}$  is the Kolmogorov time scale

$(\epsilon \nu)^{1/4} =$  is the **Kolmogorov velocity scale**

*Microscale Reynolds* number:

$$Re_K = [\eta (\epsilon \nu)^{1/4}] / \nu = 1.$$

Photo: John Collier - Copied from [johnbyrne.fireflyinternet.co.uk](http://johnbyrne.fireflyinternet.co.uk).

Cropped photo of a painting of Osborne Reynolds painted in 1904 by John Collier.



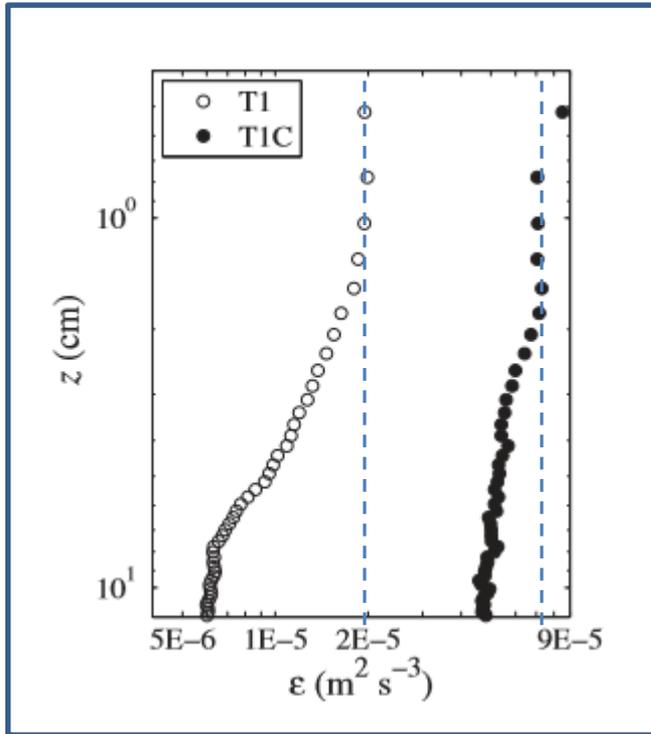


# Experiments

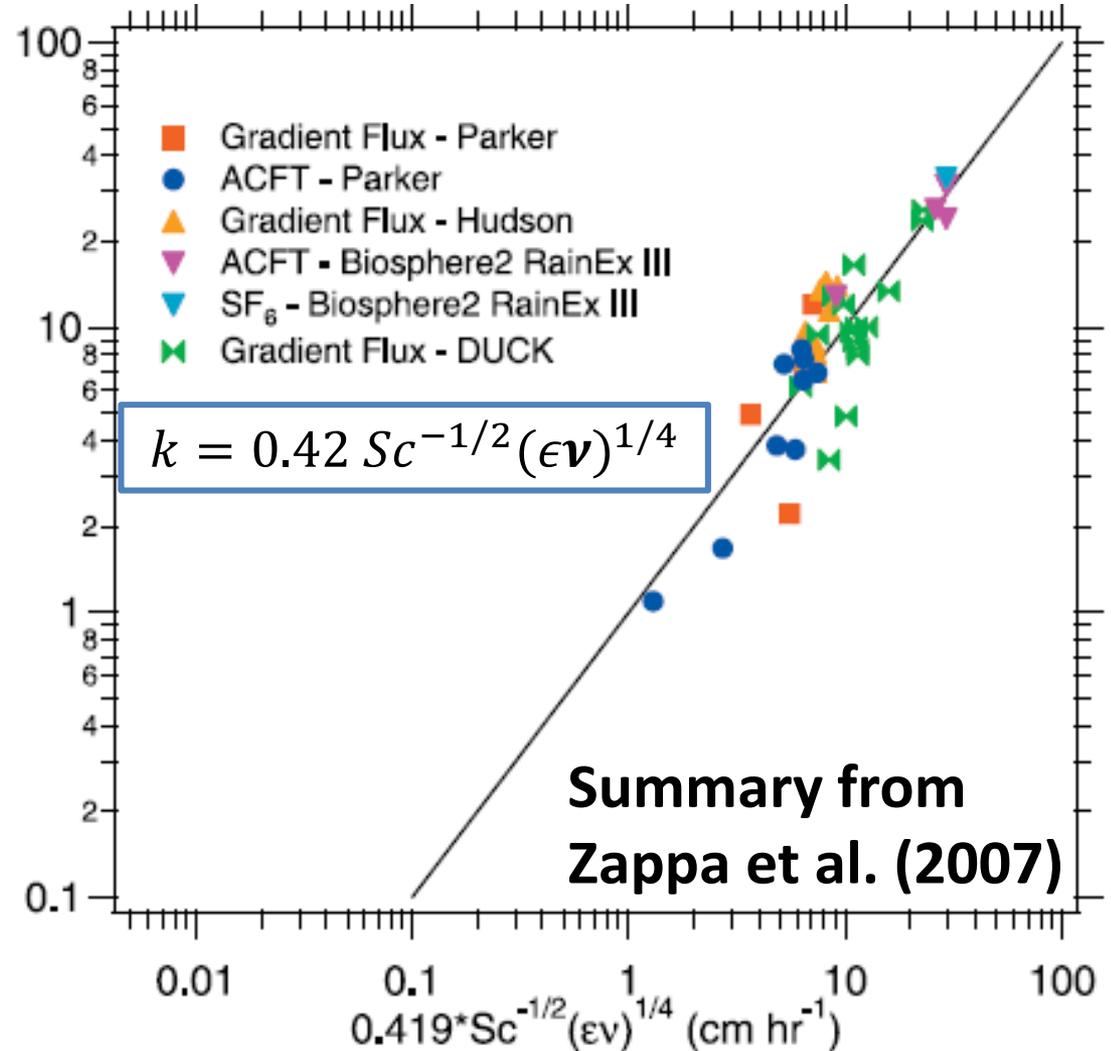
## Environmental turbulent mixing controls on air-water gas exchange in marine and aquatic systems

Christopher J. Zappa,<sup>1</sup> Wade R. McGillis,<sup>1</sup> Peter A. Raymond,<sup>2</sup> James B. Edson,<sup>3</sup> Eric J. Hints,<sup>4</sup> Hendrik J. Zemelink,<sup>5,6</sup> John W. H. Dacey,<sup>7</sup> and David T. Ho<sup>1</sup>

Received 1 December 2006; revised 5 February 2007; accepted 5 April 2007; published 17 May 2007.



From Wang et al. (2015)



# Review of gas transfer theories from rough surfaces into a turbulent atmosphere



Image from <https://ohiocountrylife.files.wordpress.com/2015/03/bare-soil.jpg>



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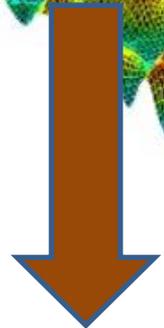
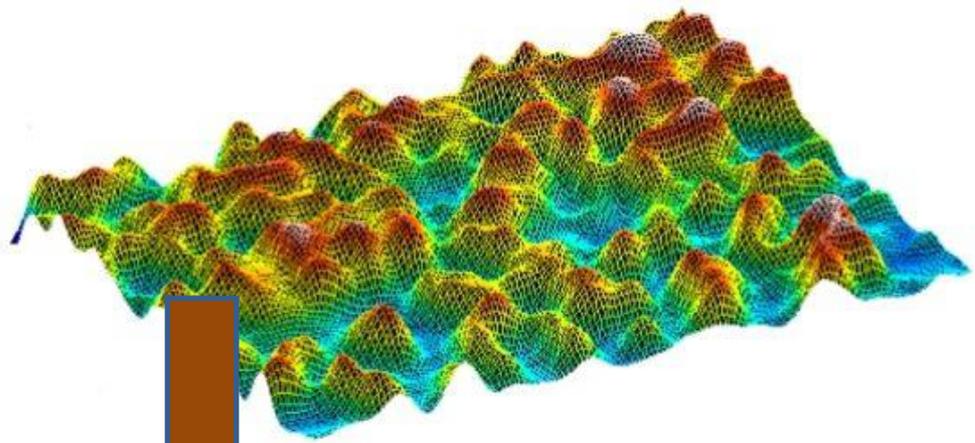
OCTOBER 15, 1965

## A Model for Evaporation as a Molecular Diffusion Process into a Turbulent Atmosphere

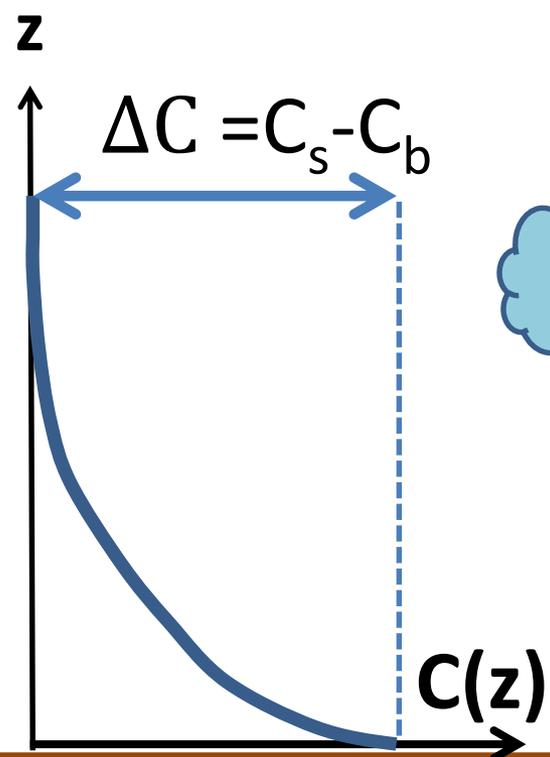
WILFRIED BRUTSAERT

*Department of Hydraulics and Hydraulic Engineering  
School of Civil Engineering, Cornell University, Ithaca, New York*

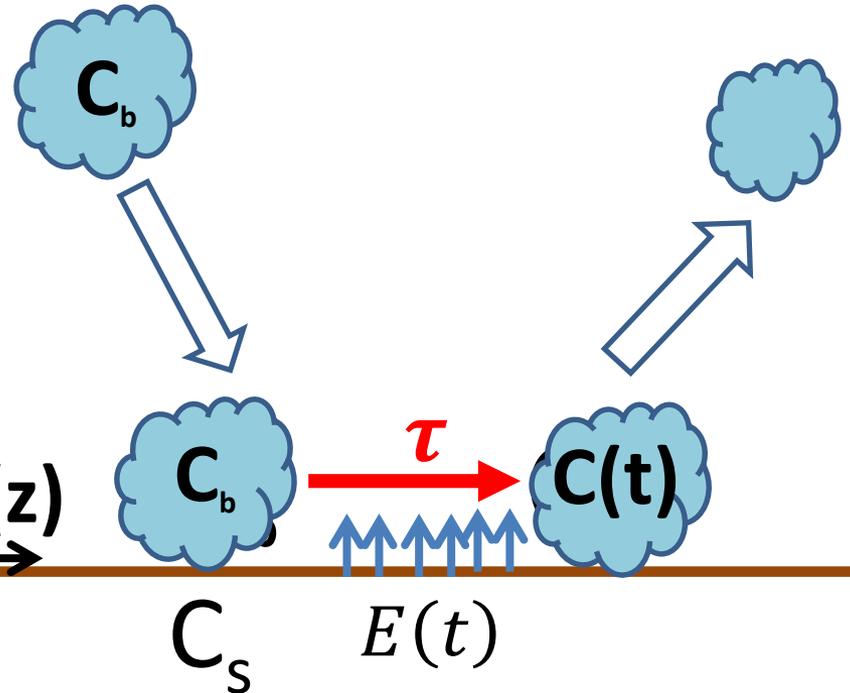
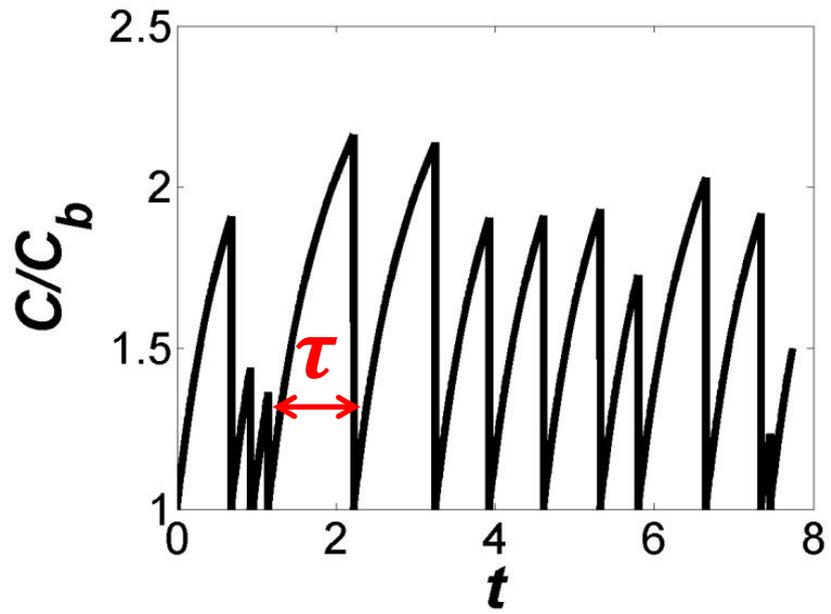
*Abstract.* Evaporation is analyzed as a phenomenon of molecular diffusion from a large rough surface into random-lived internal scale turbulent eddies. The model is based on the principles of similarity and stochastic renewal. It is shown that evaporation is proportional to the 0.75 power of the friction velocity and to the square root of the molecular diffusivity. This is in agreement with the available experimental data.



Rough surface characterized by a momentum roughness height  $z_0$



Brutsaert assumed **exponentially distributed** contact times  $\tau$ .



# Brutsaert (1965)

A simplified view of Brutsaert's renewal model:

- Evaporation at any time  $t$  is:

$$E(t) = -D_m \left. \frac{\partial C(t)}{\partial z} \right|_{z=0} \approx D_m \left( \frac{\Delta C}{\delta(\tau)} \right) \sim D_m \frac{\Delta C}{\sqrt{D_m \tau}}$$

$\Delta C = (C_s - C_b)$  assumed time independent.

$$\frac{E(t)}{\Delta C} = k(\tau) \sim \sqrt{\frac{D_m}{\tau}}; \tau > 0$$

# Brutsaert (1965)

Pdf of contact Durations<sup>+</sup>

$$\tau > 0$$

$$\frac{E}{\Delta C} = k = - \int_0^{\infty} a e^{-a\tau} \sqrt{\frac{D_m}{\tau}} d\tau$$

$$a = \frac{A}{\sqrt{\left(\frac{\nu}{\epsilon}\right)}}$$

mean contact duration  $\propto$  Kolmogorov time scale

$$k = \sqrt{A\pi D_m} \left(\frac{\nu}{\epsilon}\right)^{-1/4} = \sqrt{A\pi} S_c^{-1/2} (\epsilon \nu)^{1/4}$$

$$\epsilon = u_*^2 \left(\frac{dU}{dz}\right) = u_*^2 \left(\frac{u_*}{\kappa_\nu z_0}\right)$$

Turbulent kinetic energy budget at  $z_0$  - Dissipation = mechanical production

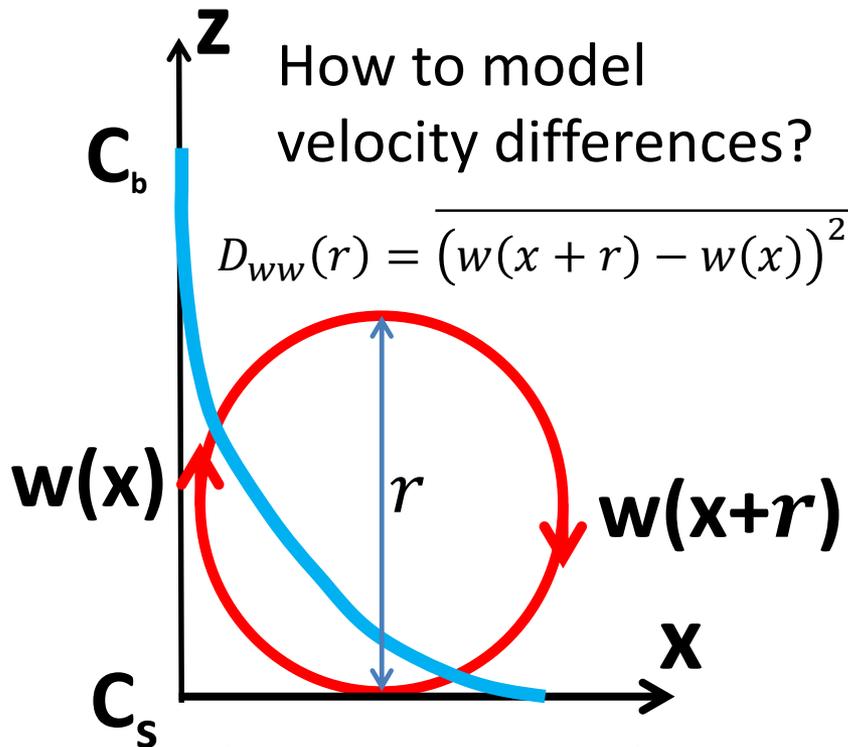
$$E = \sqrt{A\pi D_m} u_*^{3/4} (\kappa_\nu \nu z_0)^{-1/4} \Delta C$$

<sup>+</sup>Result not sensitive to assumed exponential pdf of  $\tau$  (Katul and Liu, 2017a)

# Brutsaert (1965)

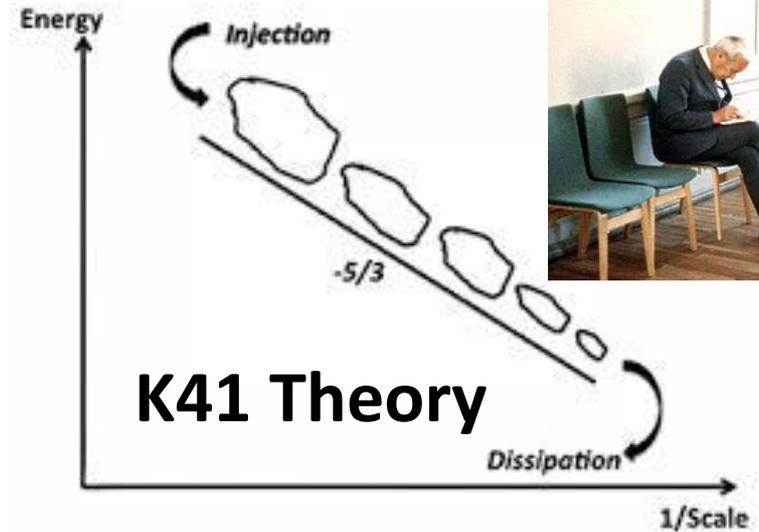
- *Average*  $\delta = - \int_0^{\infty} a e^{-a\tau} \sqrt{D_m \tau} d\tau = \frac{1}{2} \sqrt{\frac{\pi D_m}{a}}$ .
- Recall that  $a = \frac{A}{\sqrt{\left(\frac{\nu}{\epsilon}\right)}}$ ;  $\delta = \frac{1}{2} \sqrt{\frac{\pi \nu}{a Sc}}$ .
- $\delta \sim Sc^{-1/2} \eta$ . Hence, the most efficient eddy size appears to be the **Batchelor length scale** (irrespective of the Schmidt number).

# Proposed Formulation: A Structure Function Perspective



$$E = k \Delta C$$

$$\Delta C = C_s - C_b$$



$$S(k) = (C_{0,k} \epsilon^{2/3}) k^{-5/3}$$

$$D_{ww}(r) = C_0 \epsilon^{2/3} r^{2/3}$$

$$k S(k) \sim r \frac{dD_{ww}(r)}{dr}$$

In Spectral Space:  
Energy Content  
at scale  $k^{-1}$

In Physical Space:  
Energy Content  
at scale  $r$

# THEORY: A Structure Function Perspective

Image: [http://www.russia-ic.com/education\\_science/gems/817/1345938588000#.Wcl9aNEpBPY](http://www.russia-ic.com/education_science/gems/817/1345938588000#.Wcl9aNEpBPY)

Transfer Velocity:

$$k \approx \sqrt{(w(x+r) - w(x))^2} = \sqrt{D_{ww}(r)}$$



Assumption 1:  $k = \sqrt{C_0 \epsilon^{2/3} r^{2/3}}$  **K41 scaling for**  
 $D_{ww}(r)$

Assumption 2:  $r \sim Sc^{-1/2} \eta$  (Hondzo, 1998)

For many gases in the atmosphere -  $Sc \approx 1$

$$r \sim \eta; \quad \text{where } \eta = \left(\frac{\nu^3}{\epsilon}\right)^{1/4}$$

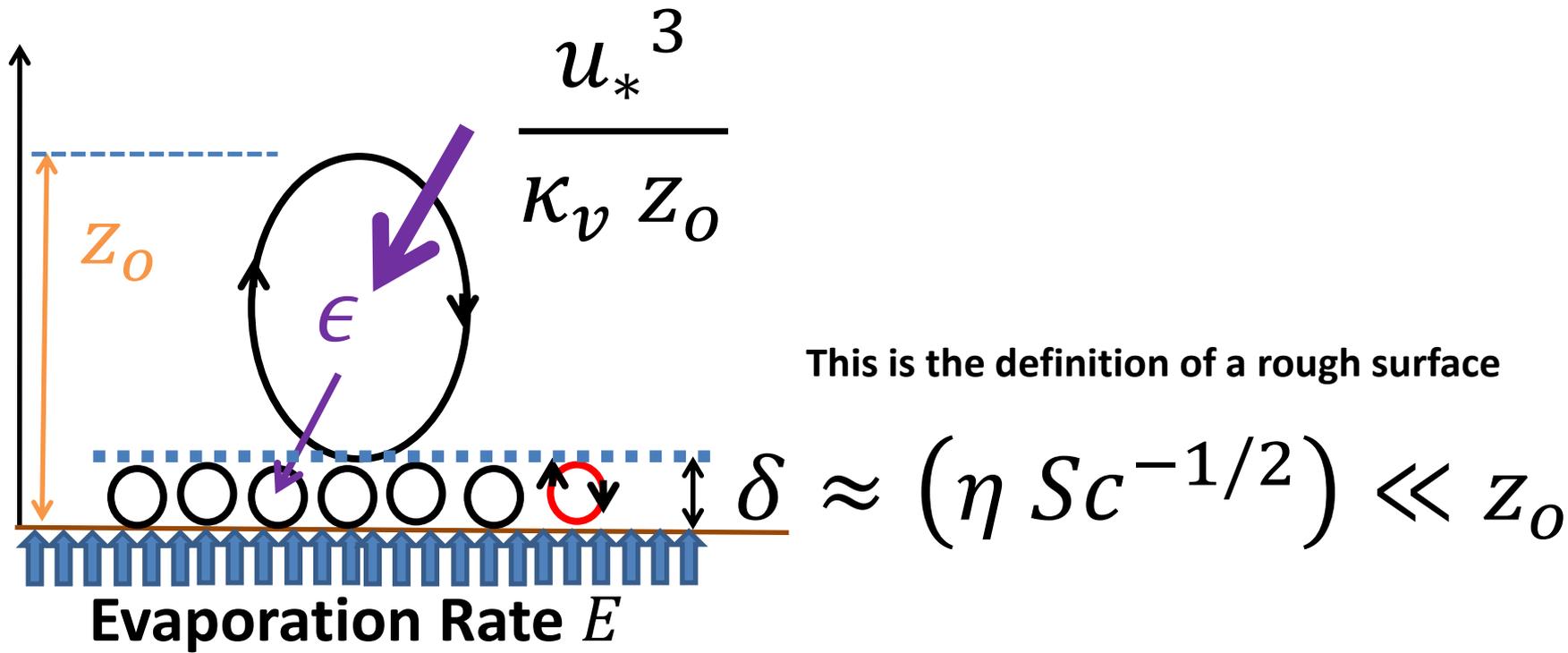
**Kolmogorov  
microscale**

# Model for Gas Transfer Velocity

$$\frac{E}{\Delta C} = k \approx \sqrt{C_o} \boxed{(\epsilon \nu)^{1/4}} \quad \text{For } Sc \approx 1$$

Brutsaert's estimate of  $\epsilon$

Kolmogorov Velocity



# Structure function model for air-water gas exchange

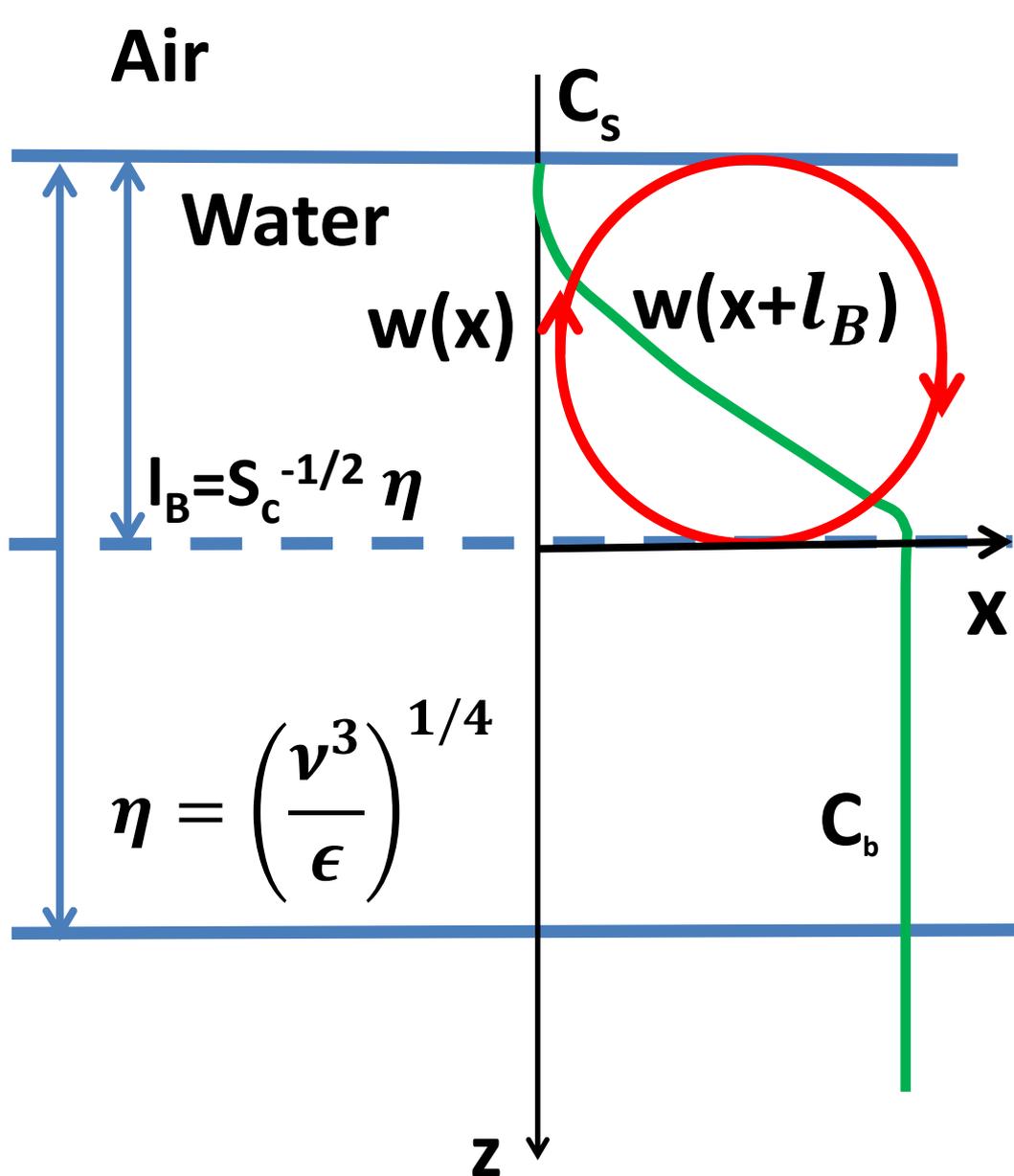
From Wanninkhof et al. (2009)

Gas	Mol. weight (g mol <sup>-1</sup> )	D (10 <sup>-5</sup> cm <sup>2</sup> s <sup>-1</sup> )	Sc
<sup>3</sup> He	3	7.29	144
He	4	6.36	165
CH <sub>4</sub>	16	1.55	677
Ne	20	3.33	315
N <sub>2</sub>	28	1.57	670
O <sub>2</sub>	32	1.78	589
Ar	40	1.82	576
CO <sub>2</sub>	44	1.59	660
N <sub>2</sub> O	44	1.5	698
(CH <sub>3</sub> ) <sub>2</sub> S	62	1.14	918
Kr	84	1.51	694
CCl <sub>2</sub> F <sub>2</sub>	121	0.86	1219
Xe	131	1.19	880
CCl <sub>3</sub> F	137	0.94	1120
SF <sub>6</sub>	146	1.05	992
CCl <sub>4</sub>	154	0.82	1286
CCl <sub>2</sub> FCClF <sub>2</sub>	187	0.68	1544
Rn	222	1.07	980
Heat	—	1.75	6

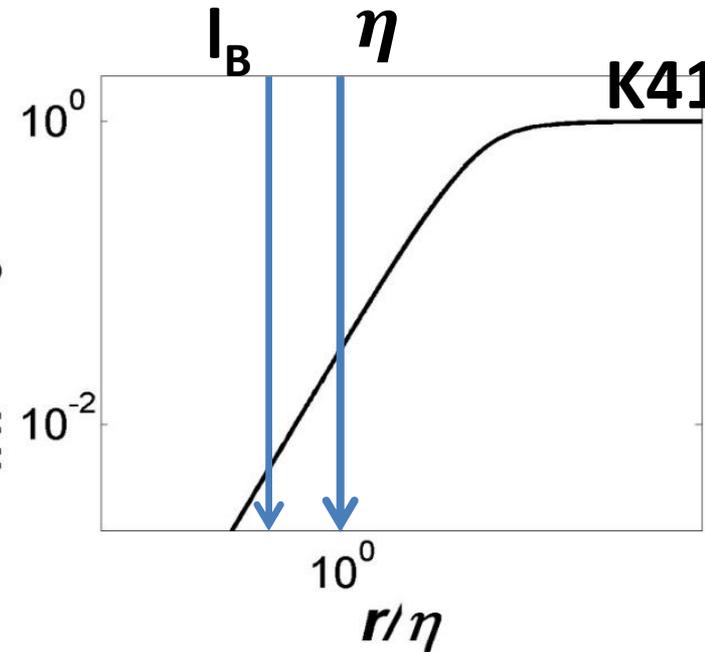
***Sc* >> 1**

Water molecules are tightly packed compared to air molecules, where *Sc* is near *unity*.

# Air-Water



$$D_{ww}(r)/C_o(\epsilon r)^{2/3}$$



Shape of vertical velocity  
Structure function can be  
predicted from the  
Karman-Howarth equation

# A Structure Function Perspective

A solution to approximated KH equation (Katul et al., 2015):

$$\frac{D_{ww}(r)}{C_o(\epsilon r)^{2/3}} = 1 - \frac{1}{\xi} Daw_F(\xi);$$

Viscous corrections to K41 scaling

$$\xi = \theta(r/\eta)^{2/3}; \theta = \sqrt{\frac{1}{10C_o}}.$$

$Daw_F(\xi) \approx \xi - \frac{2}{3}\xi^3 + \dots$  is the Dawson function.

# Recovery of $\alpha$ value

- Insert into structure function leads to:

$$k = \sqrt{\frac{2}{15}} S_C^{-1/2} (\epsilon \nu)^{1/4}.$$

$$\text{Here, } \alpha = \sqrt{\frac{2}{15}} = 0.36$$

Recall Zappa et al. (2007):  $\alpha = 0.41$

This completes the sought-after result and the study objective. A final *independent* check – recovery of surface divergence theories.

# Recovery of Surface Divergence Methods

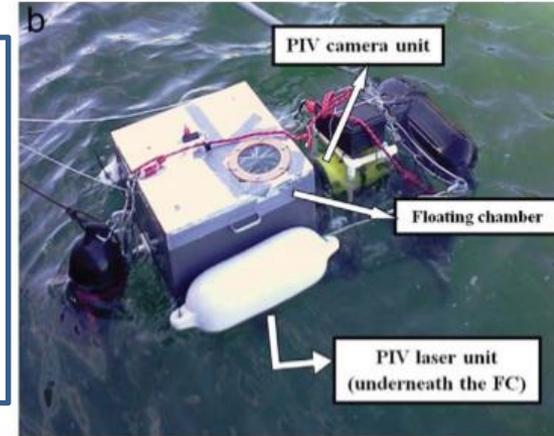
From Banerjee et al. (2004):

DNS & Measurements

0.57- 0.71

Surface divergence term

$$k = c_s Sc^{-1/2} \sqrt{\mathbf{v} \Lambda_o} \quad ; \quad \Lambda_o = \sqrt{\left(\frac{\partial w}{\partial z}\right)^2}$$



Start with  $k = \sqrt{\frac{2}{15}} Sc^{-1/2} (\epsilon \mathbf{v})^{1/4}$  (i.e. Structure function)

Recall that  $\epsilon = 15\nu \overline{\left(\frac{\partial w}{\partial z}\right)^2}$  (in locally isotropic turbulence)

$$k = \frac{\sqrt{2}}{15^{1/4}} Sc^{-1/2} (\mathbf{v} \Lambda_o)^{1/2} = 0.71$$

# Conclusion

- $k = \frac{F}{\Delta C}$  (analogous to a macroscopic resistance law).
- $k = \left[ \overline{(w(x+r) - w(x))^2} \right]^{1/2}$  - structure function describes cumulative energy content at scale  $r$  (e.g. analogous to micro-state energy content). Most *effective eddy size*  $r$  contributing to  $k$  is linked to the Kolmogorov microscale (or Batchelor scale).

The equality of these two expressions may be viewed as analogous to a '*fluctuation-dissipation*' result for gas transfer velocity across interfaces.

# Thank you

All models are wrong, but some are useful (George Box).

From [https://en.wikiquote.org/wiki/George\\_E.\\_P.\\_Box](https://en.wikiquote.org/wiki/George_E._P._Box)



## Acknowledgements

**E. Bou-Zeid, M. Novack, and W. Brutsaert** for the discussions and insights on this topic.

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Department of Energy:

DE-SC0006967 and DE-SC0011461

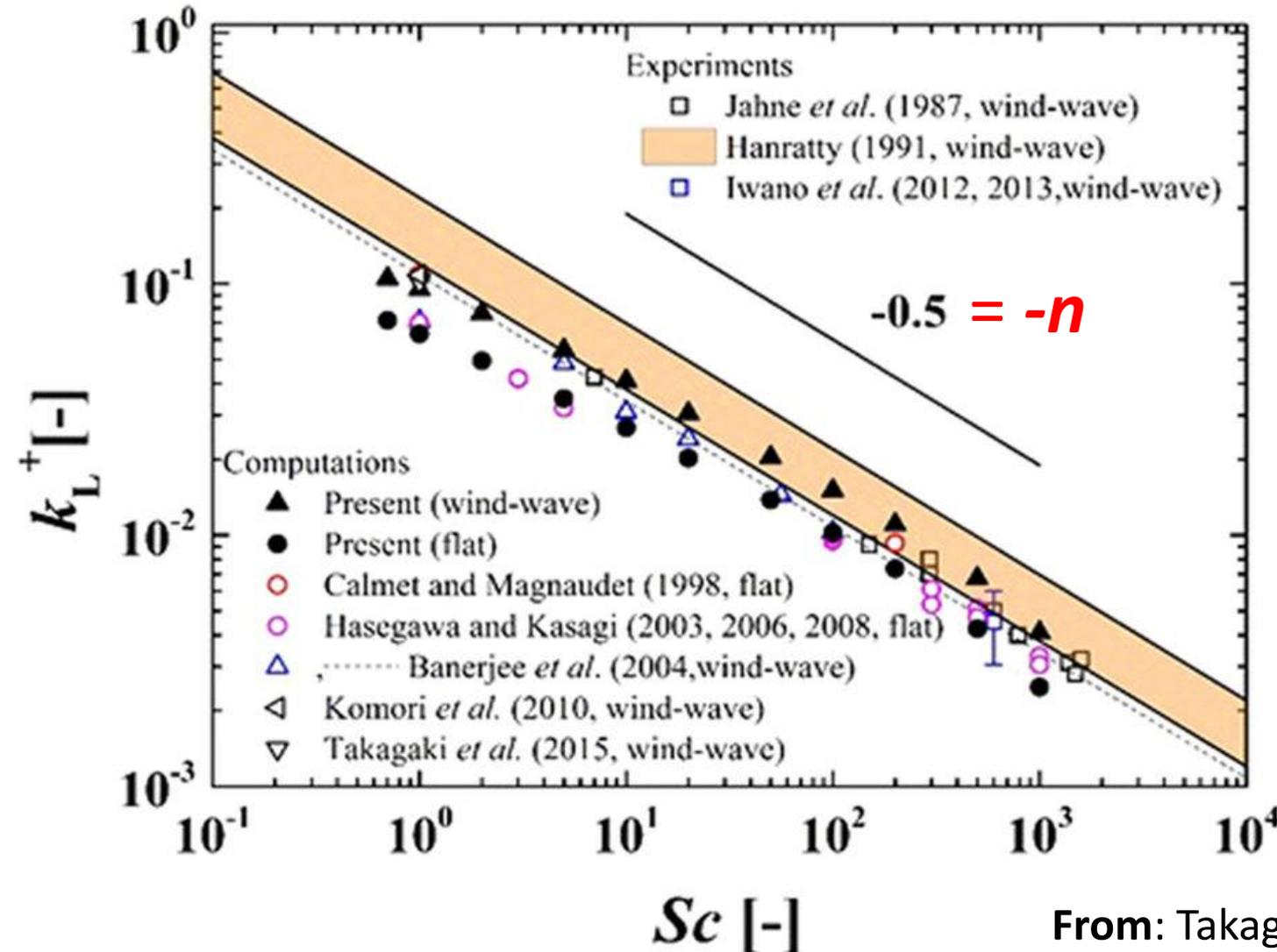
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**EXTRA SLIDES FOR QUESTIONS**

# Schmidt Number Effect

$$k = \alpha Sc^{-n} (\epsilon \nu)^{1/4}$$



# Evaporation derived from an interfacial theory and surface renewal (Brutsaert, 1965)

$$E = A \sqrt{D_m} u_*^{3/4} (\kappa_v \nu z_o)^{-1/4} \Delta C$$

Similarity constant

Friction velocity

Molecular Viscosity

Concentration difference between surface and bulk air aloft.

Molecular diffusivity

von Karman constant

Momentum roughness length

The diagram shows the equation  $E = A \sqrt{D_m} u_*^{3/4} (\kappa_v \nu z_o)^{-1/4} \Delta C$  with several terms highlighted in different colors and arrows pointing to their physical meanings. The term  $A$  is black and labeled 'Similarity constant'.  $\sqrt{D_m}$  is green and labeled 'Molecular diffusivity'.  $u_*^{3/4}$  is orange and labeled 'Friction velocity'.  $\kappa_v$  is blue and labeled 'von Karman constant'.  $\nu$  is red and labeled 'Molecular Viscosity'.  $z_o$  is brown and labeled 'Momentum roughness length'.  $\Delta C$  is blue and labeled 'Concentration difference between surface and bulk air aloft.'

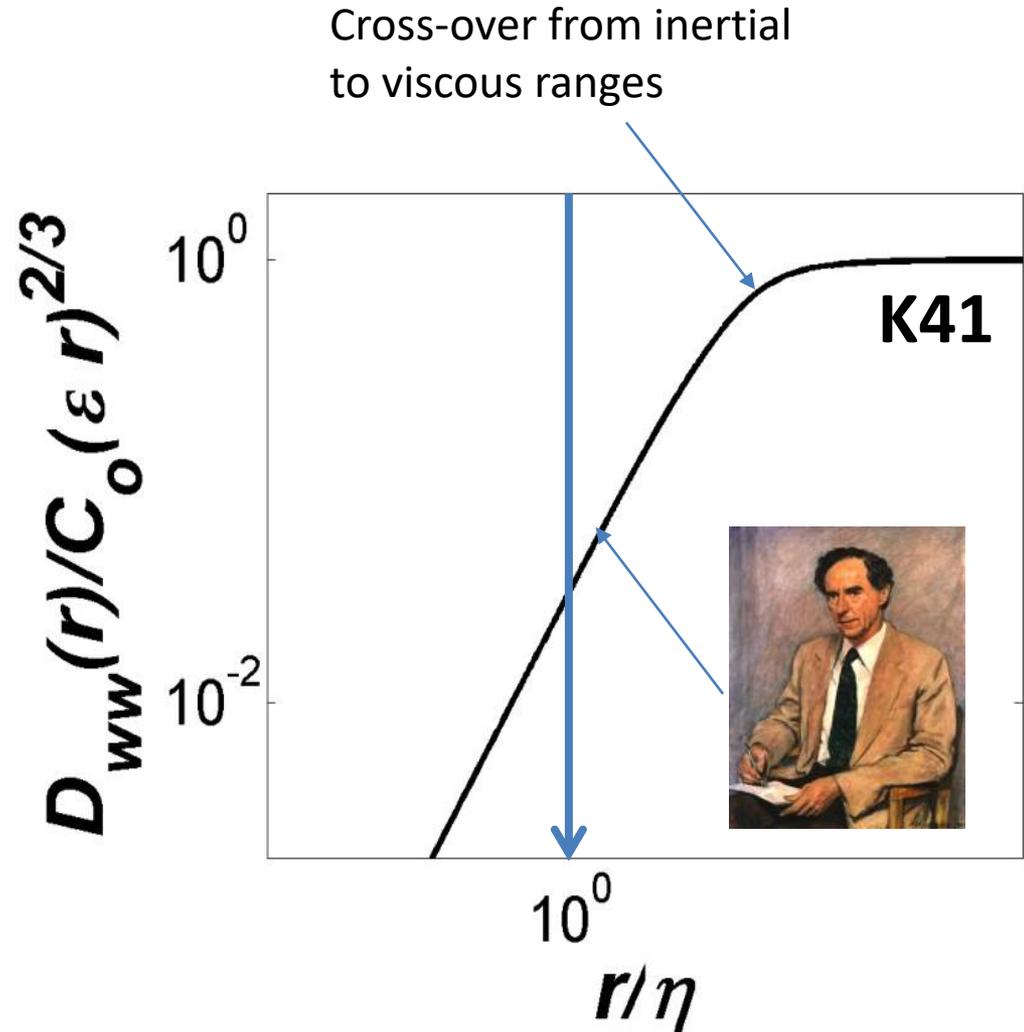
# Add Viscous Cutoff Correction to K41

Basic result

$$k \sim (\epsilon \nu)^{1/4}$$

Unaltered. Only the constant **A** needs adjustment.

(see Katul and Liu, 2017a)



# THEORY: A Structure Function Perspective

ONLY Kolmogorov Scaling:  $k = \sqrt{[C_0 \epsilon^{2/3} r^{2/3}]}$ ;

$r =$  Batchelor Scale  $l_B = S_c^{-1/2} \eta$ ; where  $\eta = \left(\frac{\nu^3}{\epsilon}\right)^{1/4}$ .

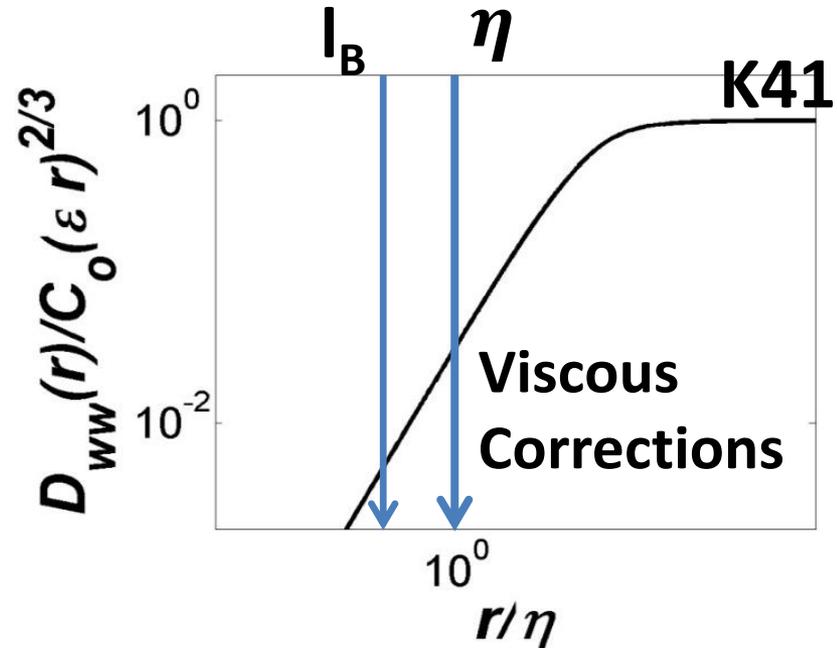
$$k = \sqrt{C_0} S_c^{-1/6} (\nu \epsilon)^{1/4}$$

## Notes:

$(\epsilon \nu)^{1/4} =$  Kolmogorov velocity

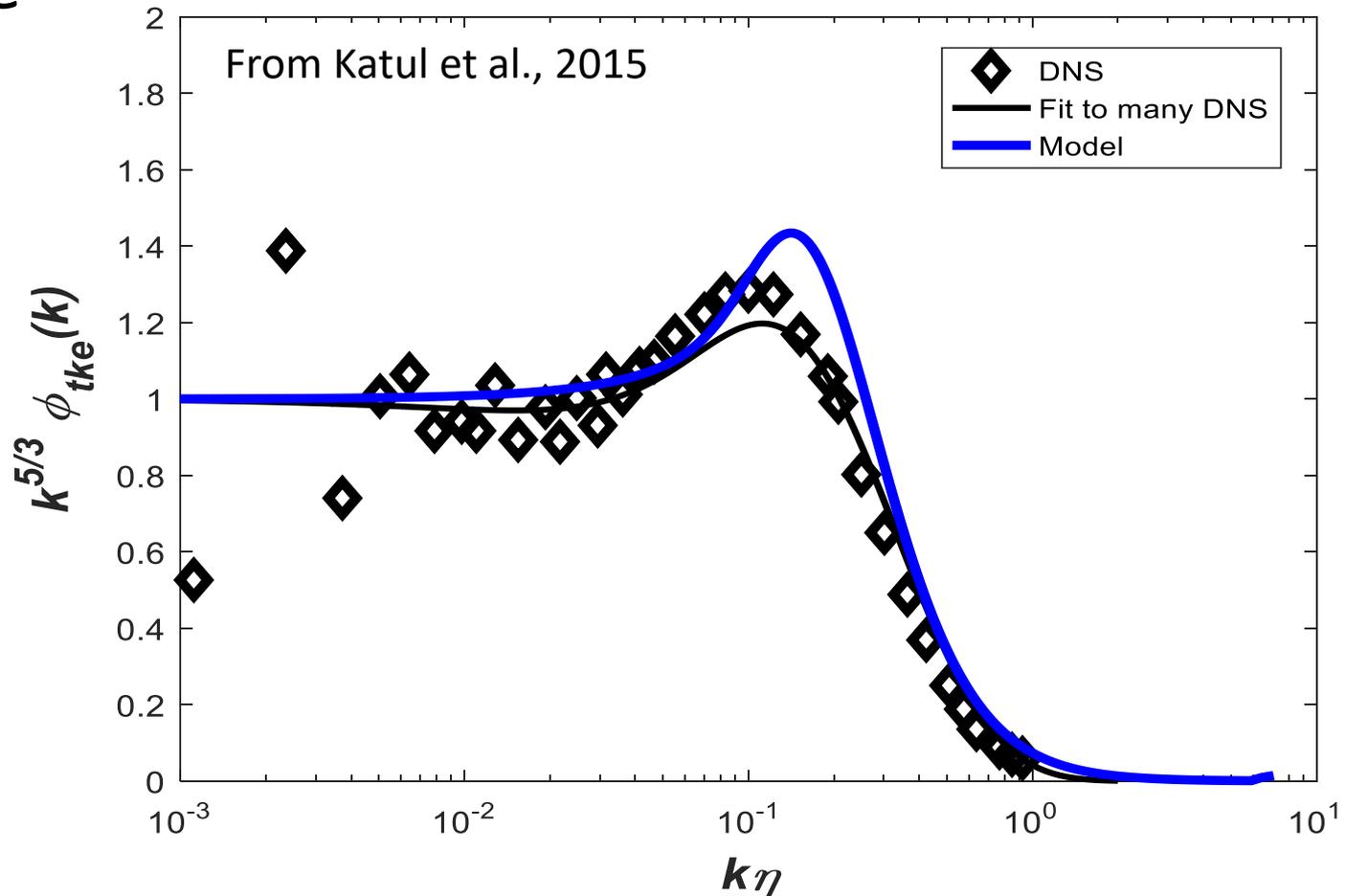
K41 scaling leads to correct  $(\nu \epsilon)^{1/4}$  but wrong Schmidt number exponent

(see Katul and Liu, 2017b).



# Inertial-to-Viscous Crossover

- Model reproduces the ‘spectral bottleneck’ when physical space is converted to spectral space



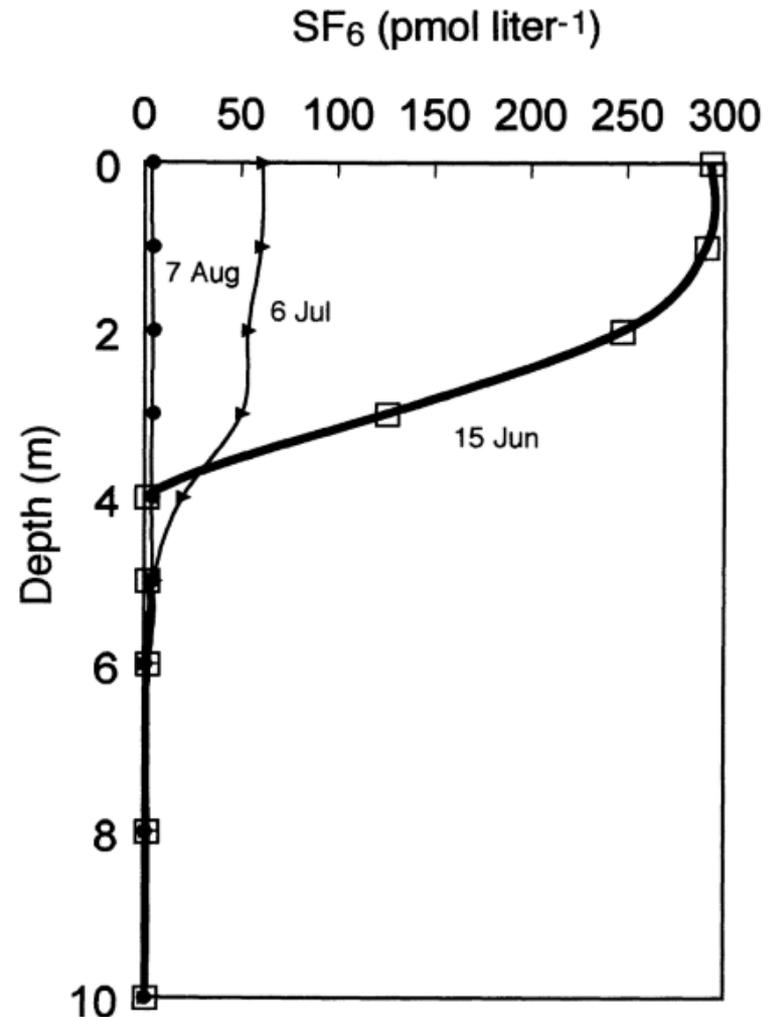
# Typical profiles of mean concentration

- The shape of the mean concentration profile over time scales much longer than turbulent mixing are 'preserved'.

This suggests that

$$\Delta C = C_s - C_b \text{ is a}$$

reasonable descriptor of the driving force for mass movement.



From Cole and Caroco (1998)

# Transfer Across the Air-Sea Interface

# 2

Peter S. Liss  
Martin T. Johnson  
Editors

## Ocean-Atmosphere Interactions of Gases and Particles

Christoph S. Garbe, Anna Rutgersson, Jacqueline Boutin, Gerrit de Leeuw, Bruno Delille, Christopher W. Fairall, Nicolas Gruber, Jeffrey Hare, David T. Ho, Martin T. Johnson, Philip D. Nightingale, Heidi Pettersson, Jacek Piskozub, Erik Sahlée, Wu-ting Tsai, Brian Ward, David K. Woolf, and Christopher J. Zappa

