SO_2 Processing During PASE

"Science is always wrong. It never solves a problem without creating ten more."

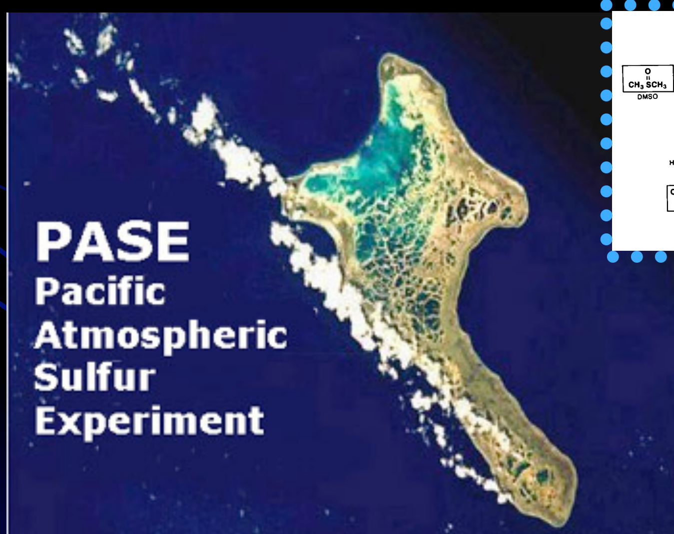
— George Bernard Shaw

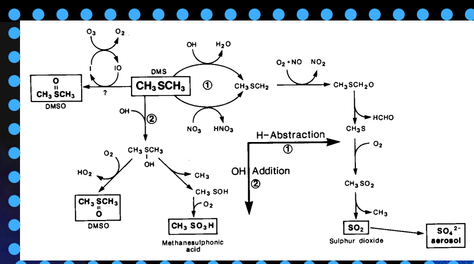
Ian Faloona & Steve Conley
Dept. of Land, Air, & Water Resources
University of California, Davis, CA

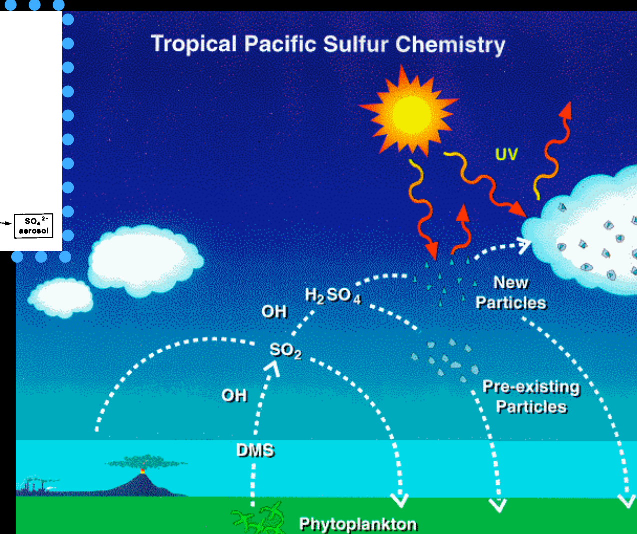
Don Lenschow
ESSL, NCAR, Boulder, CO

B. Blomquist, S. Howell, A. Clarke, V. Kapustin
University of Hawaii, Honolulu, HI

Alan Bandy
Drexel University, Philadelphia, PA







NCAR ESSL's Mesoscale & Microscale Meteorology

3rd PASE Science Meeting 2-3 Dec 2009

Table 1. Global Budgets of Main Sulfur Species (TgS/yr) and Their Lifetimes (d)

	Liu et al., 2007	Range of Other Models[a] Min	Max	Estimated Std. Deviation[b]	Approximate Diversity[c]	avg. of last two columns
	DMS					
Sources	26.1	10.7	27.6	4.3	11.7	8.0
Oxidation	25.9	10.7	27.6	4.3	11.7	8.0
Global Lifetime	2.4	0.5	3	0.6	---	
	SO_2					
Sources	99.4	83.2	126	10.9	9.9	10.4
Anthropogenic	69	55	92	9.4	5.5	7.5
Ship	---	2.5	4.7	0.6	0.3	0.4
Volcanic	4.8	3.4	14	2.7	0.4	1.5
DMS Oxidation	25.6	10	25.7	4.0	11.5	7.8
Sinks	99.1	91.7	126	8.8	---	
Dry Deposition	27.6	14	56	10.7	8.8	9.8
Wet Deposition	4.9	0	20	5.1	1.6	3.3
Oxidation (-->SO_4)	65.9	---	---	---	---	
Global Lifetime	2.4	0.6	2.6	0.5		
	NSS-Sulfate					
Sources	65.8	---	---	---	---	
Direct Emissions[d]	---	1.1	4.6	0.9	1.8	1.3
Heterogeneous Ox.	49.3	24.5	57.8	8.5	10.8	9.7
Homogeneous Ox.	16.6	6.1	16.8	2.7	5.8	4.3
Sinks	65.7	---	---	---		
Dry Deposition	3.6	2.5	18	4.0	2.0	3.0
Wet Deposition	62.1	24	74	12.8	13.7	13.2
Global Lifetime	4.3	2.6	6.8	1.1	0.8	0.9

[a]Models included: *Langner & Rodhe [1991], Pham et al. [1995], Chin et al. [1996], Feichter et al. [1996], Graf et al. [1997], Lohmann and Feichter [1997], Chuang et al. [1997], Roelofs et al. [1998], Koch et al. [1999], Lohmann et al. [1999], Haywood & Boucher [2000], Rasch et al. [2000], Chin et al. [2000], Chuang et al. [2002], Rotstayn and Lohmann [2002], Easter et al. [2004], Koch et al. [2006], and Kloster et al. [2006].*

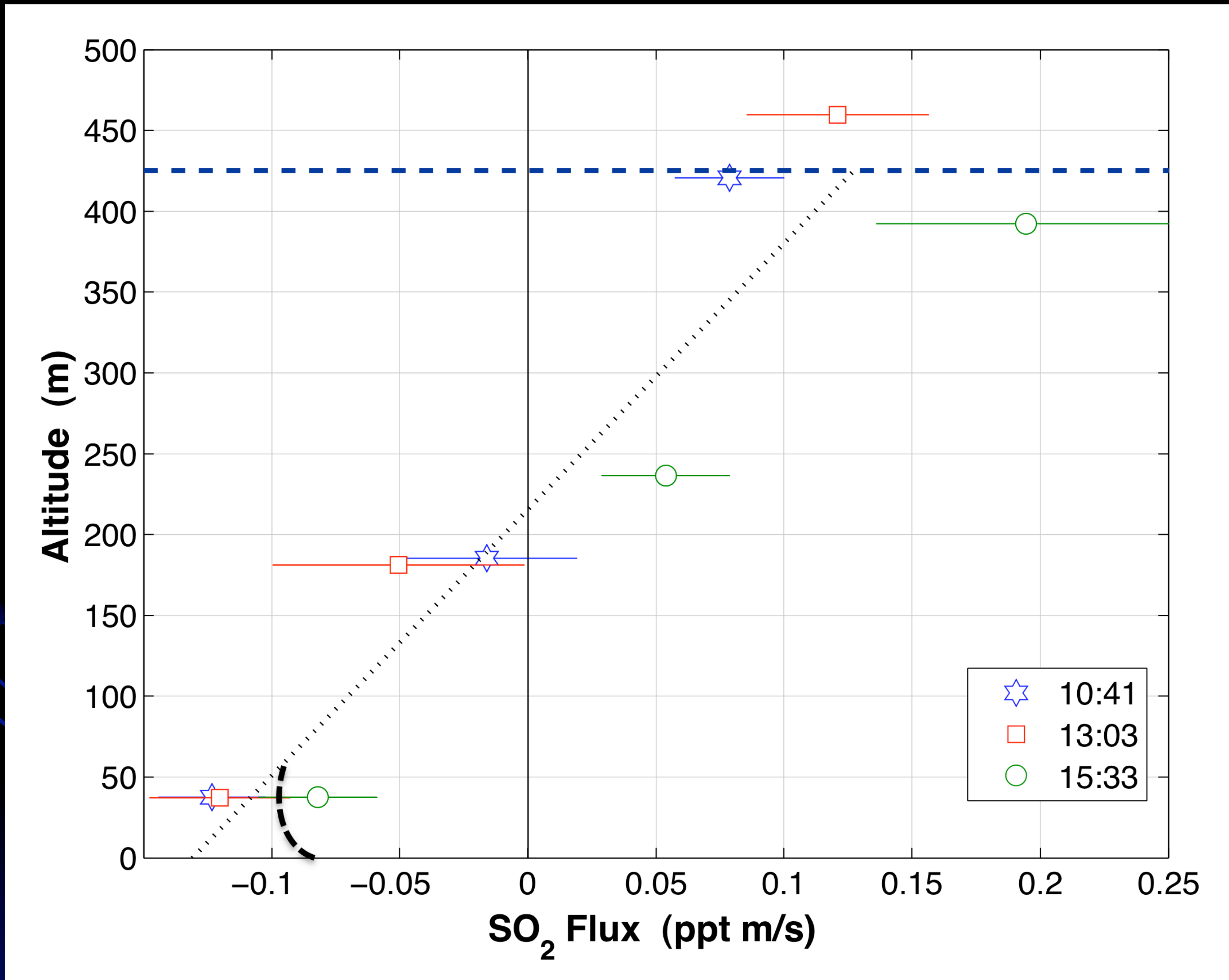
Anthropogenic Sources: fuel bound S, ore smelting, & biomass burning ~70 Tg S/yr

Largest uncertainties:
SO_4 wet dep
SO_2 dry dep
SO_2 sources

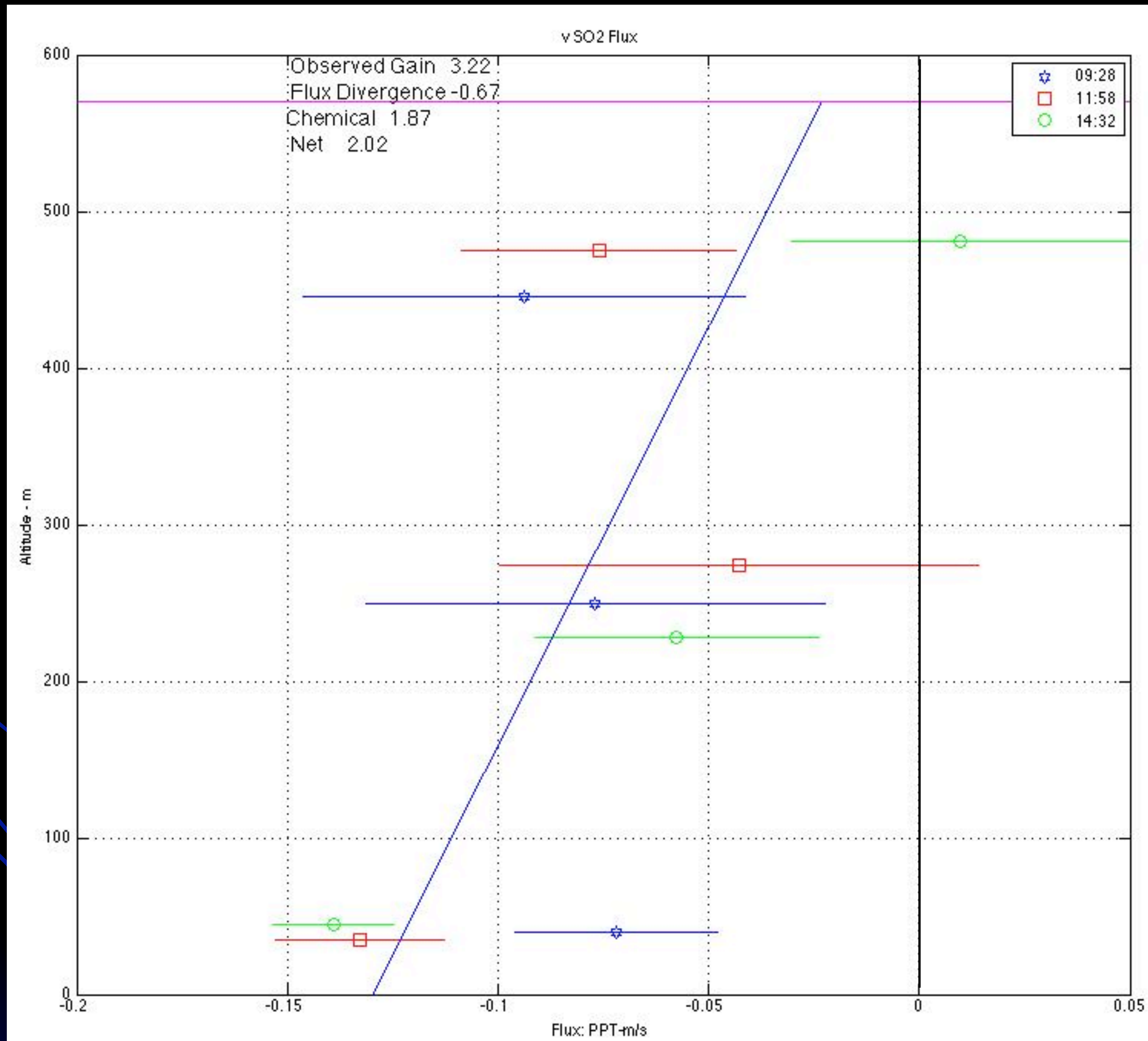
Oceanic DMS emissions: large (~25%) and very difficult to predict.

PASE can address:
SO_2 dep
& Hetero. Ox.

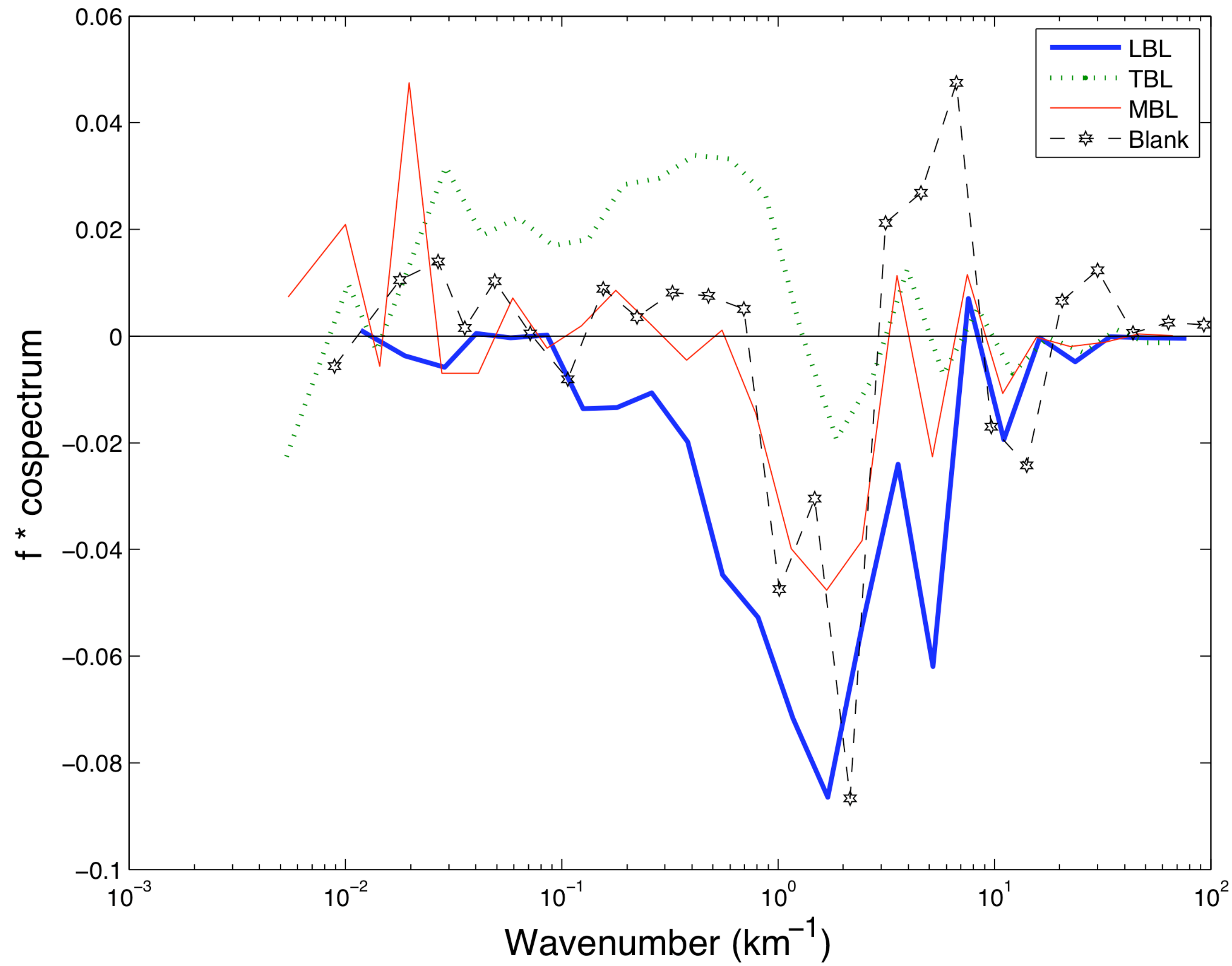
RF02 SO_2 Flux Profiles



Flux Profile RF08: BuL source

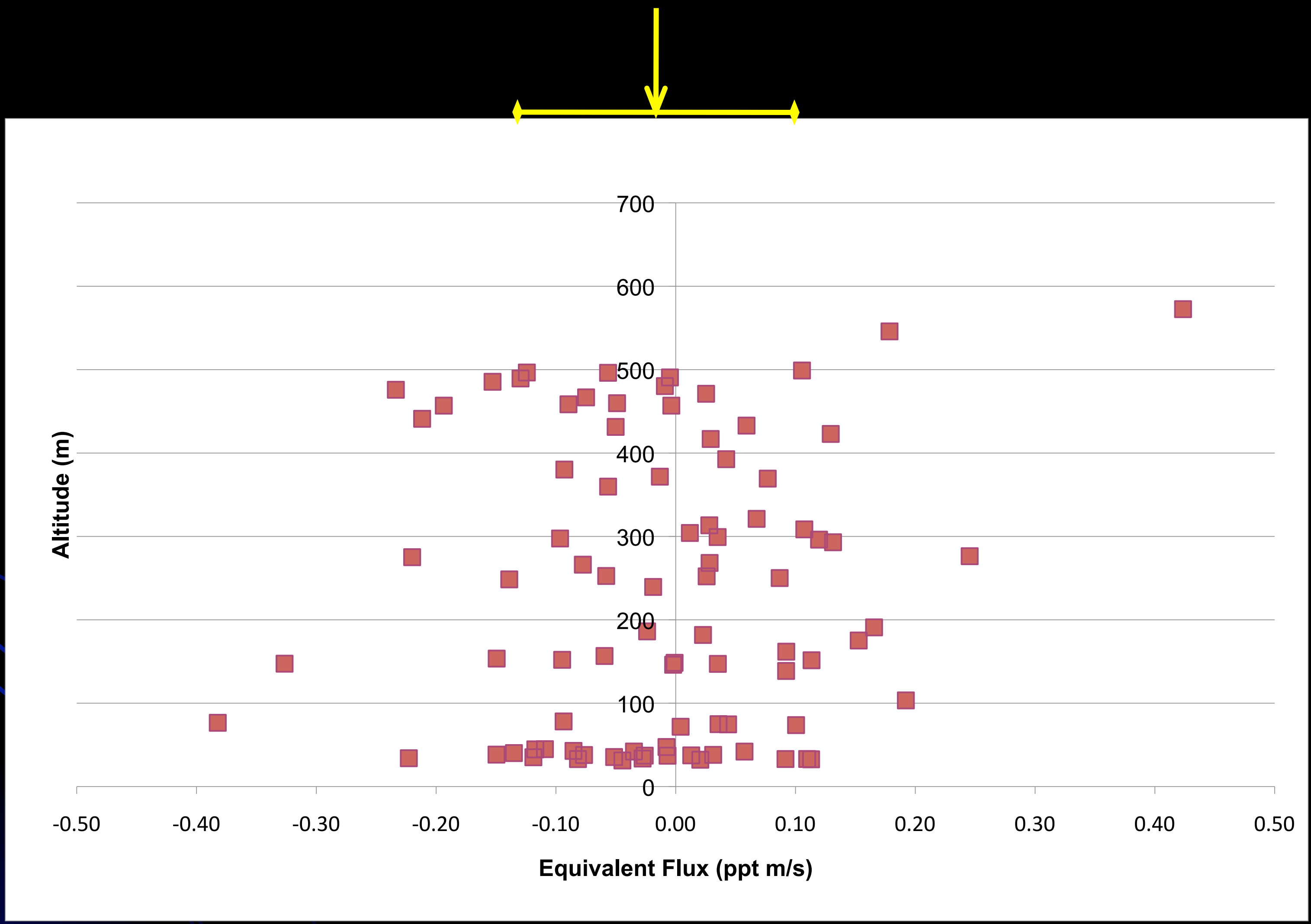


SO_2 signal & blank, w Cospectra



Statistics of Background 'flux'

Mean: -0.015 ± 0.123 ppt m/s



SO_2 Budgets & Dry Deposition

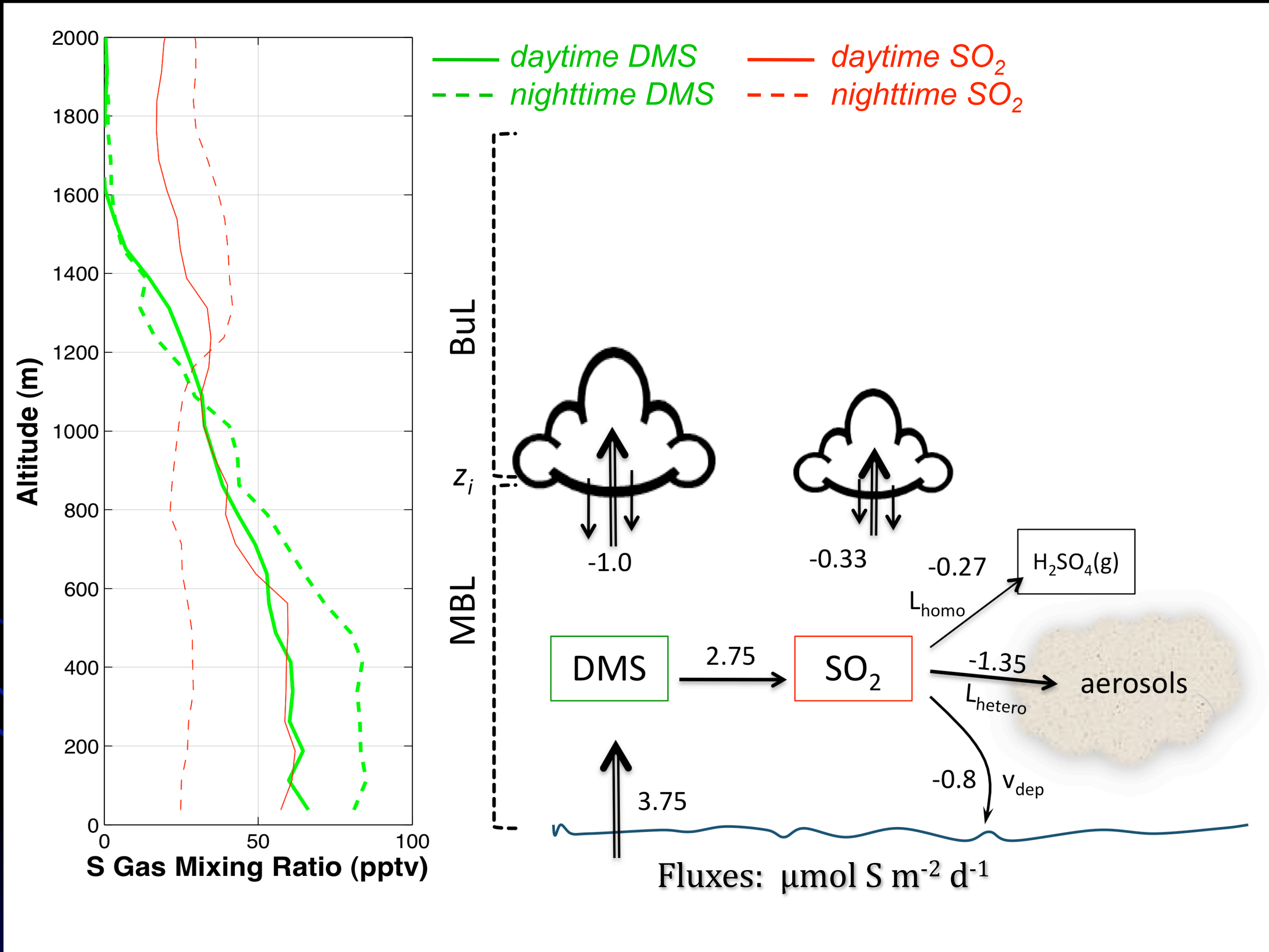
$$\frac{\partial [SO_2]}{\partial t} = -\frac{\partial}{\partial z}\langle w'[SO_2]'\rangle - \vec{U}\cdot\nabla[SO_2] + P_{DMS} - L_{chem}$$

Flight (RF)	SO_2 Trend (ppt/hr)	Flux Div. (ppt/hr)	Advection (ppt/hr)	DMS decay (ppt/hr)	Net Loss (ppt/hr)	Aerosol Loss (h^{-1})	V_{dep} (cm/s)	$[SO_2]$ (ppt)	Net Error (ppt/hr)	Surface Area ($\mu m^2/cm^3$)	Aerosol pH
1	0.00	-2.19	0.11	N/A	N/A		0.21	63.8	0.15		
2	0.76	-3.14	0.51	7.36	-3.97	-0.058	0.37	54.9	0.20	94.6	7.0
3	4.50	-1.81	-0.45	7.43	-0.67	0.002	0.31	55.2	0.25	98.1	N/A
5	4.96	-3.14	-0.38	11.23	-2.75	-0.033	0.43	57.4	0.48	90.8	6.9
6	-4.35	-2.10	-0.50	0.00	-1.75	-0.065	0.53	26.9		115.7	6.9
7	1.20	-3.23	-1.77	10.47	-4.27	-0.046	0.56	69.8	1.06	90.1	6.9
8	2.77	-0.46	1.81	5.88	-4.47	-0.095	0.33	40.7	0.21	58.8	7.2
11	2.60	-3.57	3.36	6.78	-3.96	-0.052	0.53	59.0	0.34	48.1	7.1
12	3.41	-0.63	0.73	7.39	-4.08	-0.078	0.35	43.9	0.23	87.3	7.0
13	-1.08	-0.59	0.63	0.00	-1.12	-0.040	0.29	28.1		121.0	6.8
14	5.85	-2.21	-2.06	11.29	-1.17	-0.002	0.46	68.1	0.33	91.9	6.4
Day Avg	**3.3**	**-2.3**	**0.2**	**8.5**	**-3.2**	**-0.045**	**0.42**	**56.1** ÷	**0.39**	= 6 d **82**	**6.9**
Std Dev (day)	1.8	1.2	1.8	2.2	1.5	0.034	0.09	10.2		18	0.3
Night Avg	-2.7	-1.3	0.1	0.0	-1.4	-0.052	0.41	27.5		118	6.9
Diel Avg	**0.3**	**-1.8**	**0.1**	**4.2**	**-2.3**	**-0.049**	**0.41**	**41.8**		**100**	**6.9**

$$P_{DMS} = \gamma \cdot k_{OH+DMS}[OH][DMS] \quad \Rightarrow \quad \gamma \geq 0.95$$

$$L_{chem} = \left\{ k_{OH+SO2}[OH] + \left(\frac{1}{k_{mt}} + \frac{1}{k_{O3} + k_{H2O2}} \right)^{-1} \right\} [SO_2]$$

Diel Pattern of S Processing



Previous Estimates of L_{hetero}

Table 4. Estimates of S(IV) Oxidation in Marine Boundary Layer

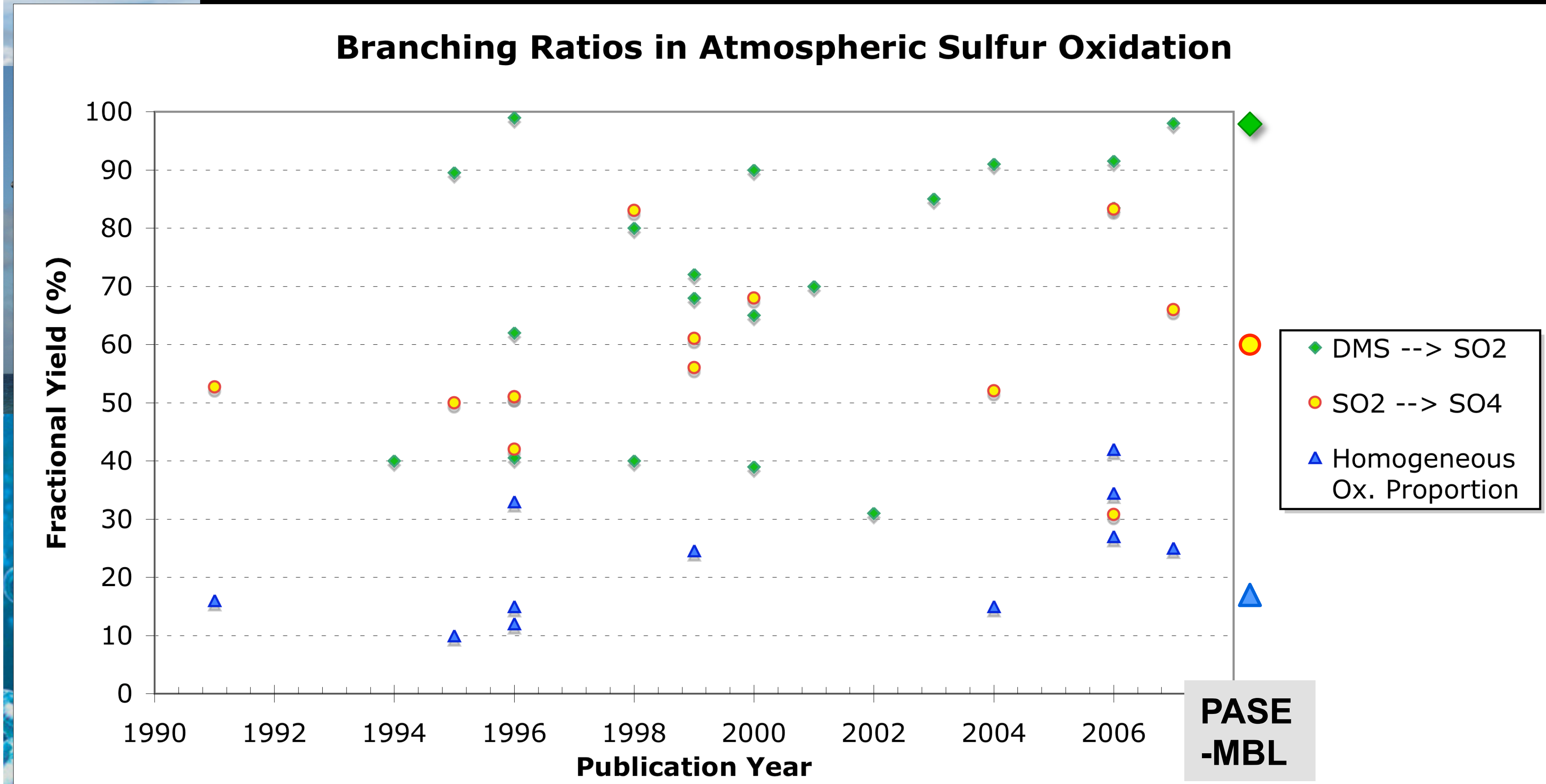
Sulfur Uptake/Oxidation (h^{-1})	Notes	Source
0.12 - 0.20	pH = 7	*Sievering et al. [1991]*
0.16	uptake limit	*Sievering et al. [1992]*
0.08 - 0.68	model	*Suhre et al. [1995]*
0.05 - 0.35	model (10 m)	*Mari et al. [1999]*
0.04	model	*Chen et al. [2000]*
0.06	NSS-SO_4 budget	*Huebert et al. [1996]*
0.02	SO_2 budget	*Bandy et al. [1996]*
0.02 - 0.04	NSS-SO_4 budget	*DeBruyn et al. [1998]*
0.015	SSA only	*Luria & Sievering [1991]*
0.03	unconstrained	*Mihalopoulos et al. [2007]*
0.11	Approx. Average	*All Above*

PASE Results: ~0 to 0.095 h^{-1}, Average: **0.045 h^{-1}**

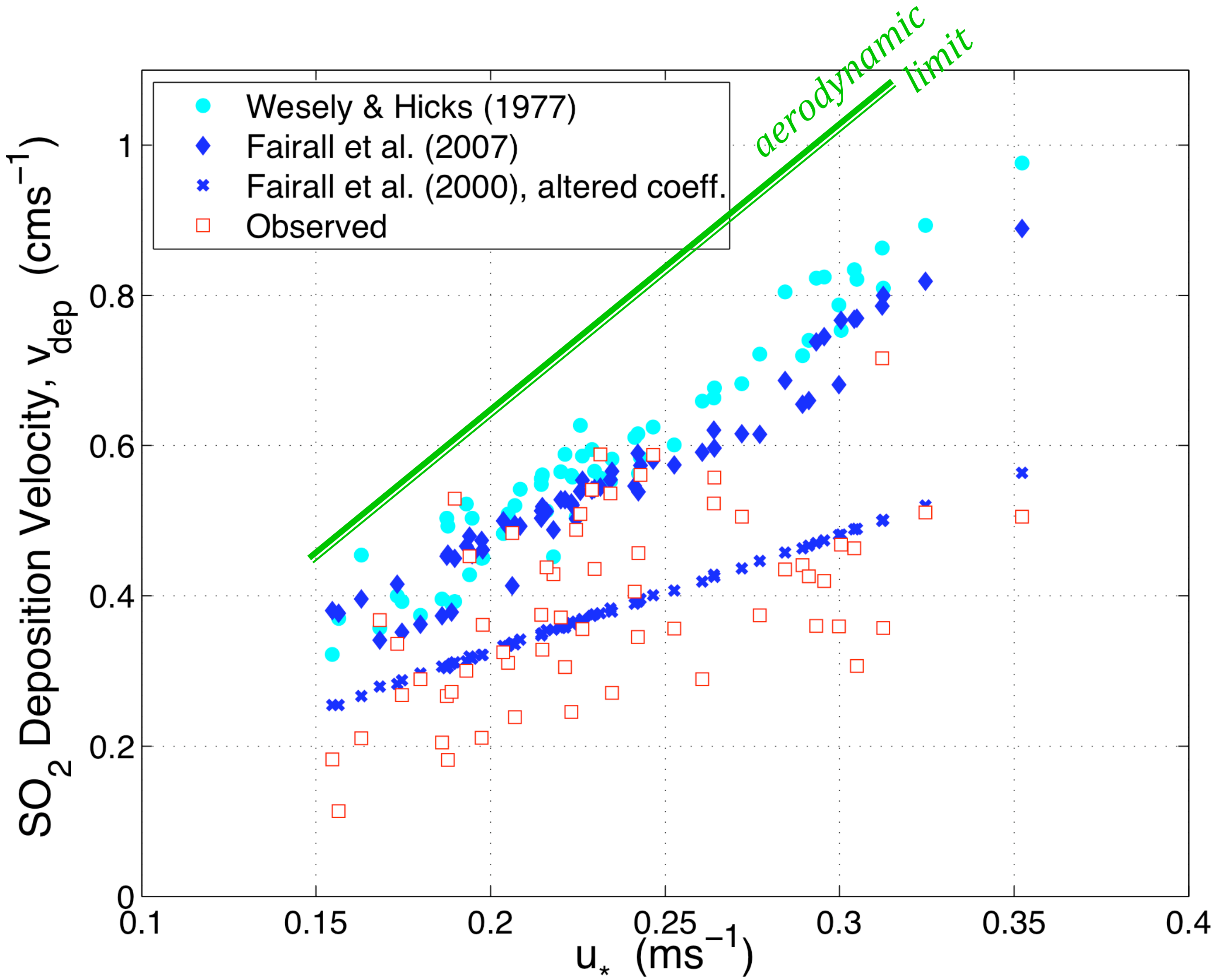
Comparing to Consensus

DMS $\xrightarrow{\sim 70\% (\pm 20\%)}$ SO_2 $\xrightarrow[\text{Aqueous/Gas: 75/25}]{\sim 60\% (\pm 15\%)}$ $H_2SO_4(g)/SO_4^{2-}(aq)$

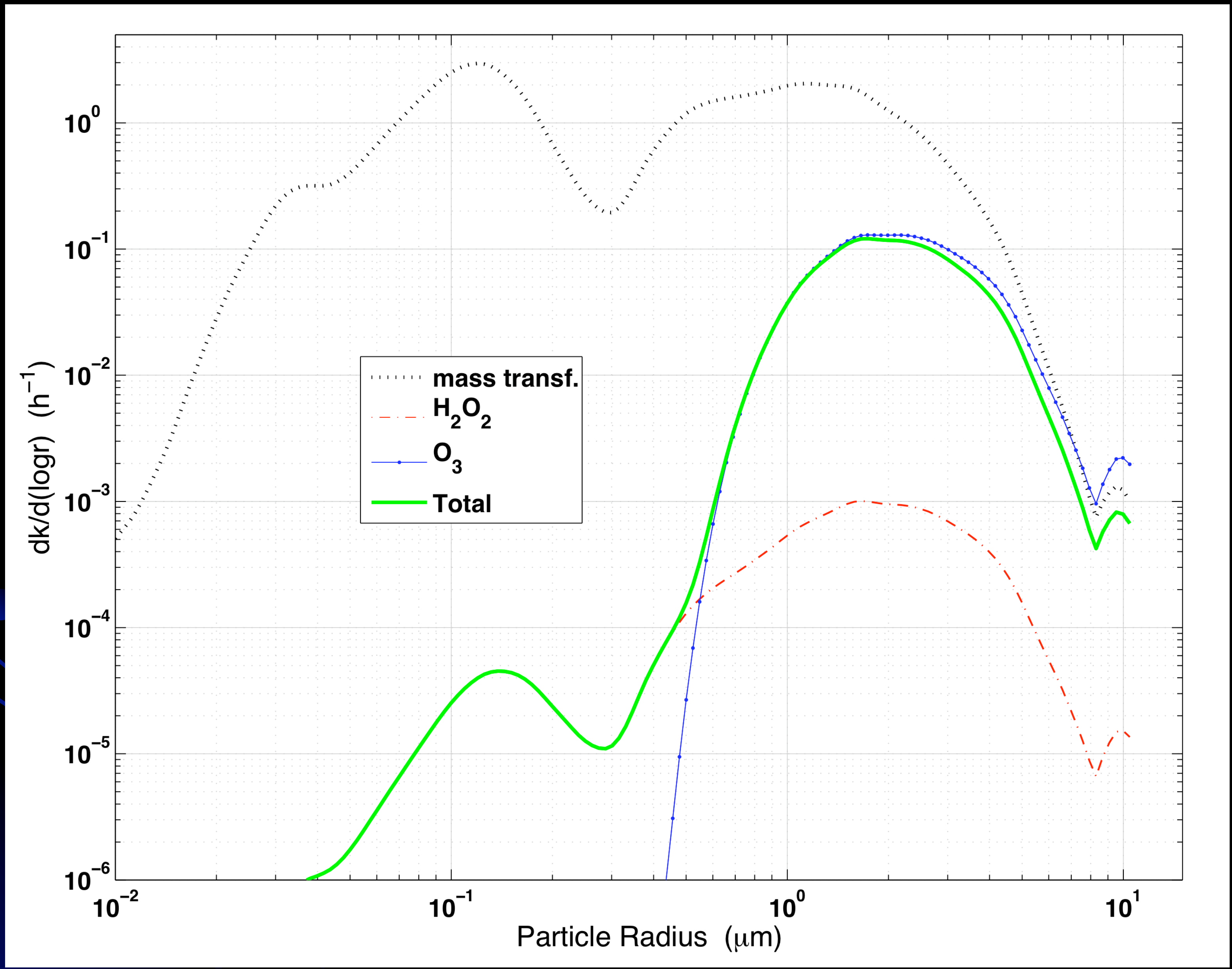
Number of refs:	19	13	11	
AVERAGES:	70.3	57.4	23.1	76.9
Standard Deviation:	22.4	14.9	10.4	10.4



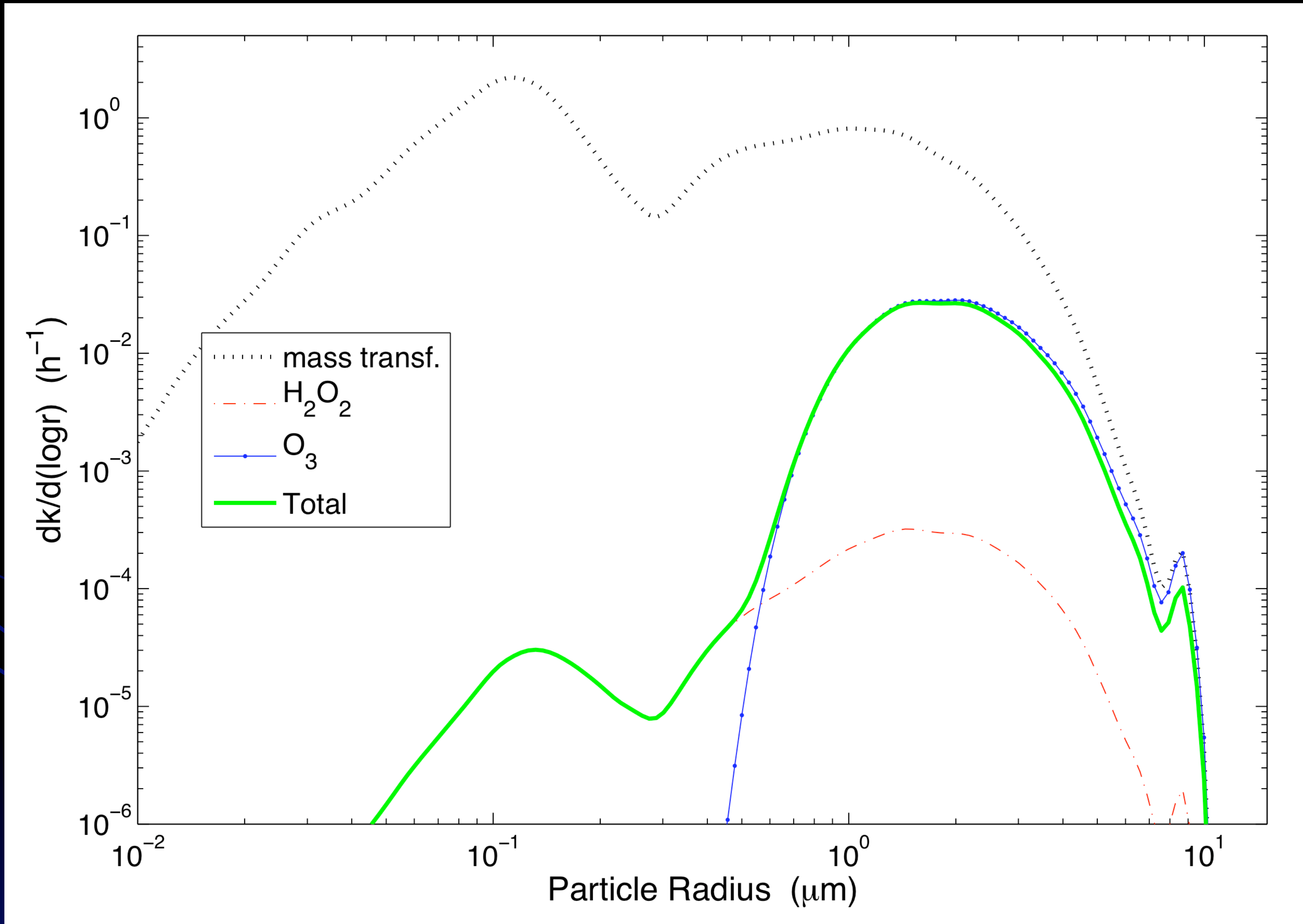
Dry Deposition vs. Friction Velocity



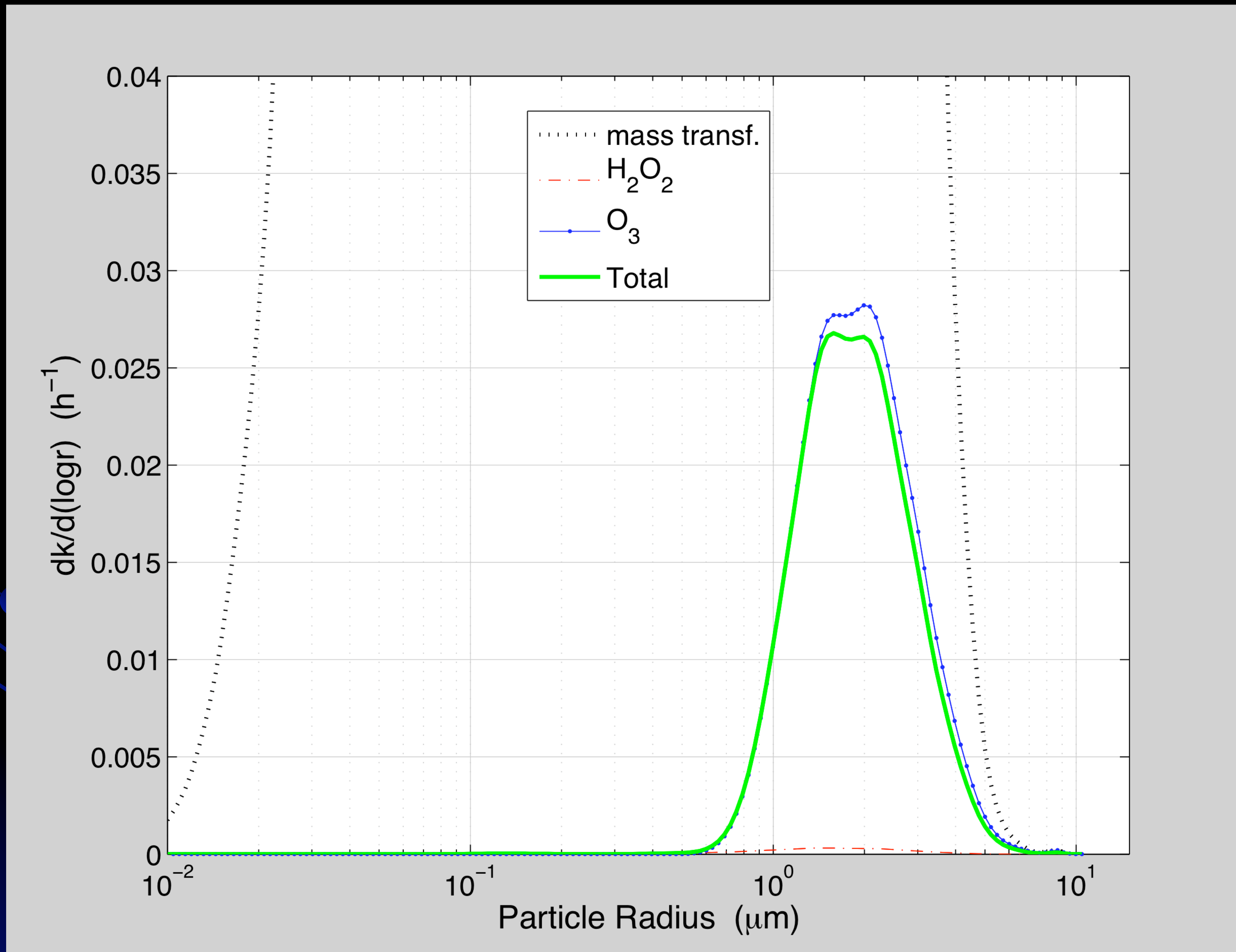
Heterogeneous Processing: RF13



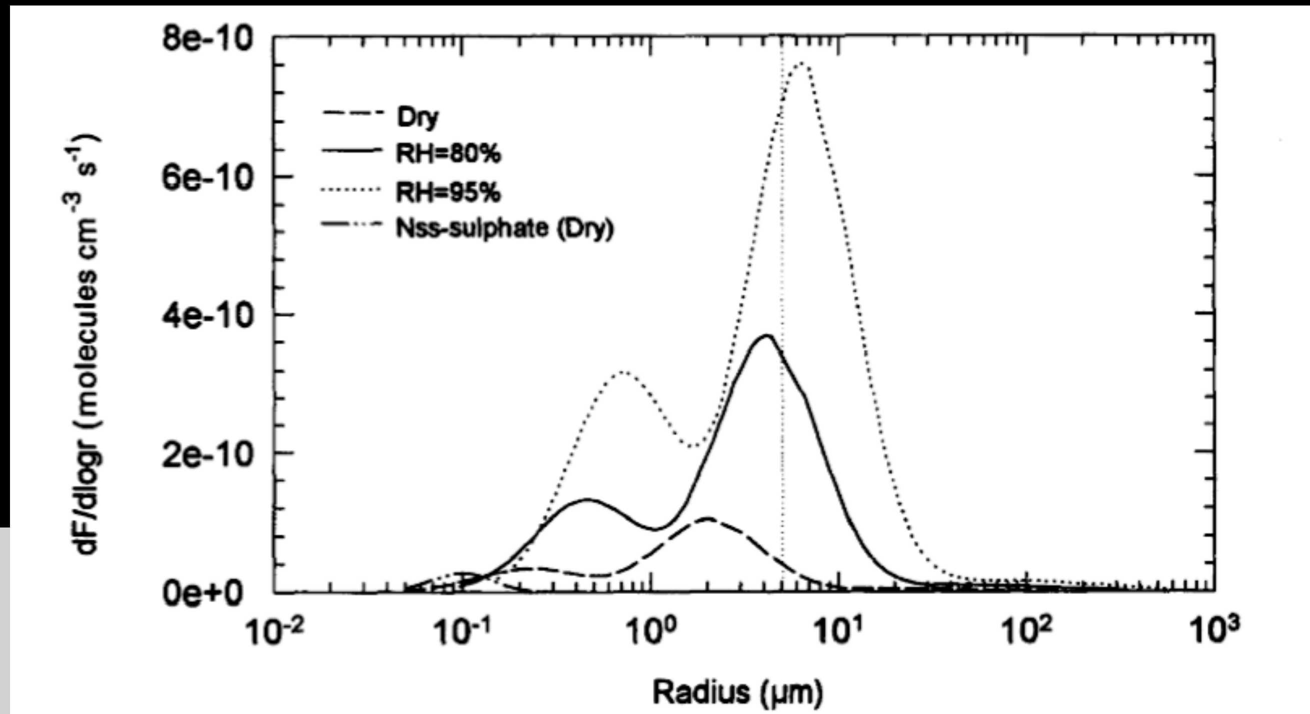
Heterogeneous Processing: RF08

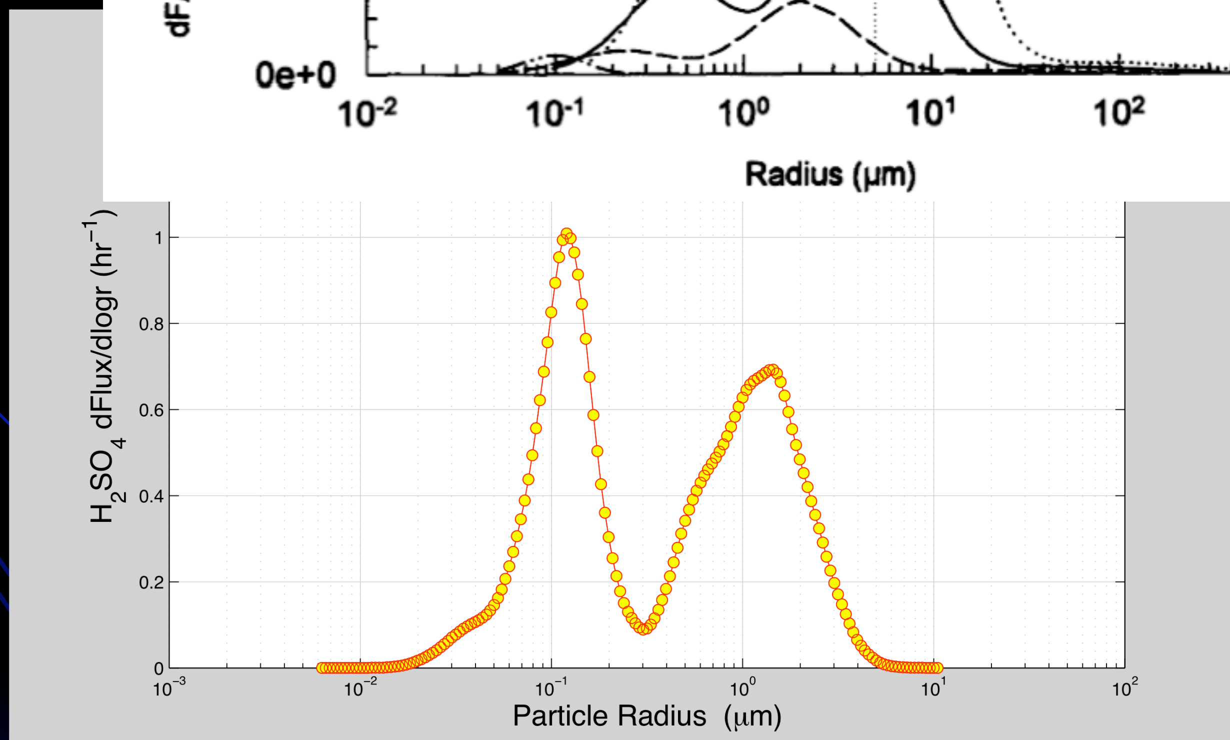


Bulk of S(IV) oxidation on coarse mode

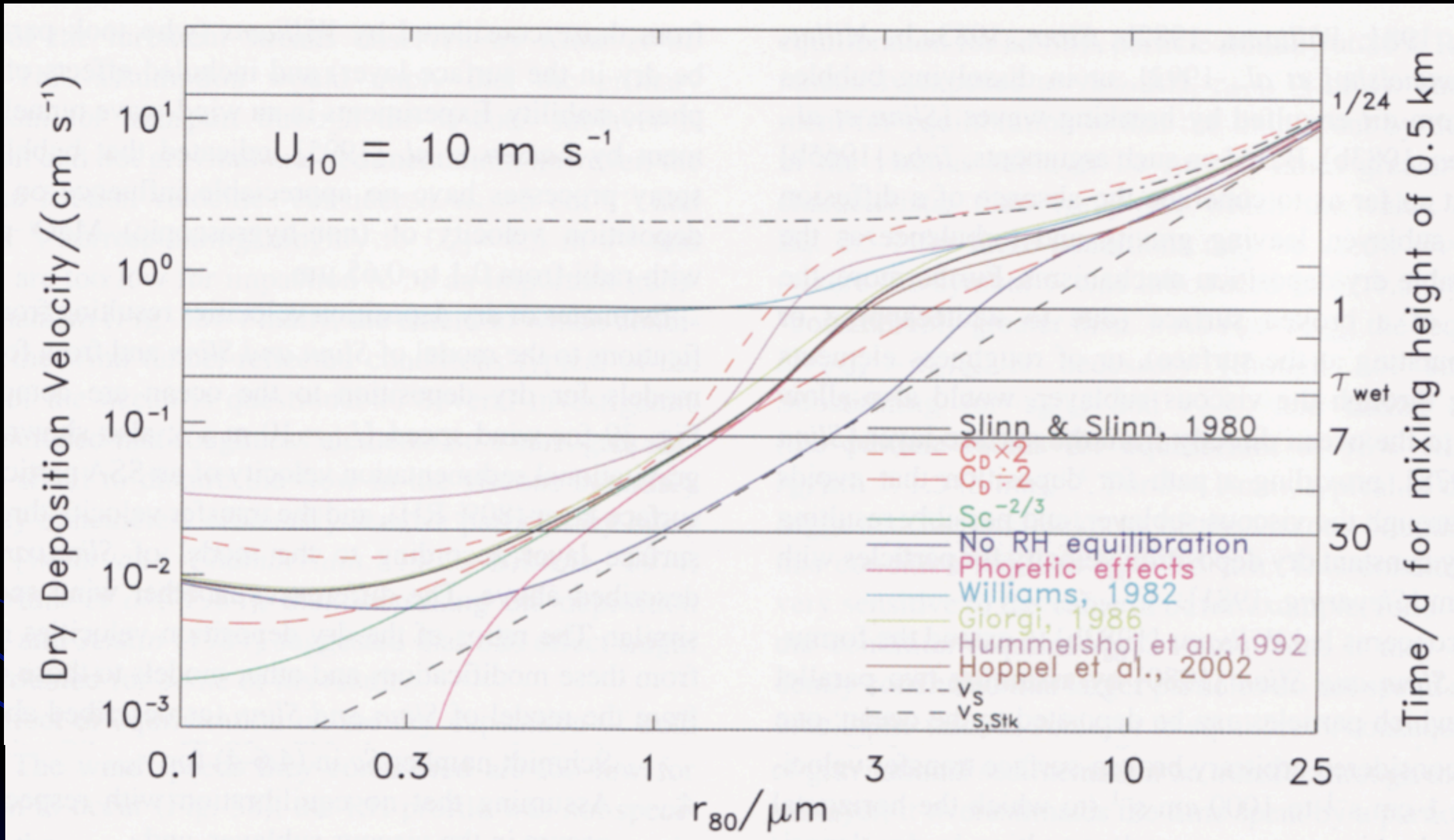


H_2SO_4 Estimated Uptake: O'Dowd & RF13



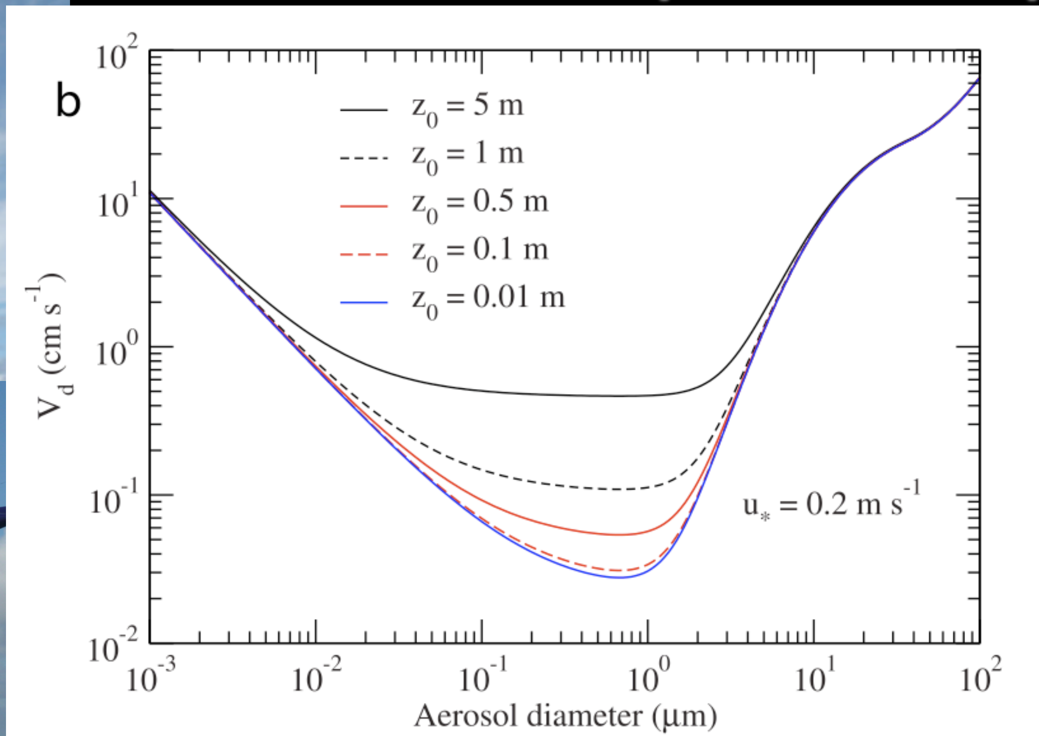


Aerosol Dry Deposition

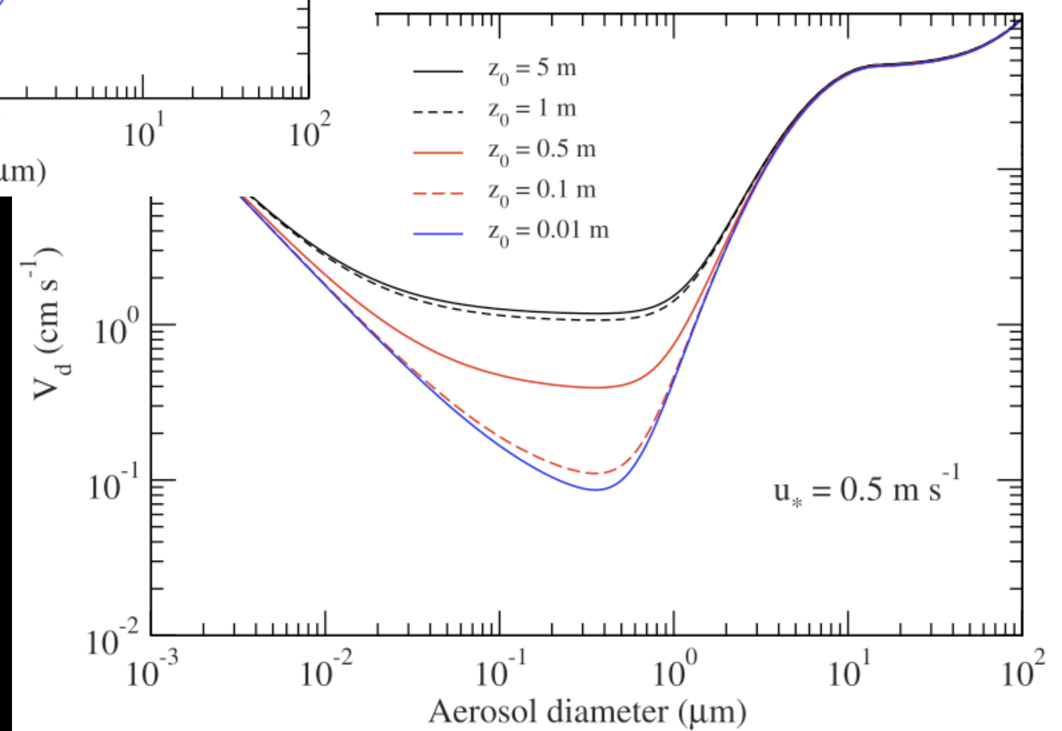


[Lewis & Schwartz, 2004]

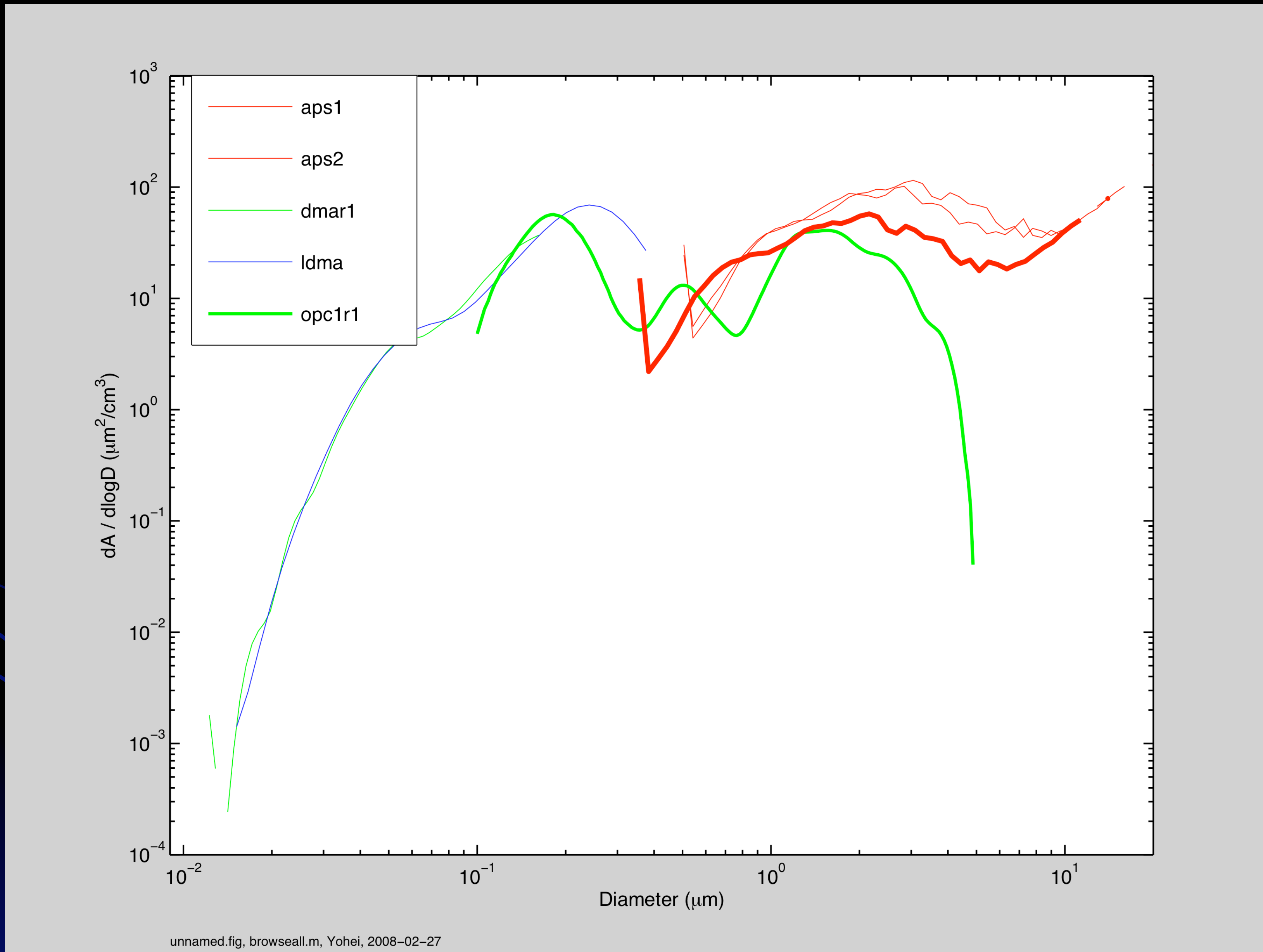
Recent turbophoresis parameterization



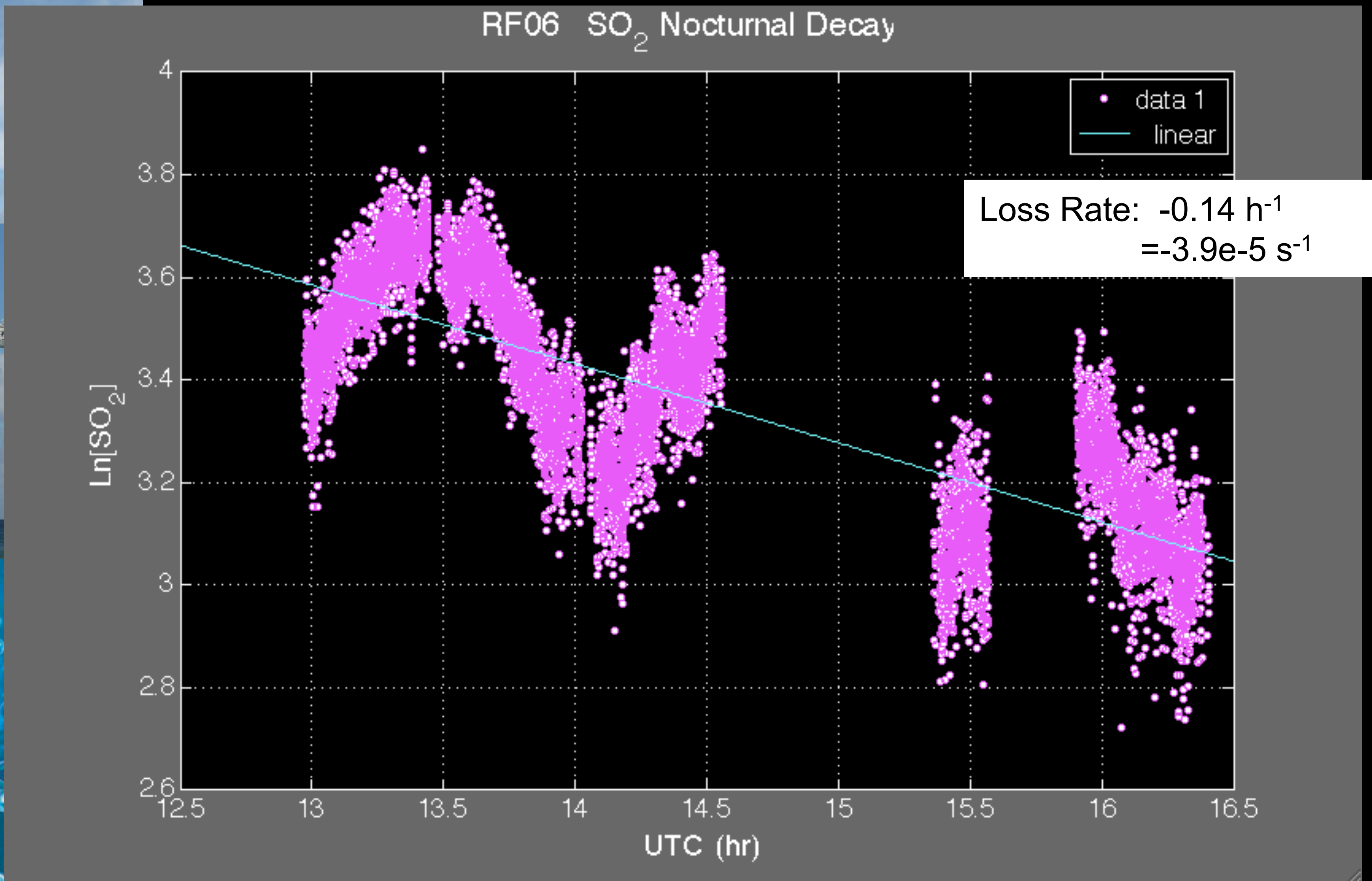
[Feng, 2008]



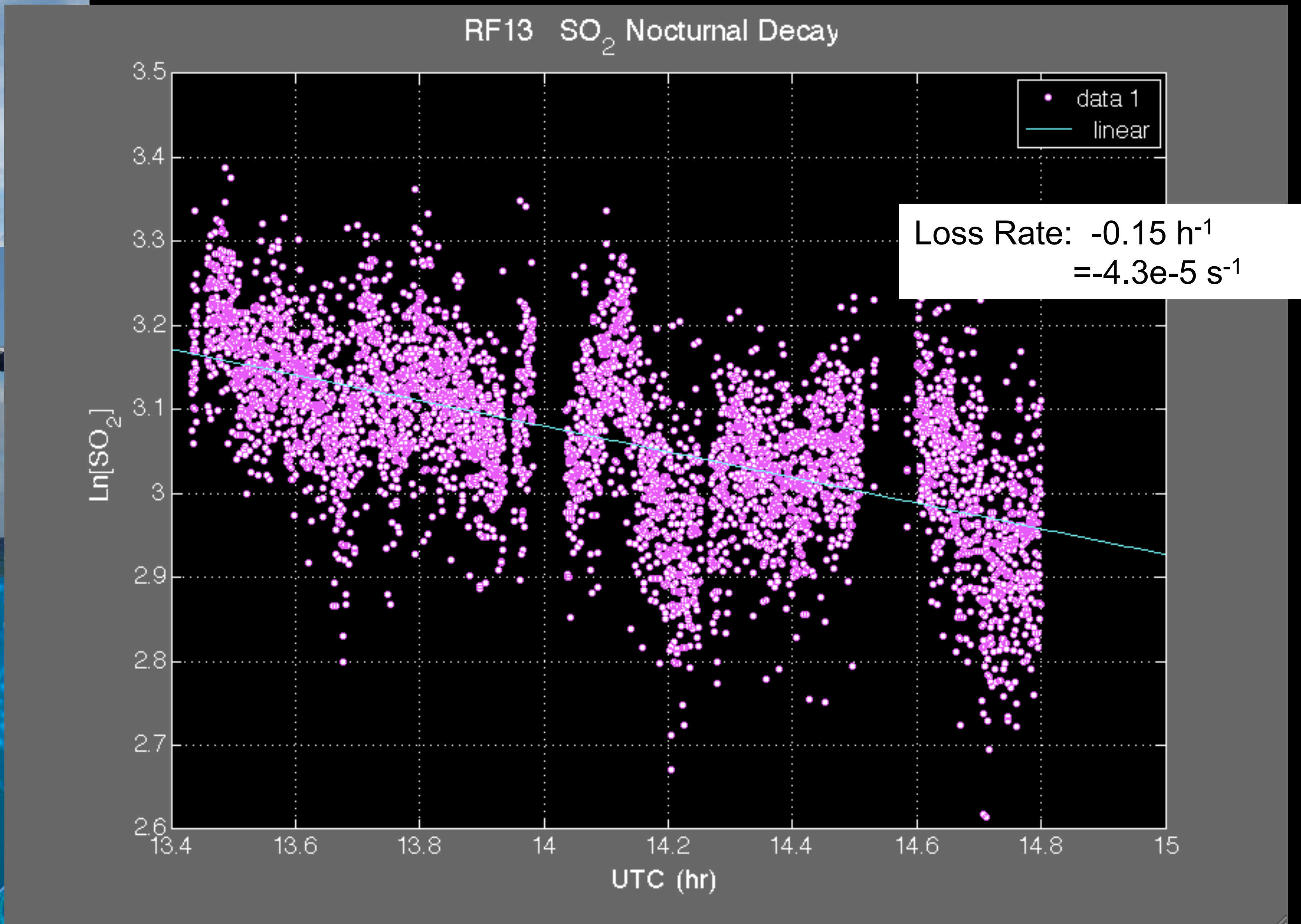
Larger aerosols?



Inferring Heterogeneous Uptake



Heterogeneous Loss on RF13



Huebert's Complaint

GEOPHYSICAL RESEARCH LETTERS, VOL. 23, NO. 7, PAGES 737-740, APRIL 1, 1996

Production and loss of methanesulfonate and non-sea salt sulfate in the equatorial Pacific marine boundary layer

B. J. Huebert, D. J. Wylie, L. Zhuang, and J. A. Heath

Department of Oceanography, University of Hawaii at Manoa, Honolulu

Abstract. We measured the concentrations of aerosol methanesulfonate (MSA) and non-sea salt sulfate (NSS) in the remote Pacific marine boundary layer (MBL) at Christmas Island (157° W, 2° N) in July and August of 1994. The project-average MSA displayed a distinct diurnal variation, decreasing to 8.6 ppt at sunrise and increasing to 12.1 ppt by sunset. The average NSS diurnal variation ranged from 196 ppt at sunrise to 235 ppt at sunset. Large-particle dry deposition may account for 10-20% of the observed nighttime decrease, with entrainment of cleaner free tropospheric air responsible for the rest. The entrainment velocity inferred from the nighttime decrease averaged 0.5 ± 0.2 cm/s. A simple model suggests that NSS and MSA were produced at rates of about 74 and 6 ppt per day, respectively. Between 30 and 40 % of the daily dimethylsulfide (DMS) flux forms NSS and 3 % forms MSA.

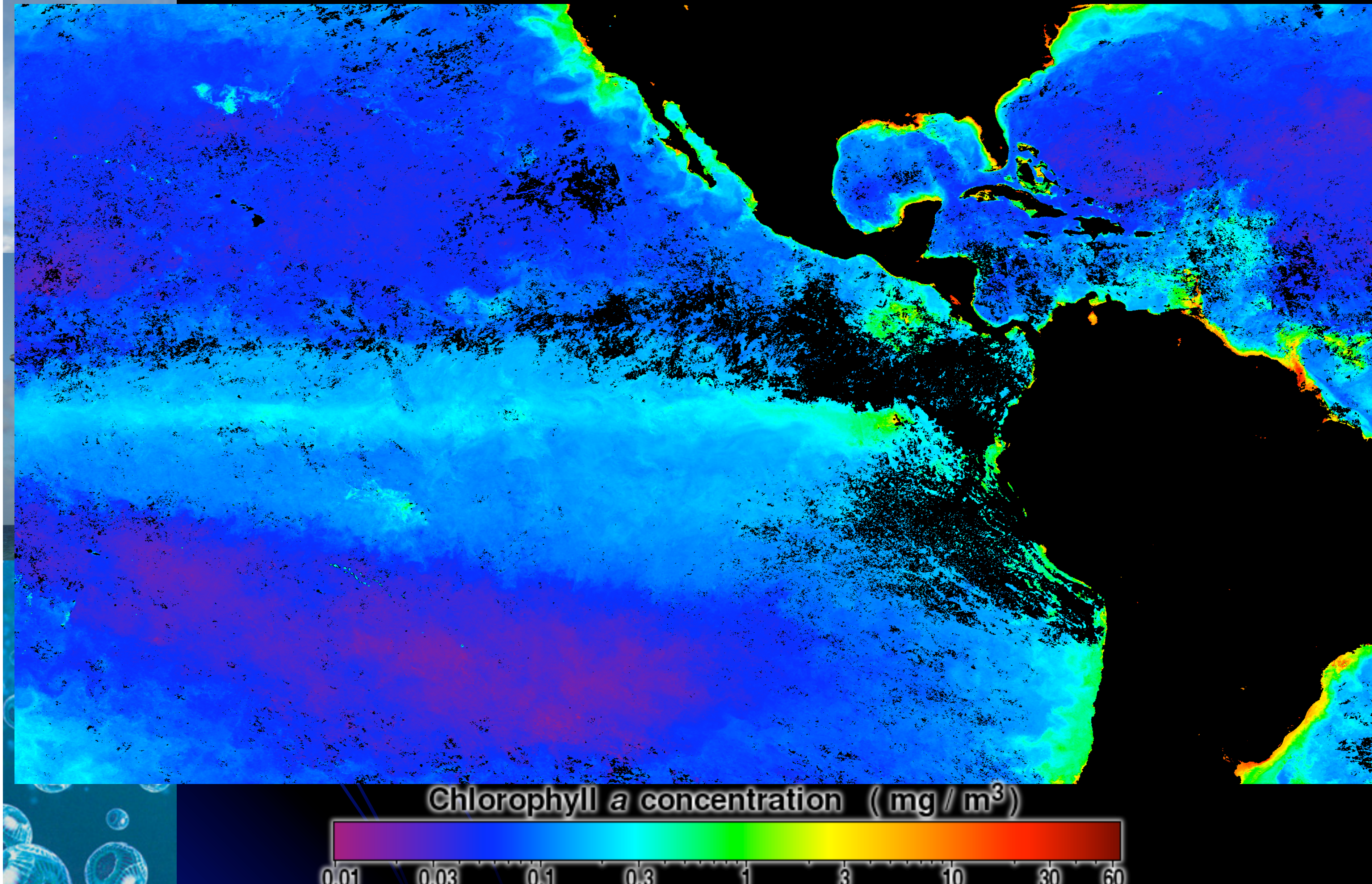
(157° W, 2° N), Republic of Kiribati. For most of the experiment our aerosol samplers were positioned atop a 30 m aluminum walkup tower situated about 10 m from the windward Pacific shoreline. We measured bulk concentrations of sulfate, MSA, sodium, and ammonium using open-faced 47 mm Teflon filters (Gelman Zefluor, 1 μm pore size). Samples were extracted and analyzed by ion chromatography [*Huebert et al.*, 1995]. The chemical size distribution of aerosols was measured with a pair of MOUDI impactors [*Marple et al.*, 1991]. To assess the depth of the MBL and its state of mixing, we launched between 4 and 8 balloons per day from an NCAR CLASS sounding system.

Results and Discussion

Our discussion will focus on two intensive sampling

PASE Results: ~42% DMS Flux → NSS
~30 ppt of NSS in 12 h day

Primary Productivity During PASE (Aug)



Tropical Precipitation by Satellite