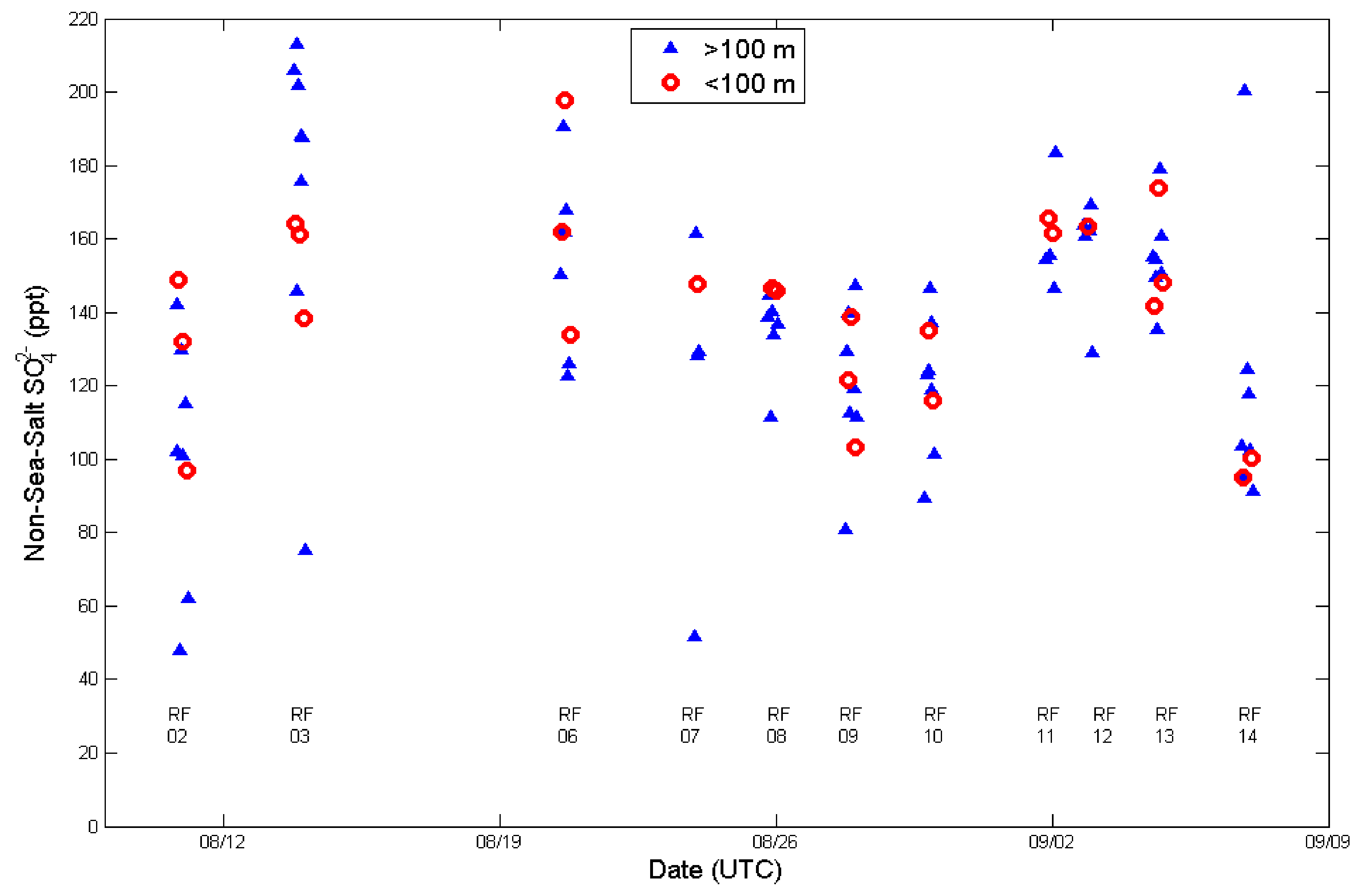
Aerosol Chemistry and Composition

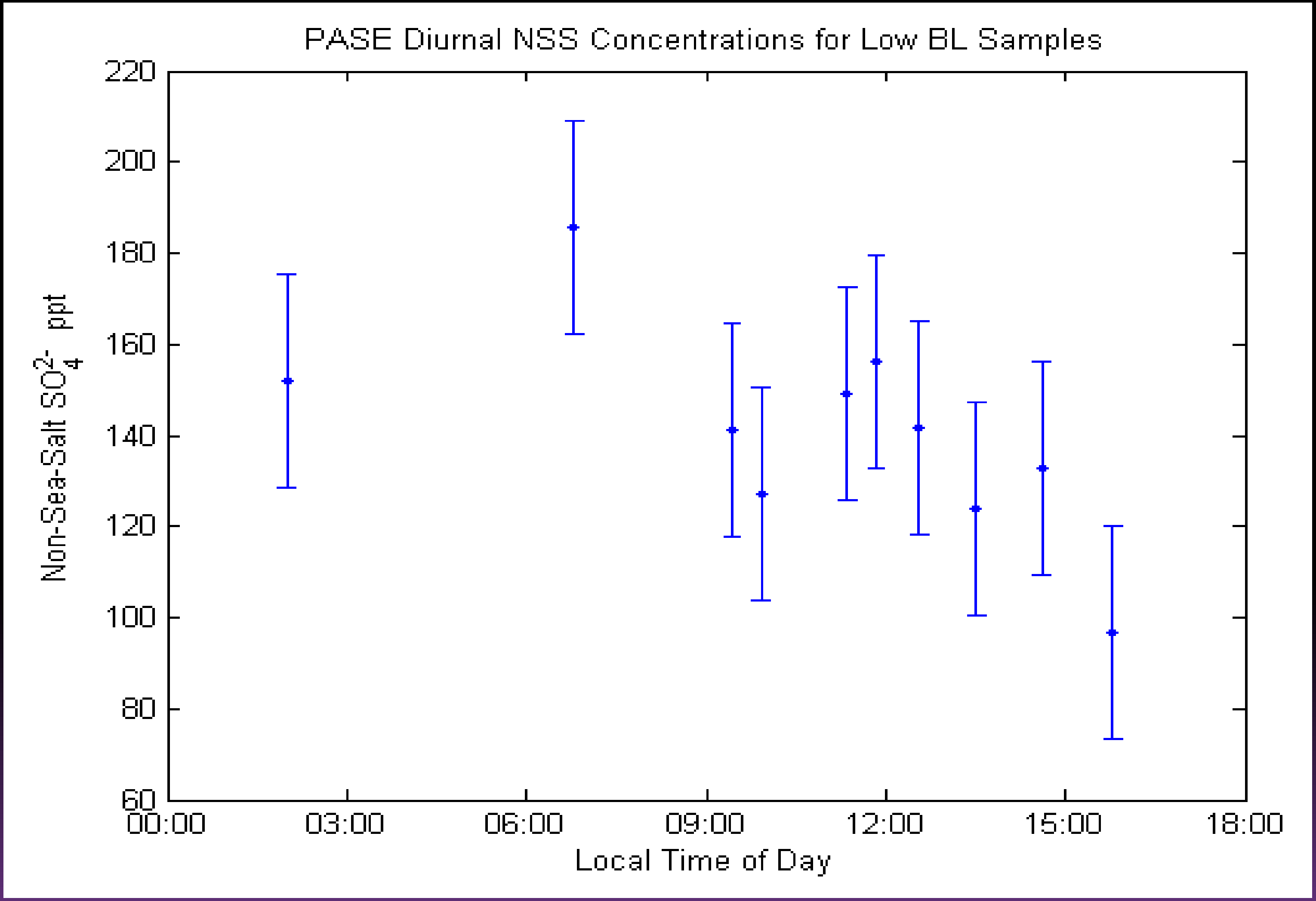
Rebecca Simpson

PASE Observations

NSS time series



No Diurnal Trends



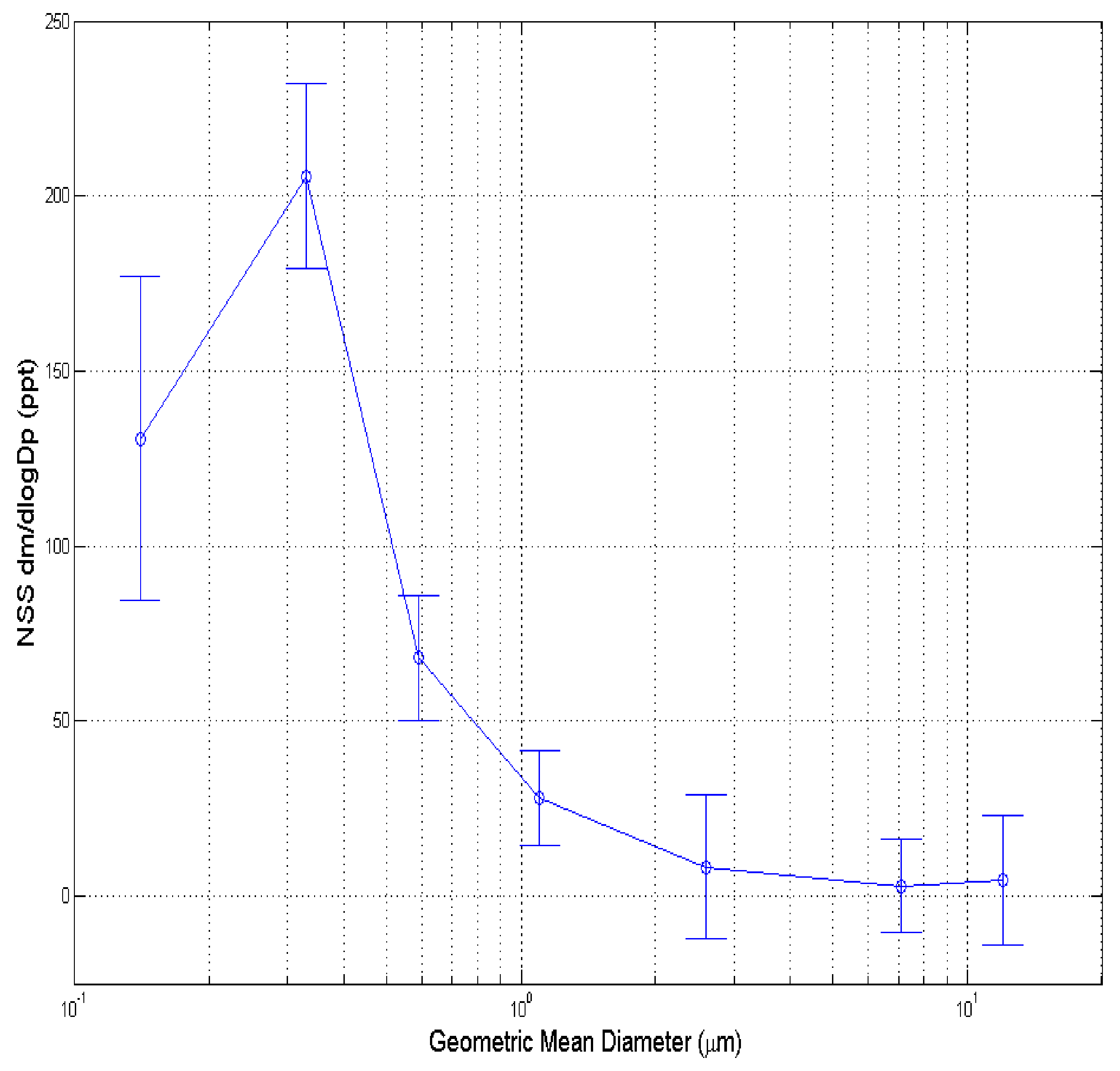
Project avg NSS: 135   45 ppt

MOI NSS Mass Size Distribution

RF03: typical

Fine mode peak

Little coarse mass

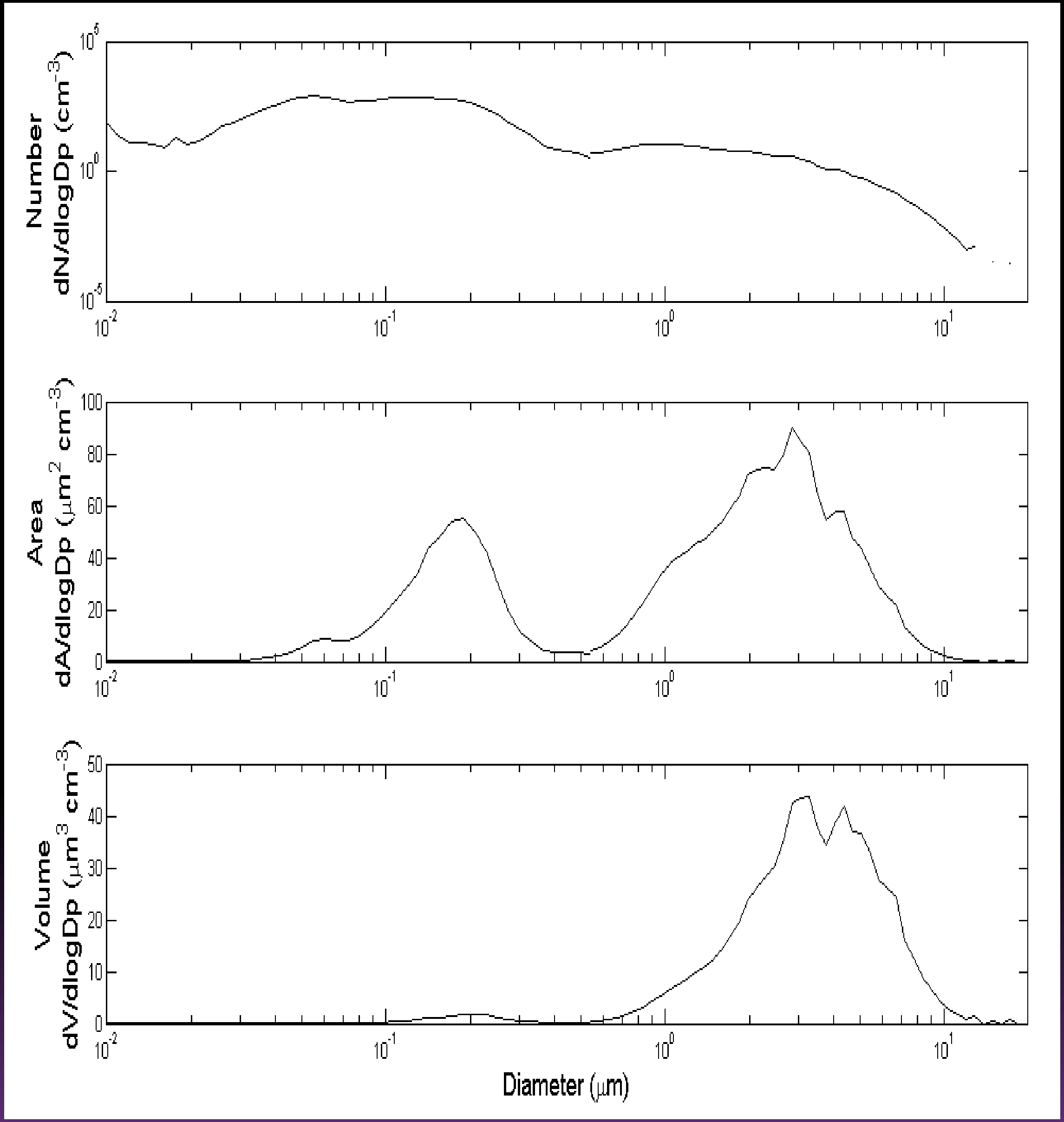


BL Number, Area, Volume

Fine mode dominates the number

Coarse mode dominates the volume

More area in the coarse mode



RF12 BL

Comparisons with PASE

1994 Christmas Island Experiment

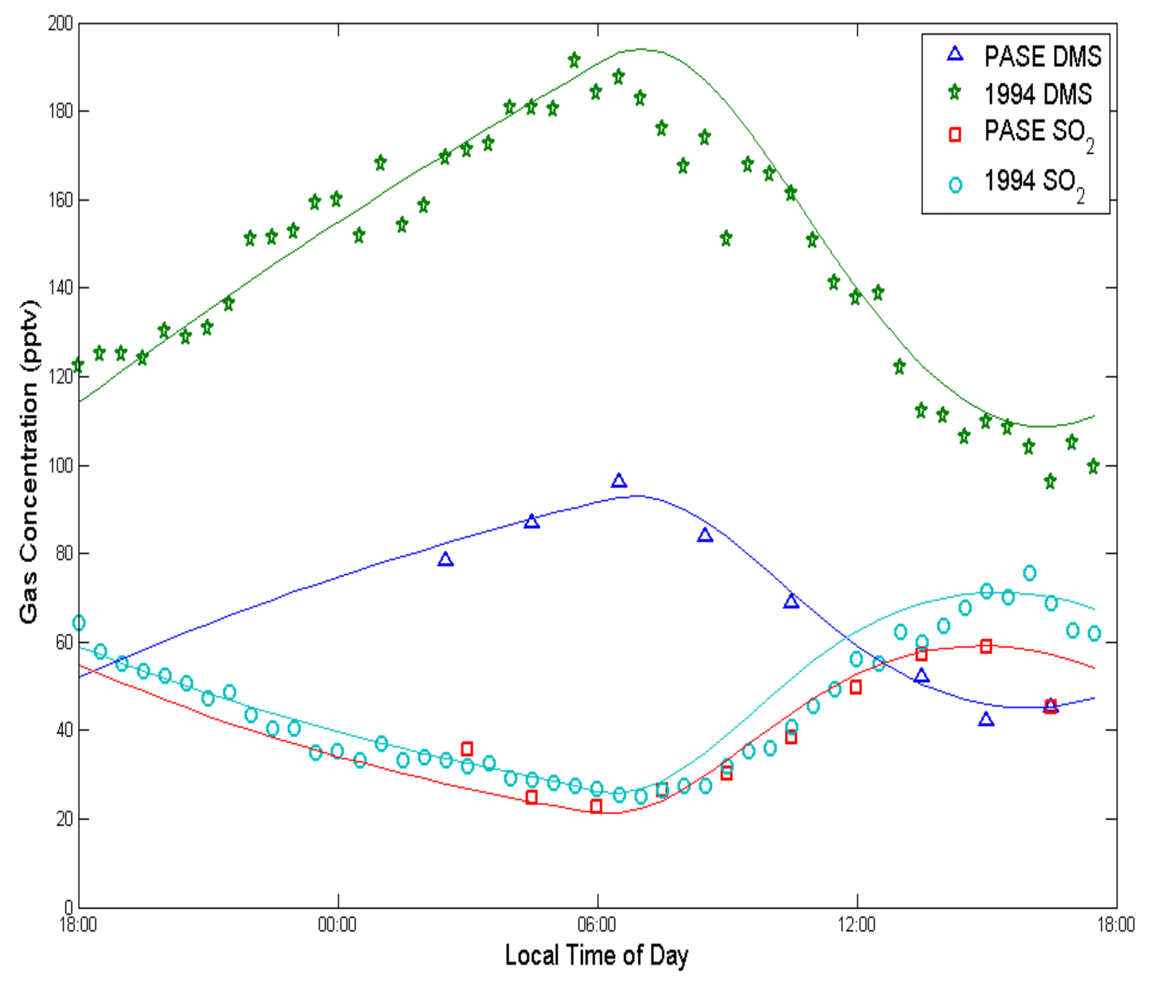
DMS and SO_2

PASE DMS<1994 DMS

PASE SO2≈ 1994 SO2

Assume different DMS source:

SO2 losses must be smaller in PASE relative to 1994



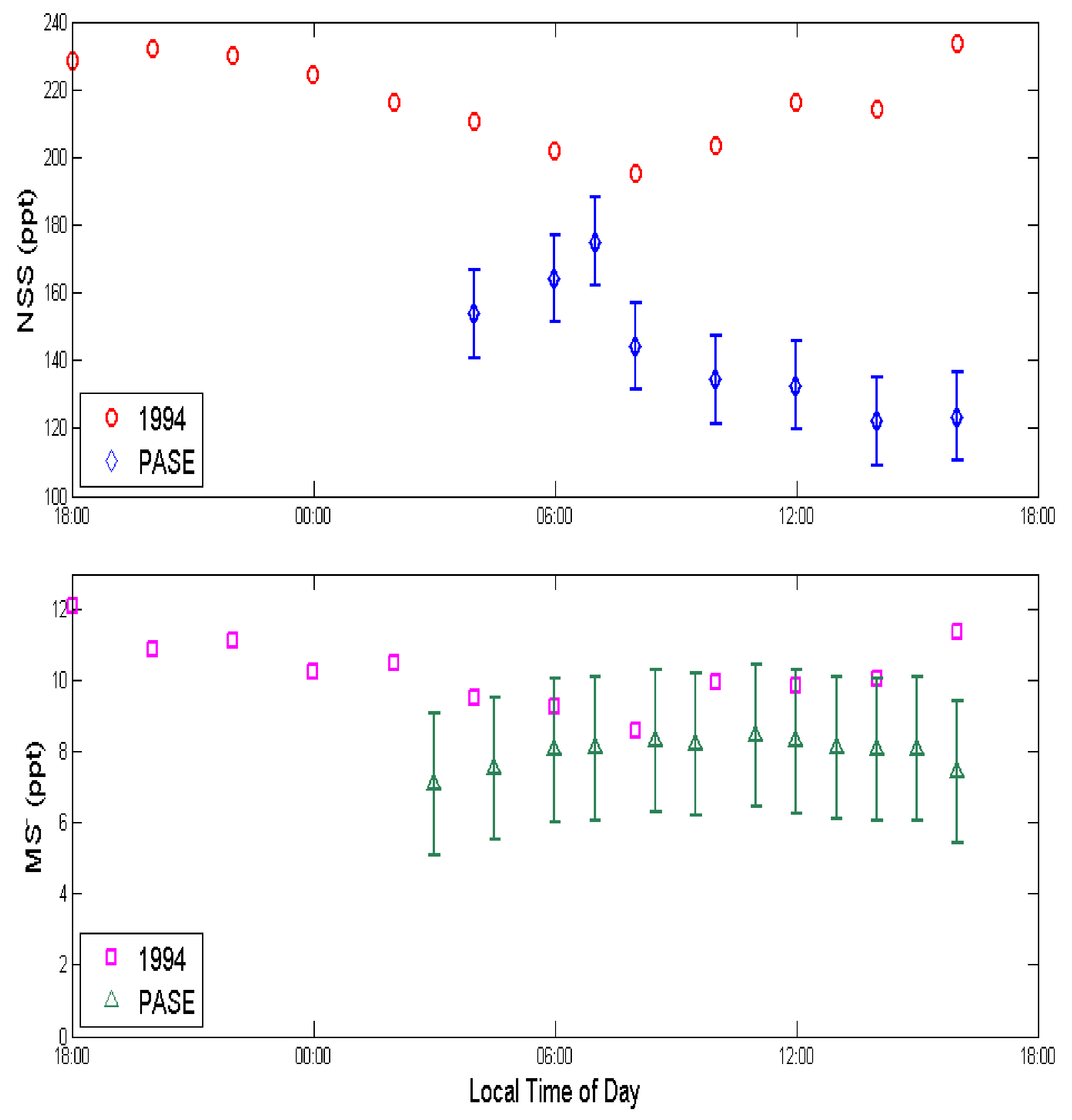
$$\frac{[SO_2]}{[DMS]} = \frac{k_{DMS}[OH]}{\Sigma k_{losses}[oxidants] + V_d}$$

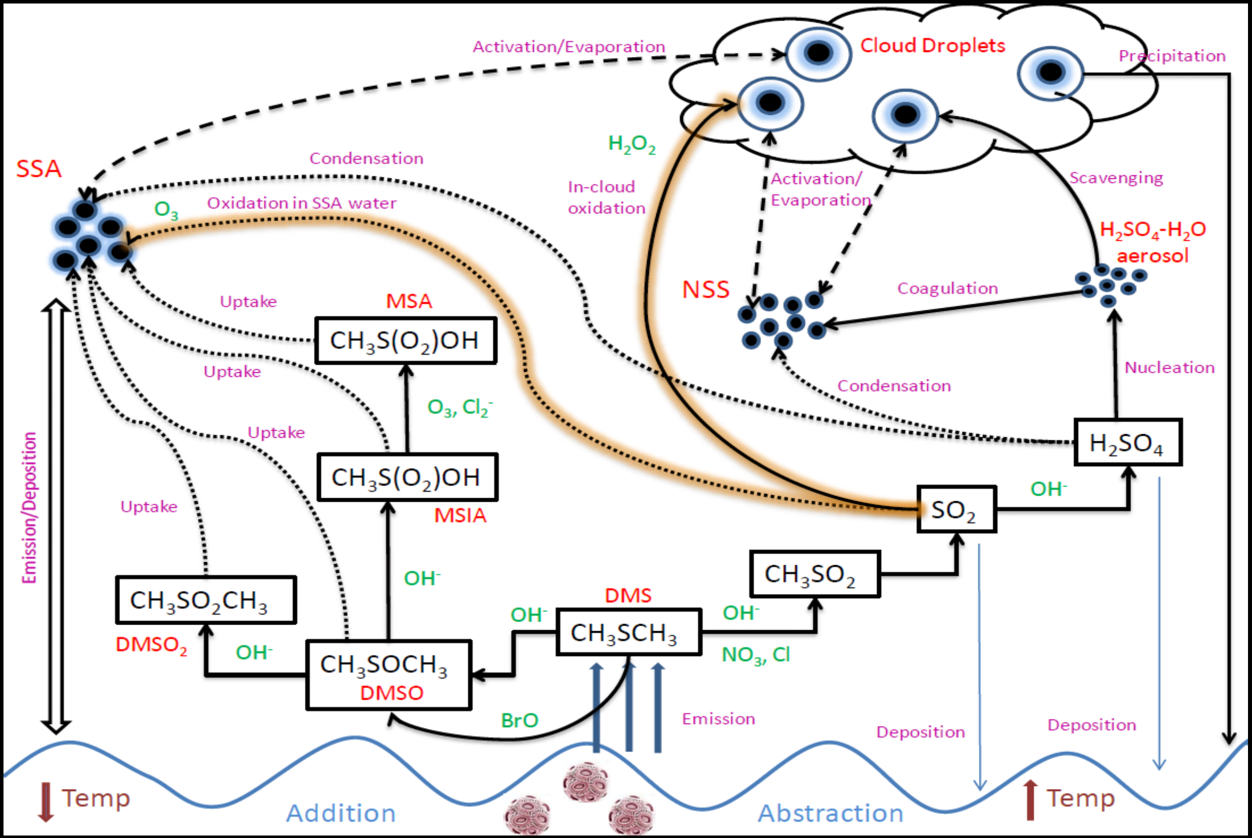
NSS and MS^-

PASE NSS < 1994 NSS

Smaller PASE NSS is consistent with fewer SO2 losses (to aerosol)

MS^- is not that different



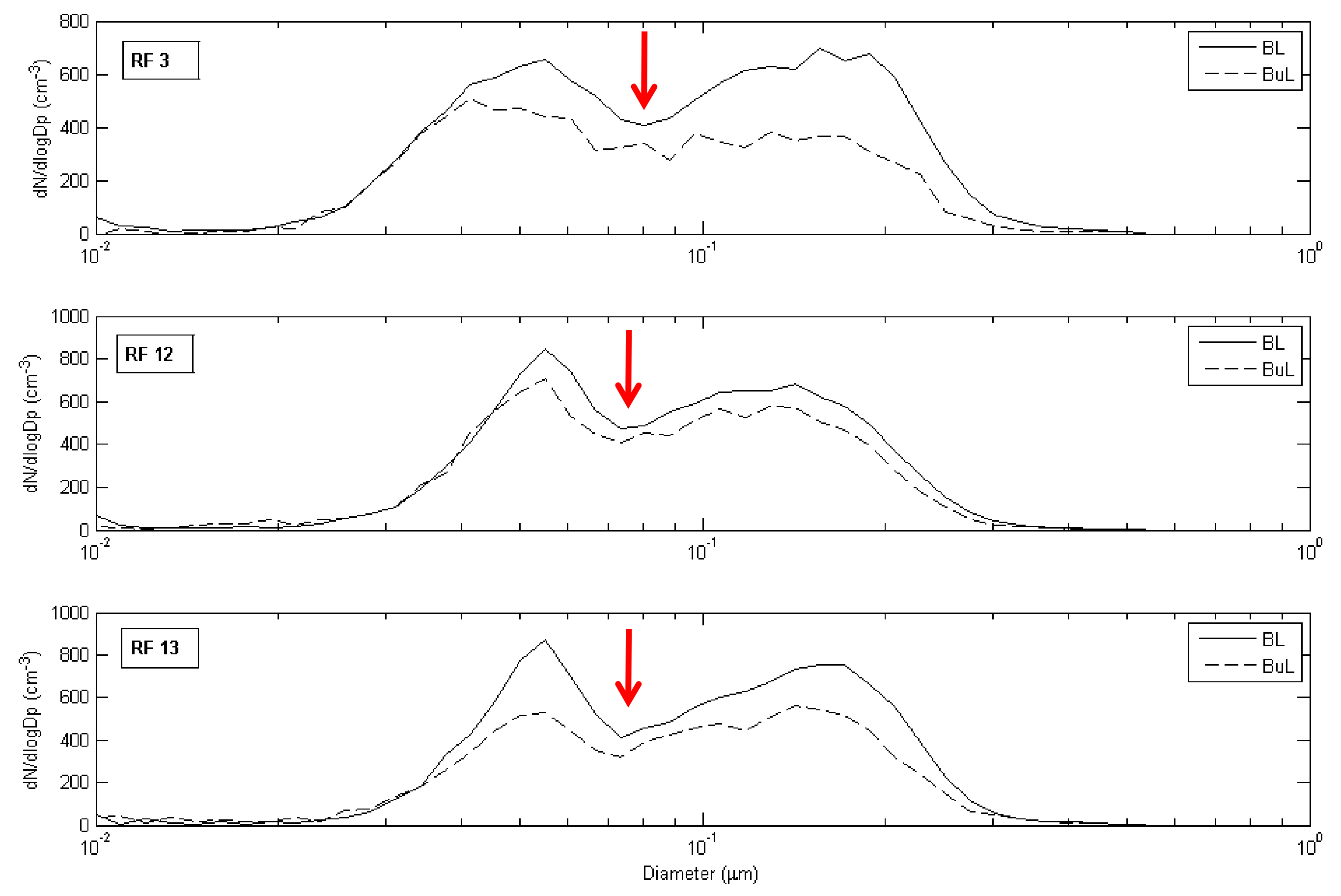


Largest heterogeneous loss term

Reveals strength of BL-BuL interactions

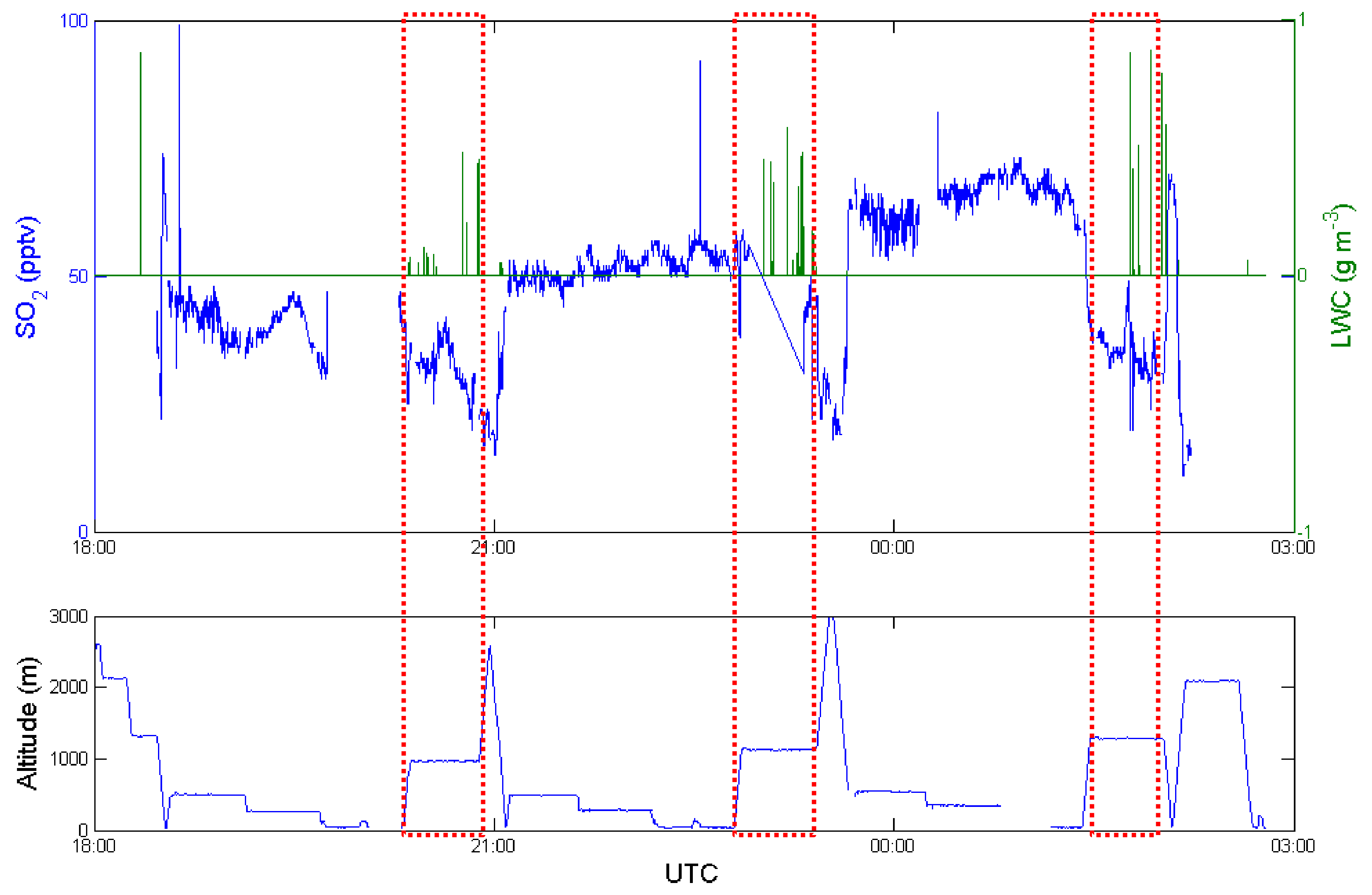
Cloud Processing

Number Distributions

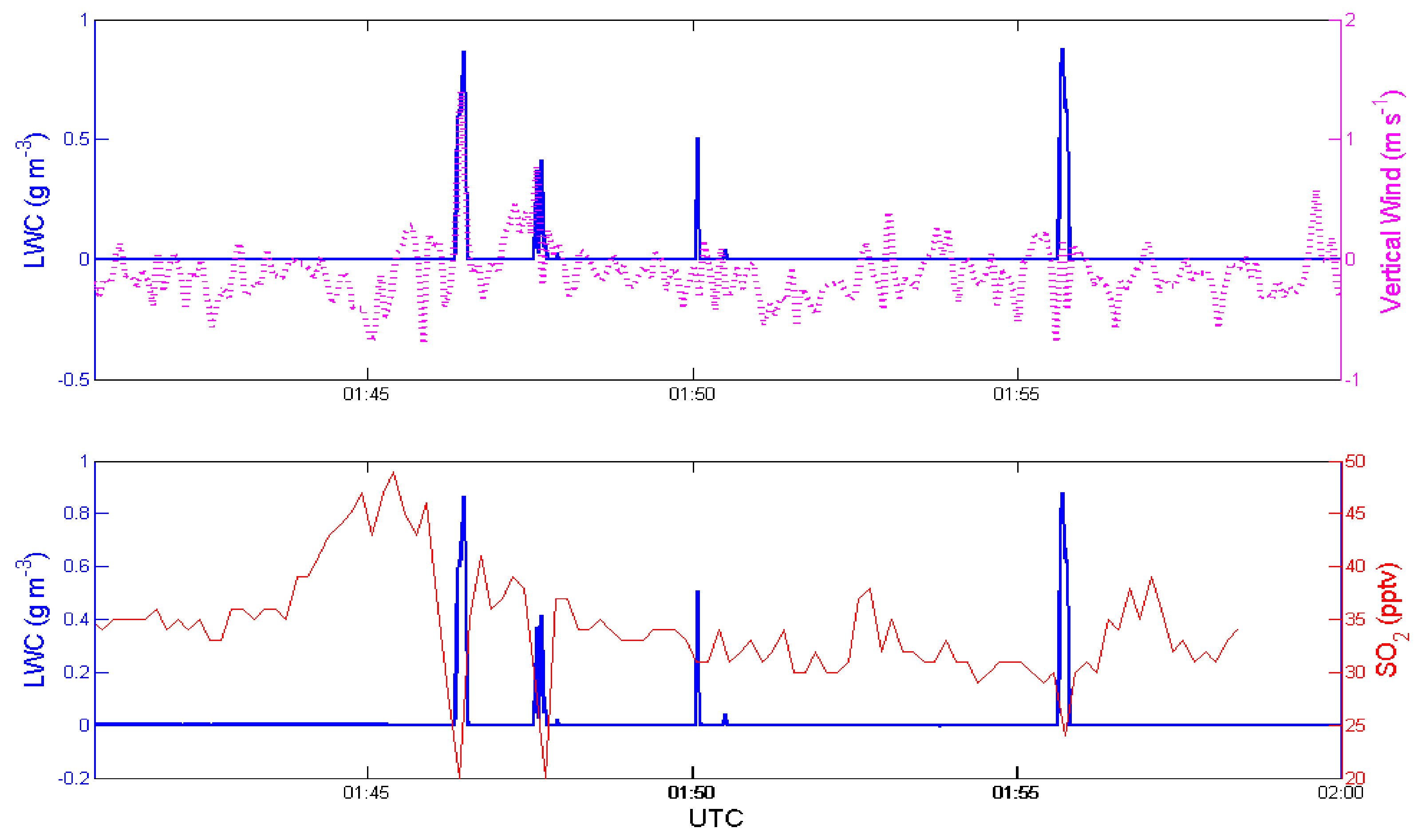


Hoppel minima show cloud processing

BuL Cloud Penetrations

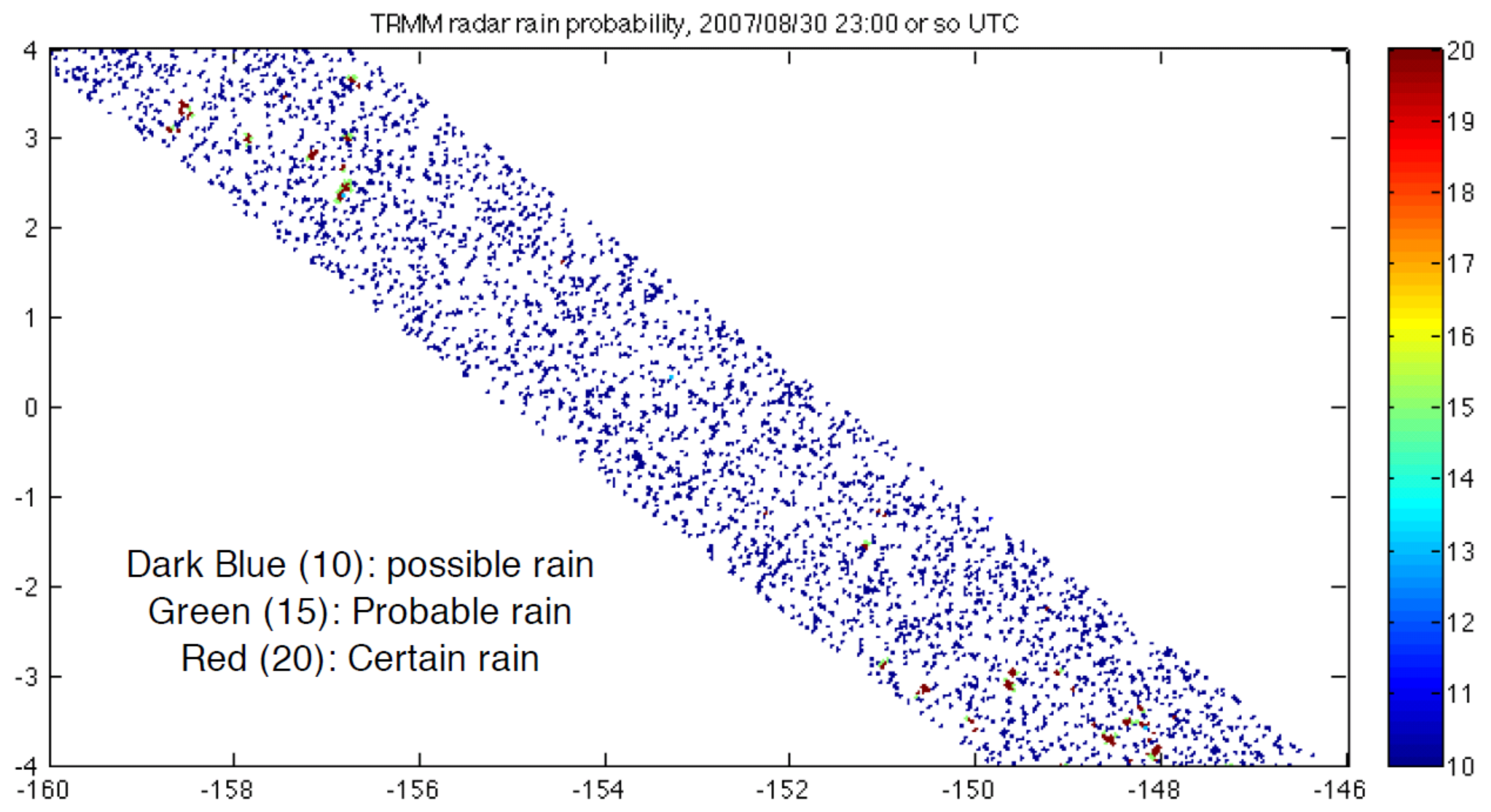


BuL Cloud Penetrations

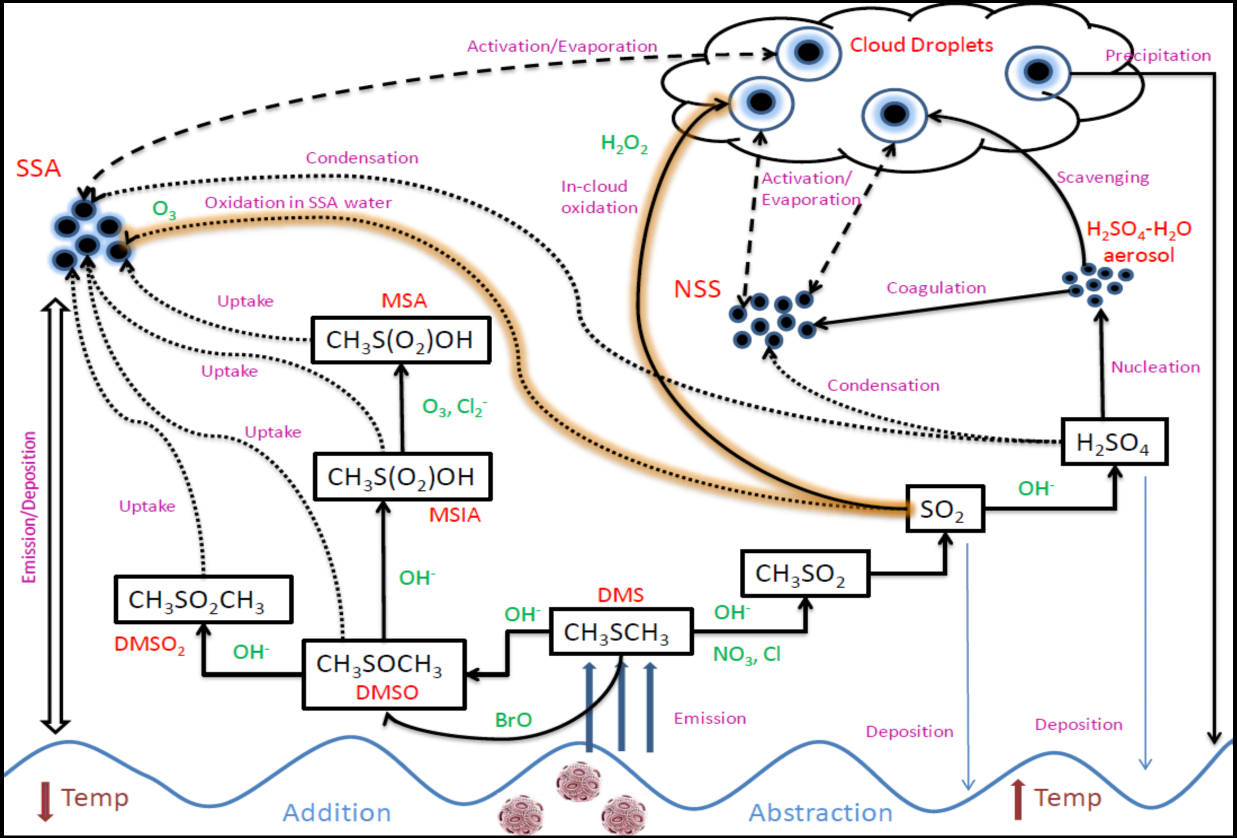


Sharp updrafts (pink) and SO$_2$ (red) accompanying LWC spikes (blue)

Precipitation??



Any ideas on how to estimate this?
We are currently assuming wet removal is small



Observations

Constraining heterogeneous loss

Coarse NSS

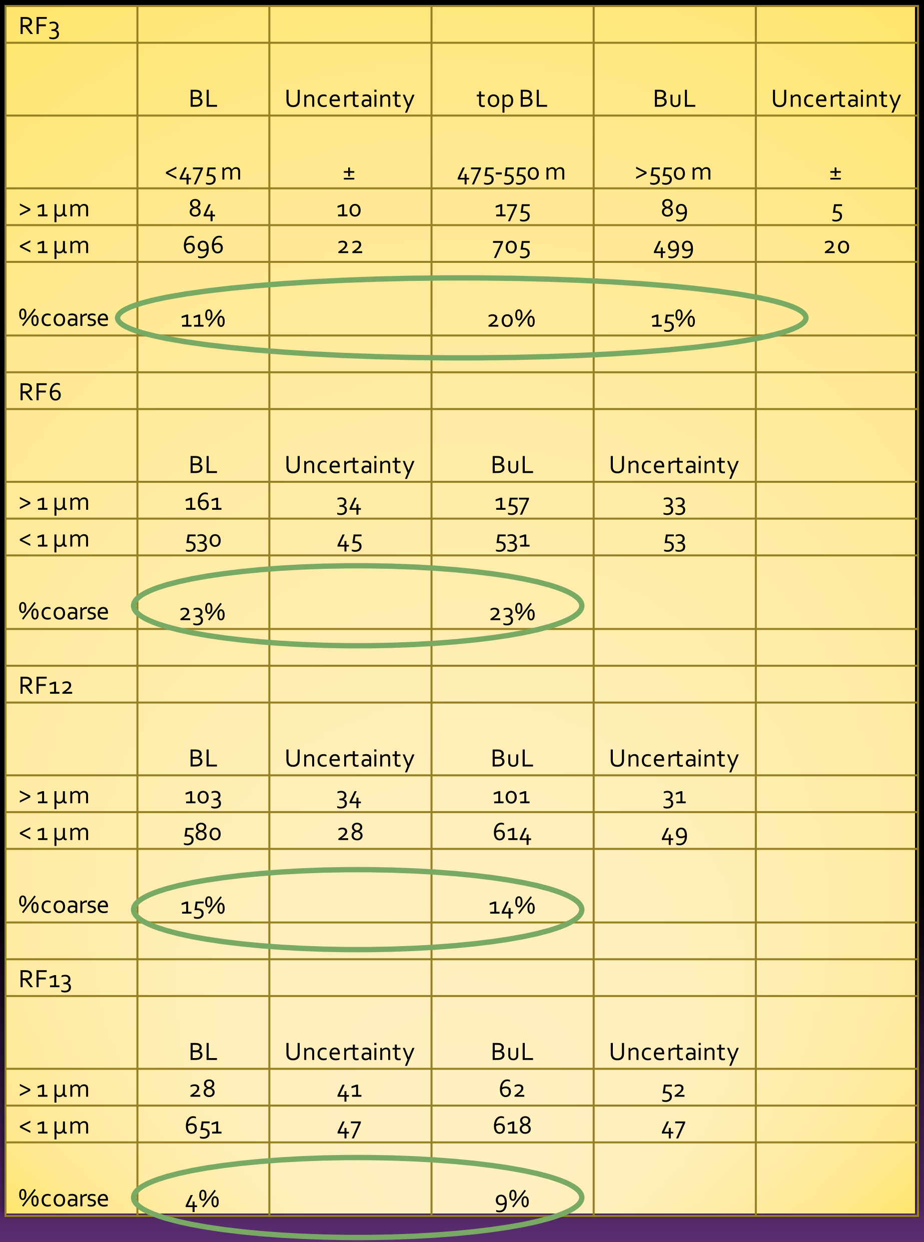
NSS (ng m^{-3}) for each case study

% coarse with RF06:

%coarse without RF06:

Relative to the BuL, shouldn't coarse NSS be higher in the BL where the sea salt is?

Coarse NSS is enhanced at lower BuL and upper BL



RF3					
	BL	Uncertainty	top BL	BuL	Uncertainty
	<475 m	±	475-550 m	>550 m	±
> 1 µm	84	10	175	89	5
< 1 µm	696	22	705	499	20
%coarse	11%		20%	15%	
RF6					
	BL	Uncertainty	BuL	Uncertainty	
> 1 µm	161	34	157	33	
< 1 µm	530	45	531	53	
%coarse	23%		23%		
RF12					
	BL	Uncertainty	BuL	Uncertainty	
> 1 µm	103	34	101	31	
< 1 µm	580	28	614	49	
%coarse	15%		14%		
RF13					
	BL	Uncertainty	BuL	Uncertainty	
> 1 µm	28	41	62	52	
< 1 µm	651	47	618	47	
%coarse	4%		9%		

Relationship between sea salt and NSS

- Is dust more of a sink for NSS than sea salt (Na$^+$)?
- More sea salt ≠ more % >1µm NSS

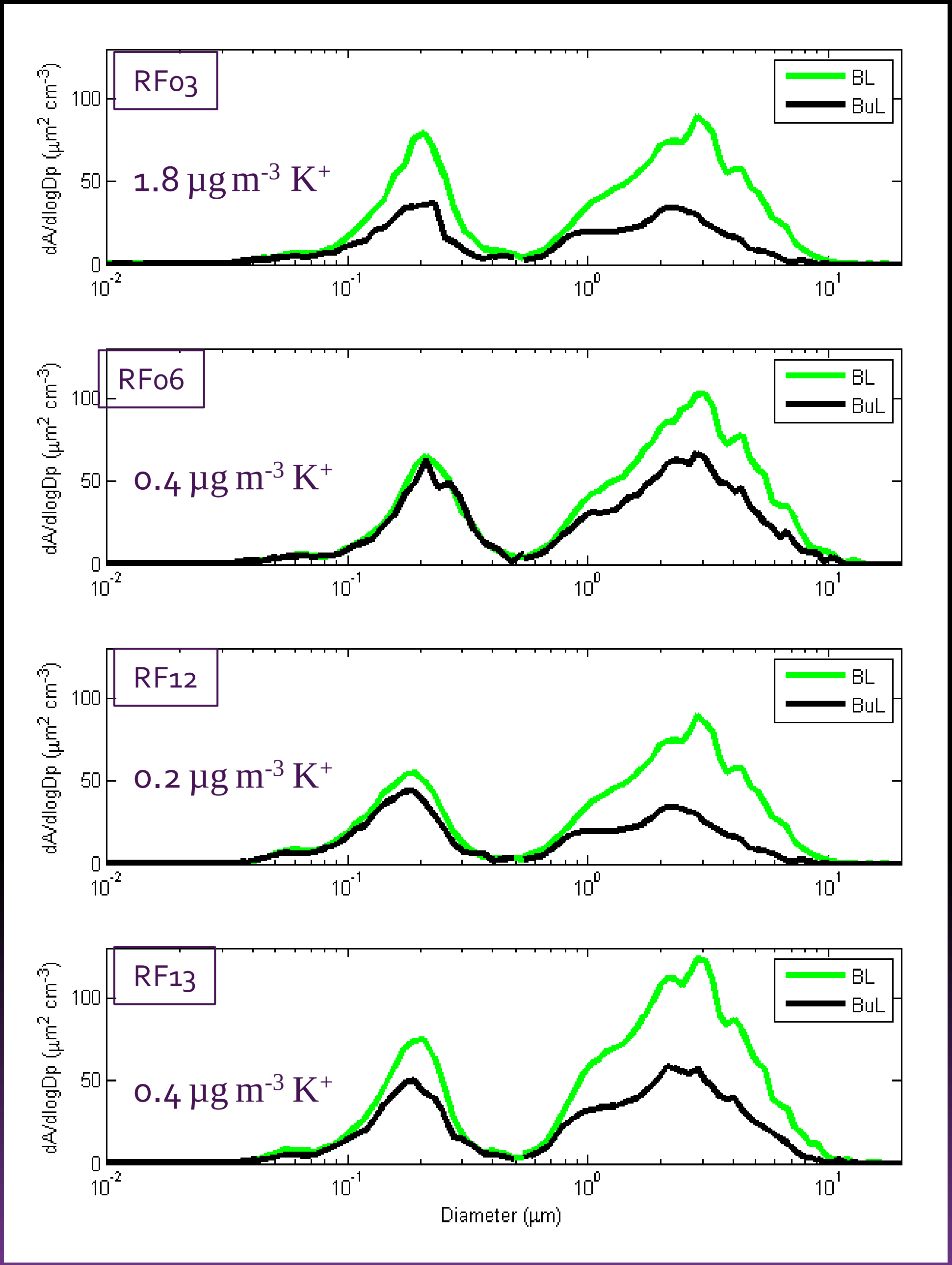
	% NSS	Na$^+$	xs Ca^{2+}	xs Mg^{2+}
	>1 µm	µg m^{-3}	ng m^{-3}	ng m^{-3}
1994	**6%**	4.8	150	0
PASE: no dust	**7%**	2.2	210	320
PASE: with dust	**14%**	1.5	450	960

Area

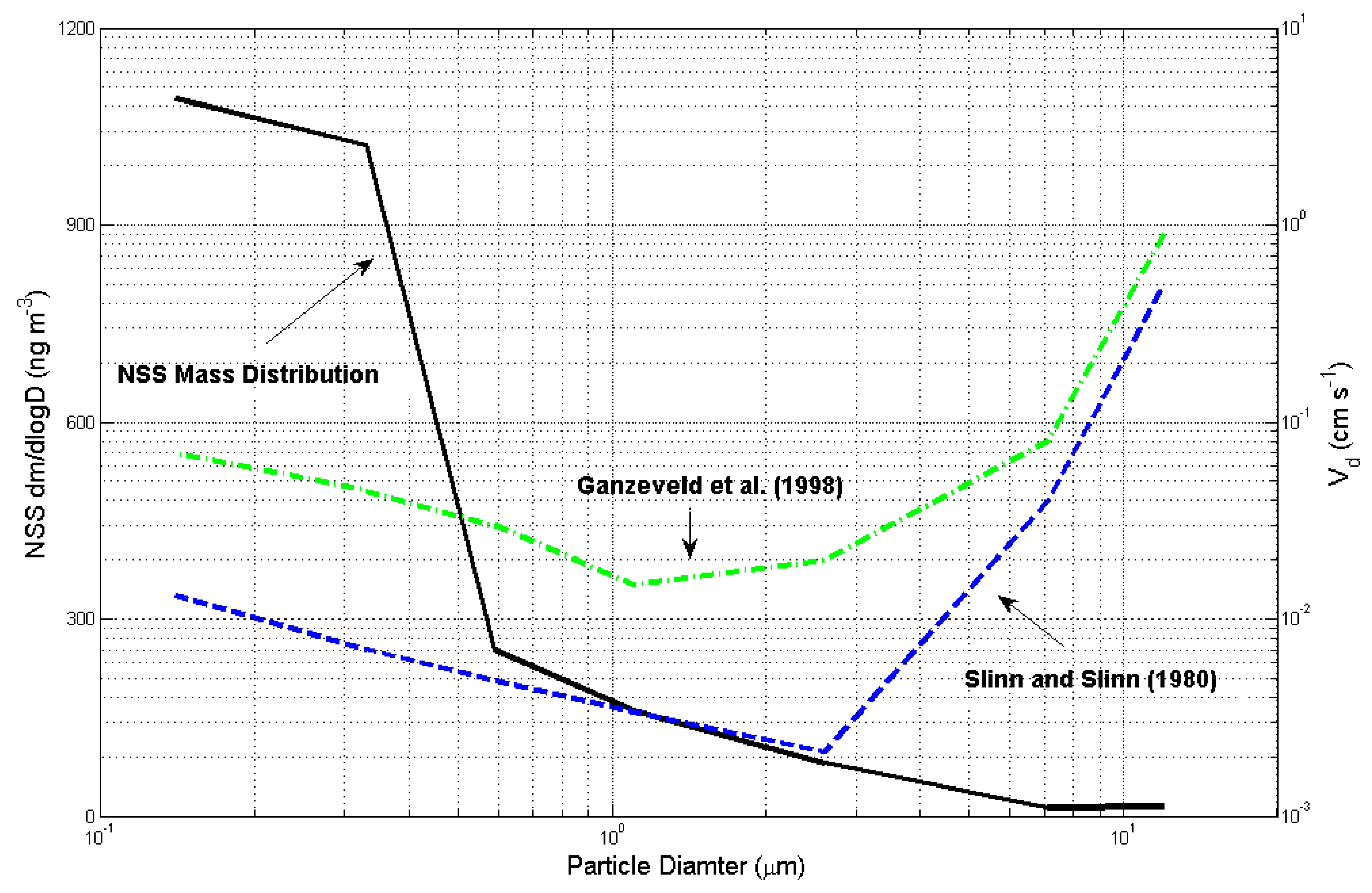
Greater in the supermicron mode in the BL

A few big particles in RF06…which is also one of the most polluted flights

Is SSA responsible for a “significant” fraction of NSS formation?



Dry Deposition



NSS Dry Deposition Fluxes

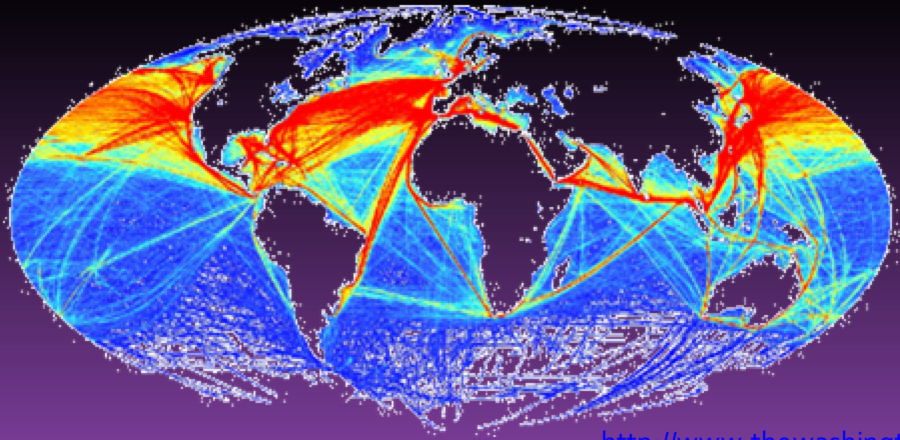
D_p	V_d	τ_d	NSS	NSS Flux
μm	cm s^{-1}	days	% $mass_{tot}$	nmol m^{-2} day^{-1}
12	0.5	1	0.7	29
7.1	0.08	8	1	4
2.6	0.002	300	2	0.6
1.1	0.004	200	6	1
0.59	0.005	100	13	3
0.33	0.009	80	47	15
0.14	0.02	40	33	48

Significant NSS formation on sea salt particles??

- Sievering et al. : oxidation of SO_2 to NSS by O_3 in sea salt liquid water content supported by alkalinity of seawater
  - Further supported by biogenic alkalinity from calcareous plankton shells (Sievering et al., 2004)
- Much of Sievering et al.'s attempts to explain coarse NSS based on Luria et al. (1986), who reported 45% coarse NSS
- An assumed deposition velocity of 1 cm/s for coarse aerosol is means of quickly removing sulfur (SO_2) from BL

Luria et al. (1986)

- N. Atlantic near Bermuda (not remote, though claimed to be)
- Use of cyclone with poorly-characterized cutoff
- >1 µm aerosol dry dep velocity used: 1 cm/s
- CLOUD-FREE



http://www.thewashingtonnote.com/shipping%20routes.jpg

Cl^- enrichments

K^+, Ca^{2+}, Mg^{2+}, oxalate

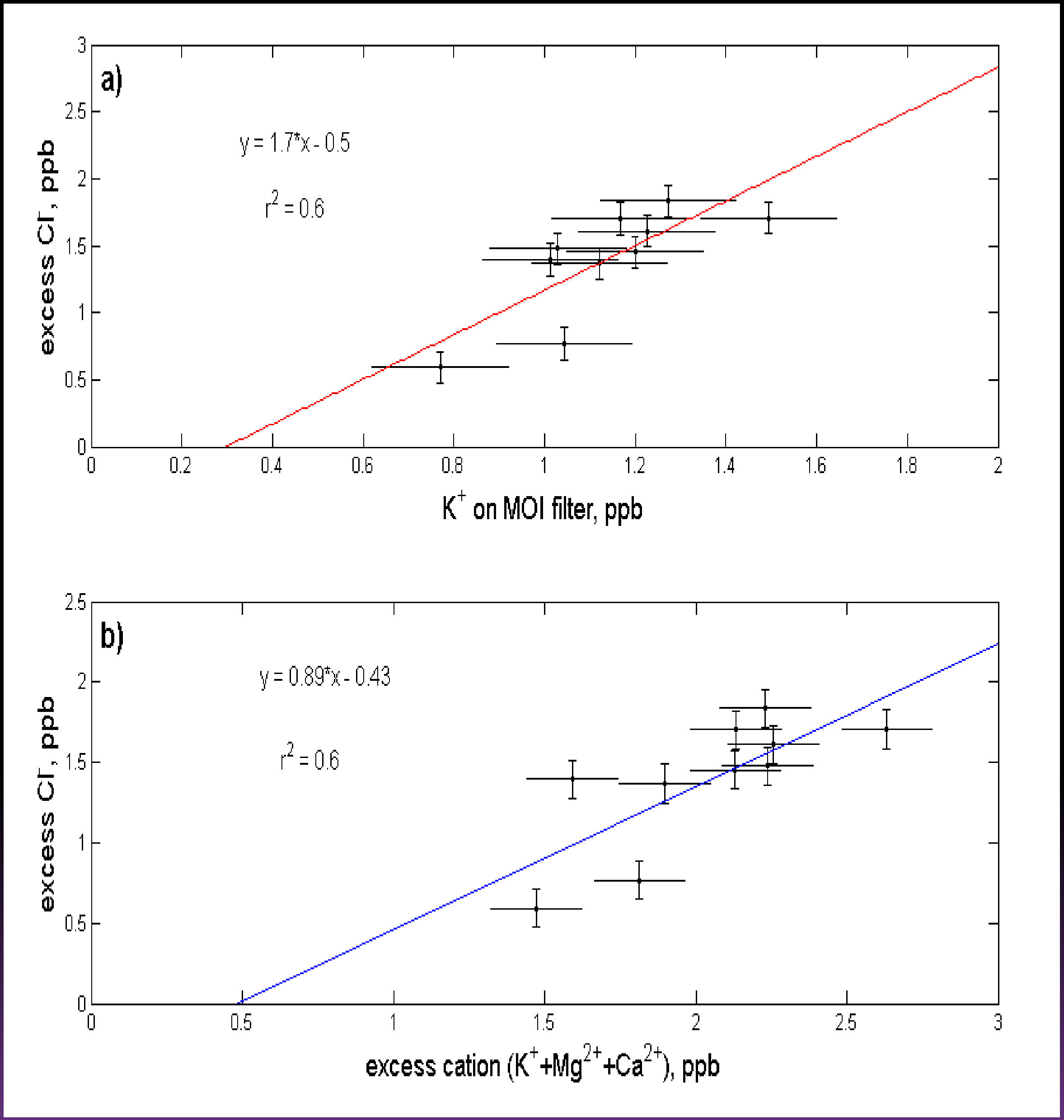
Long-range Transport

Excess Cl^-

Cl enrichments observed on every flight, especially those with greater non-local influence

KCl is a known constituent of biomass burning aerosol

HCl is also emitted by passively degassing volcanoes, esp. subduction-zone volcanoes

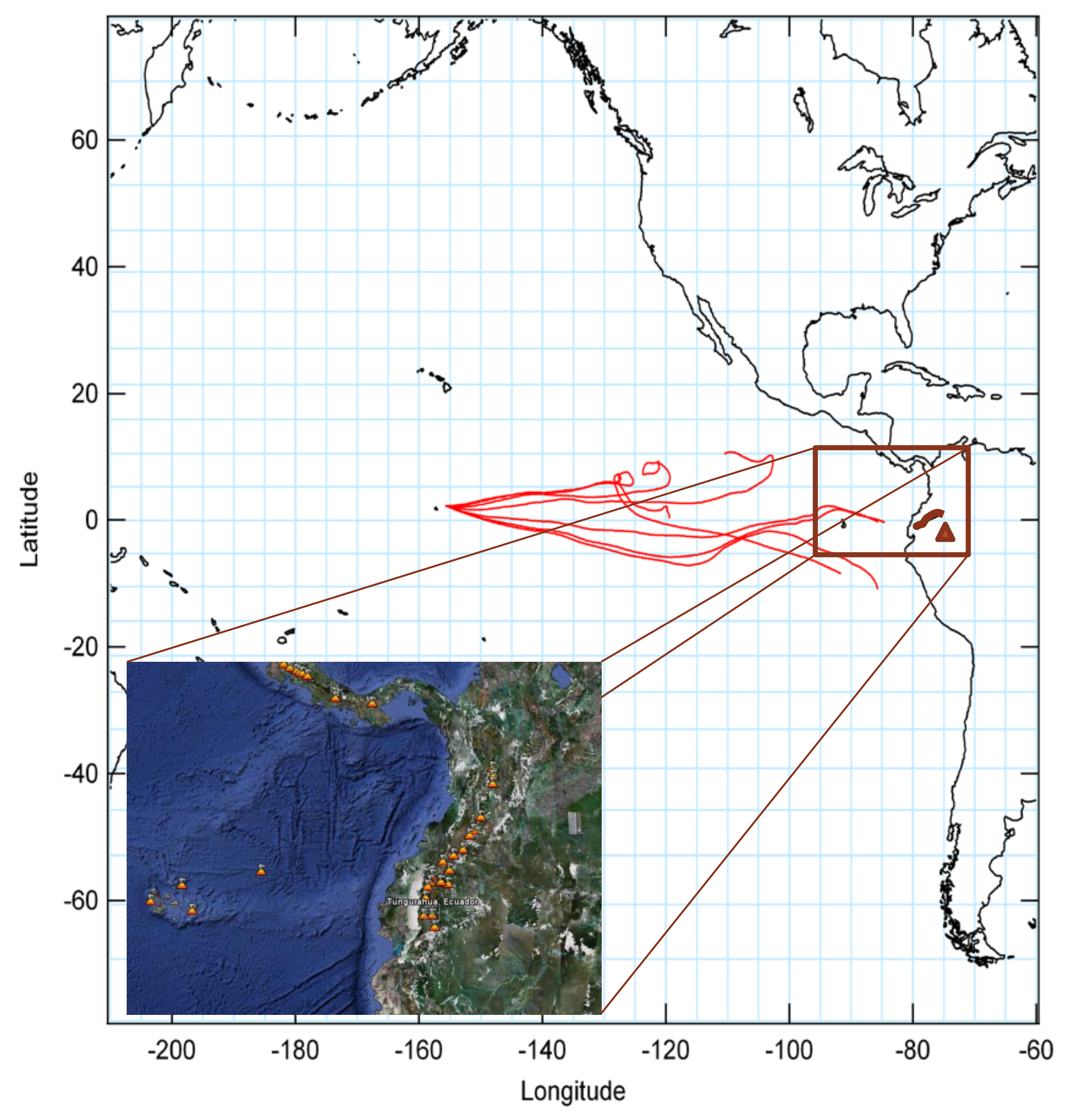


RF03

RF14: volcanogenic?

Tungurahua (Ecuador) was actively emitting large plumes kms high

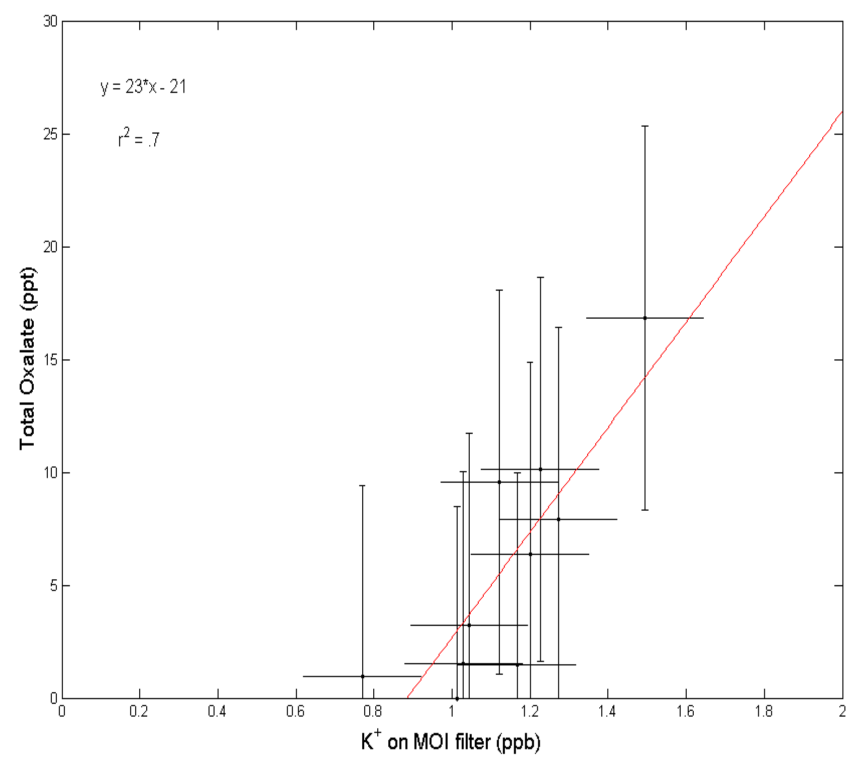
SO_2/HCl molar ratios of 0.1-10 in subduction zone volcanoes



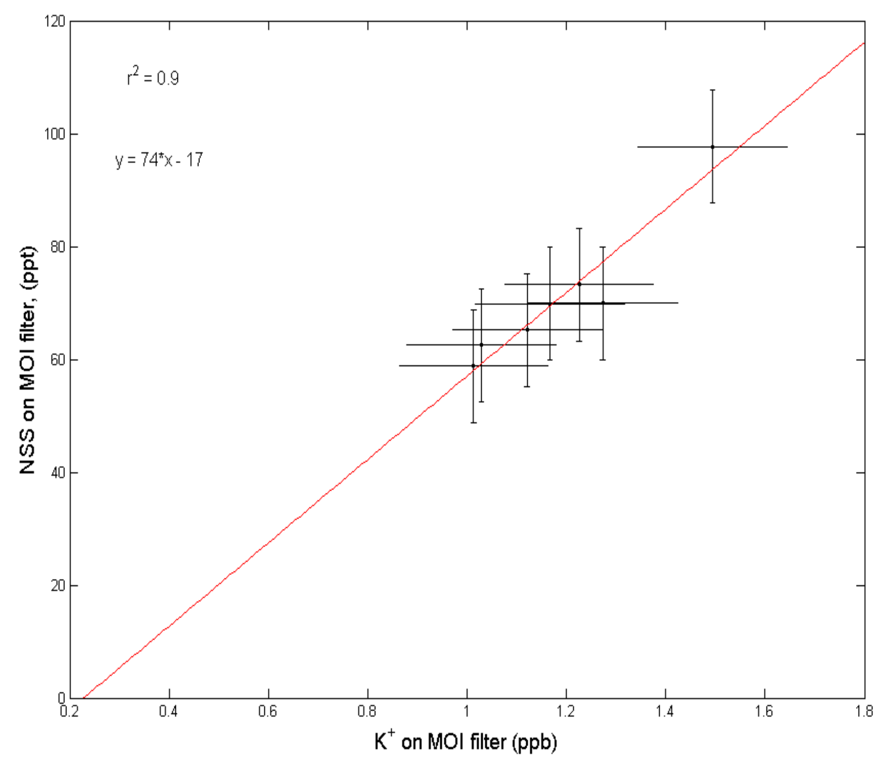
RF14: 09/06/2007

Biomass Burning Tracers

Potassium and Oxalate



Potassium and NSS

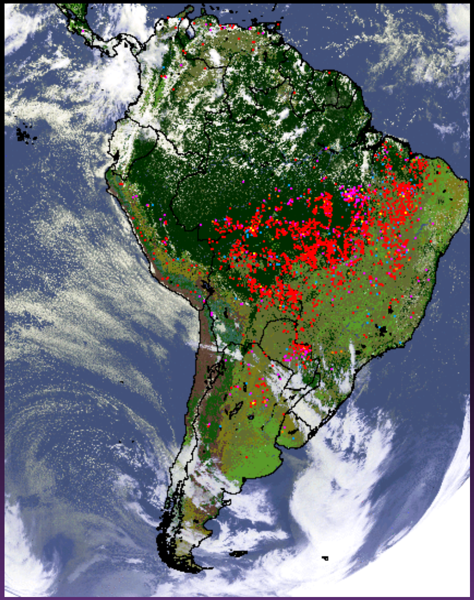


Non-local Influence: RF06

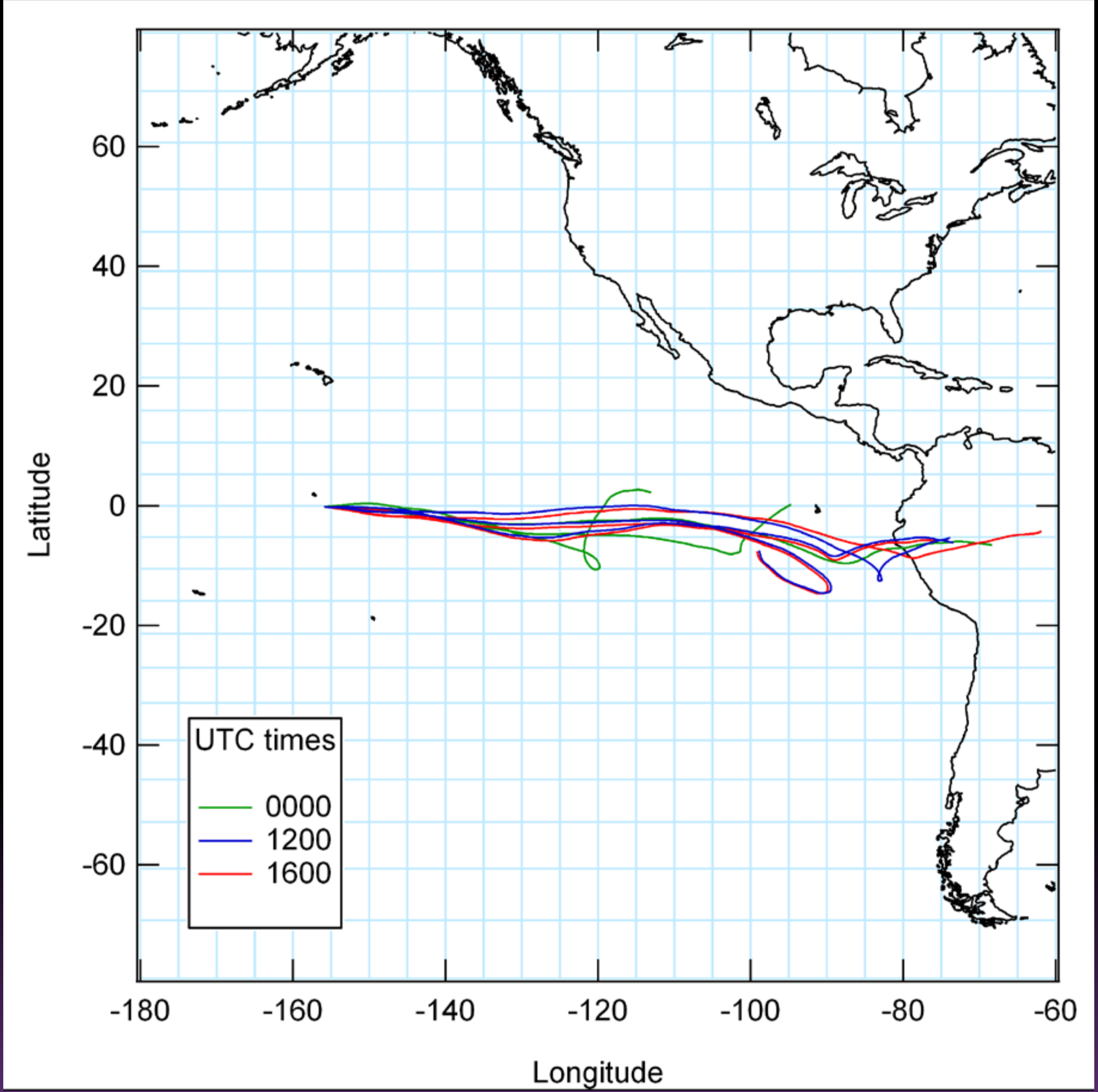
HYSPLIT 10-day back trajectories

Most coarse NSS (23%)

Most excess Ca^{2+}



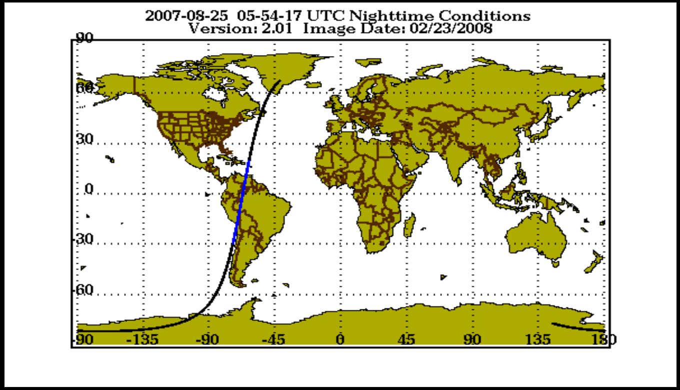
FLAMBE Images
08/10/2007

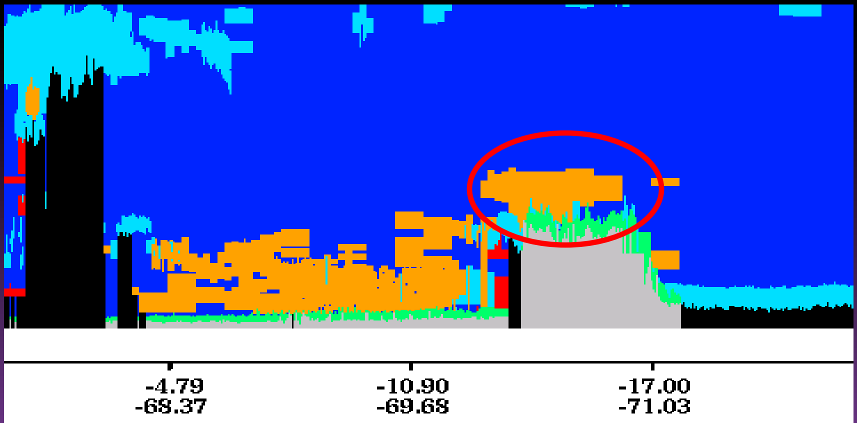


RF06: 08/20/2007

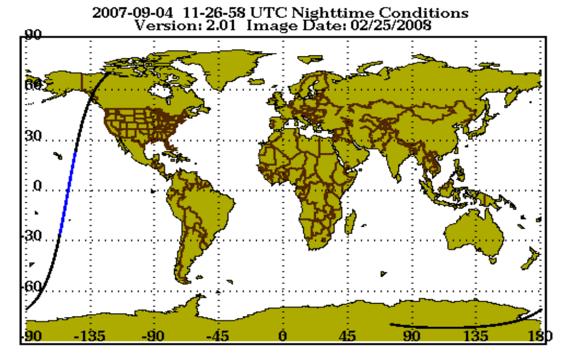
CALIPSO Images

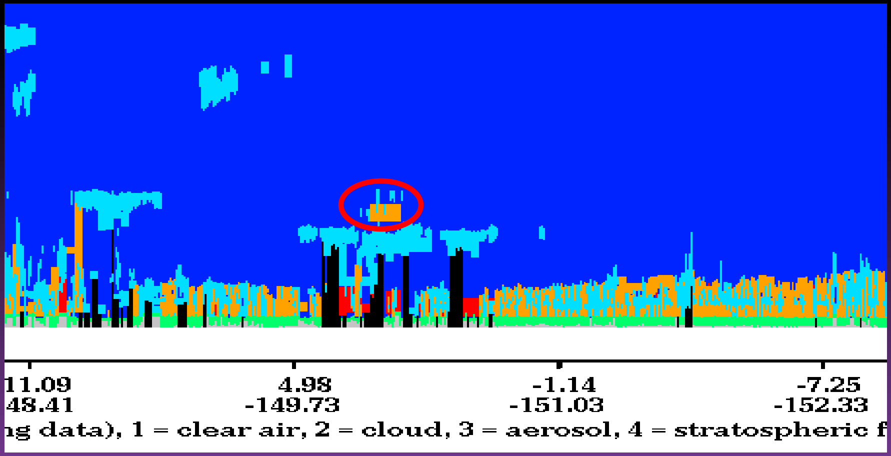
South America (8/25/07)





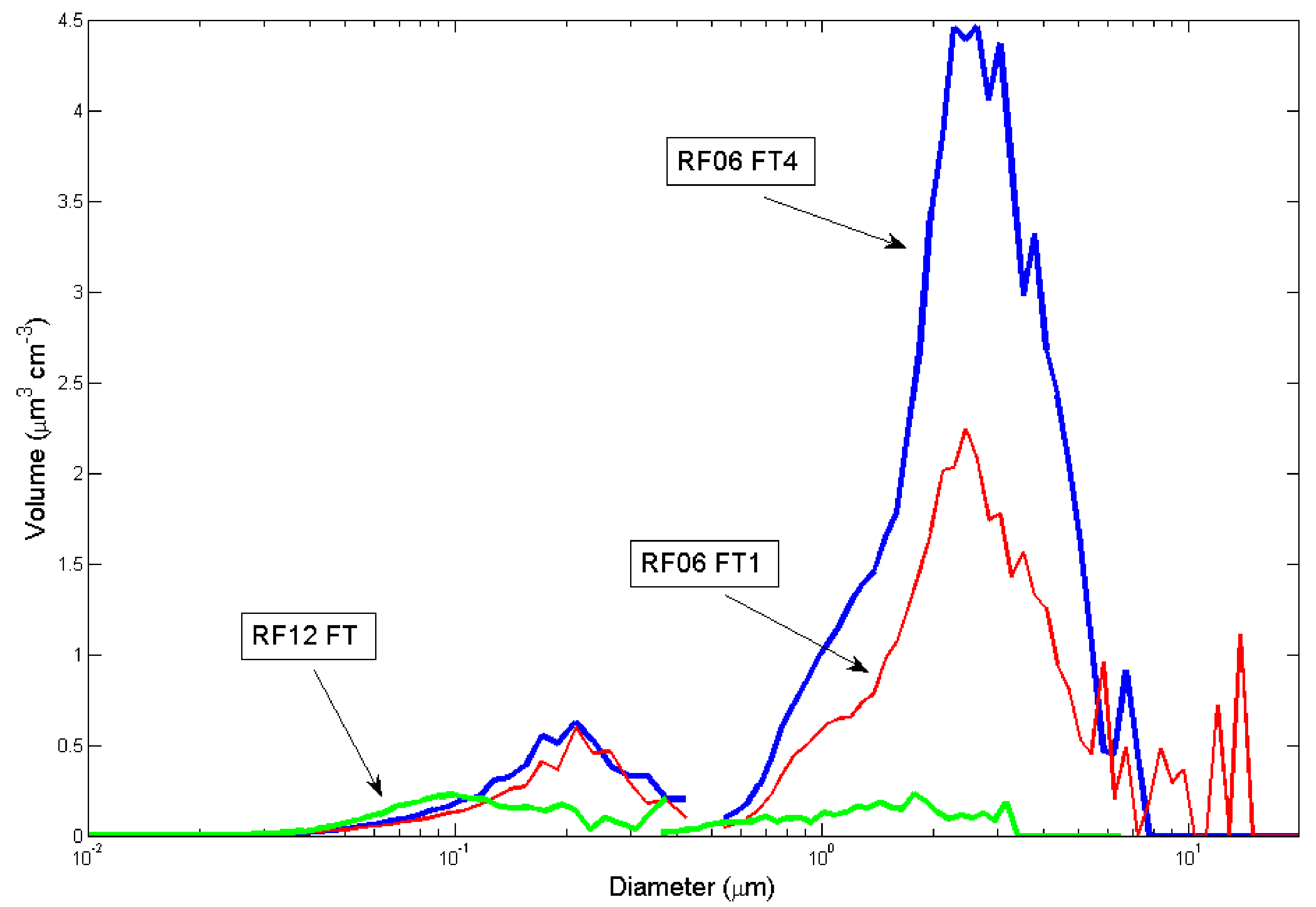
Near RF13 Sample Site (9/4/07)





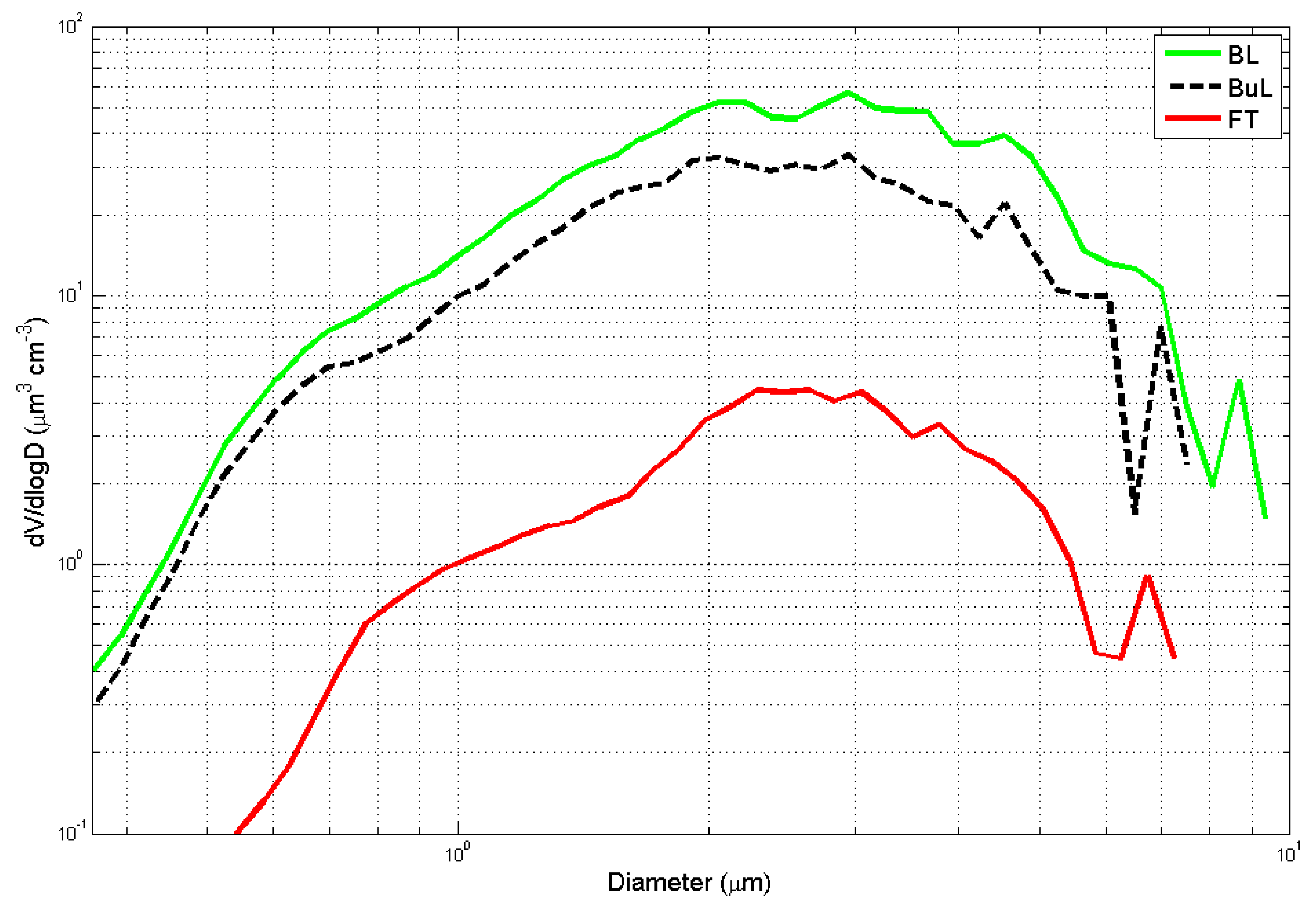
PASE Case Studies

Free Troposphere Volume



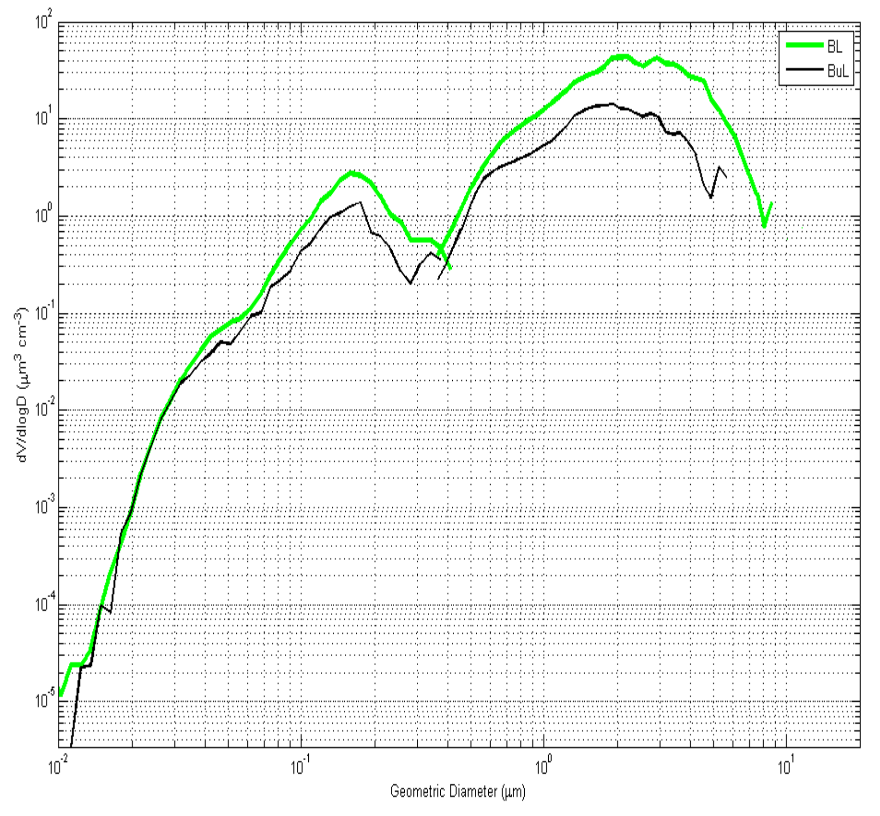
RF06 had the most mass in the FT, most of it coarse

RF06: >1µm Volume (all layers)

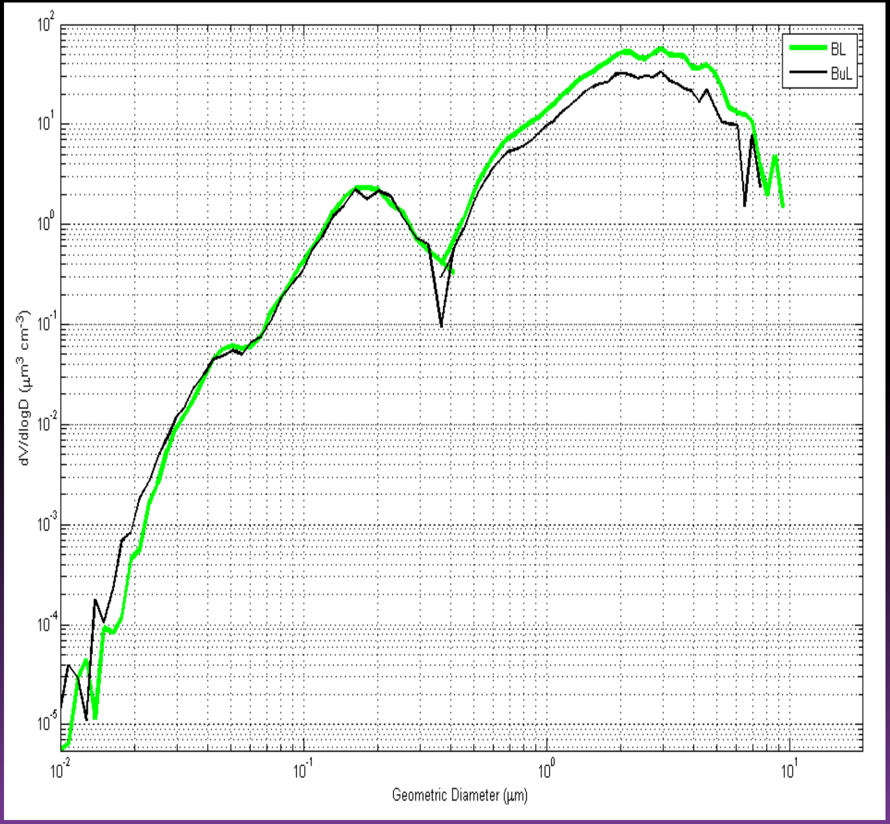


BL and BuL Volume

RF3: daytime flight, some biomass burning pollution

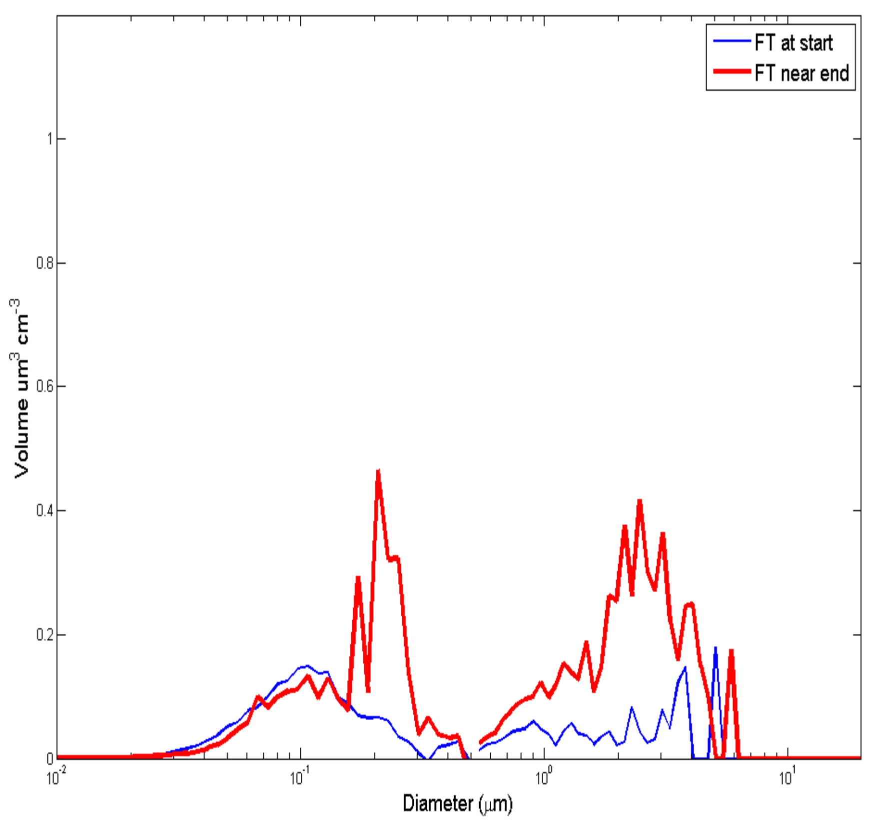


RF6: nighttime flight, polluted

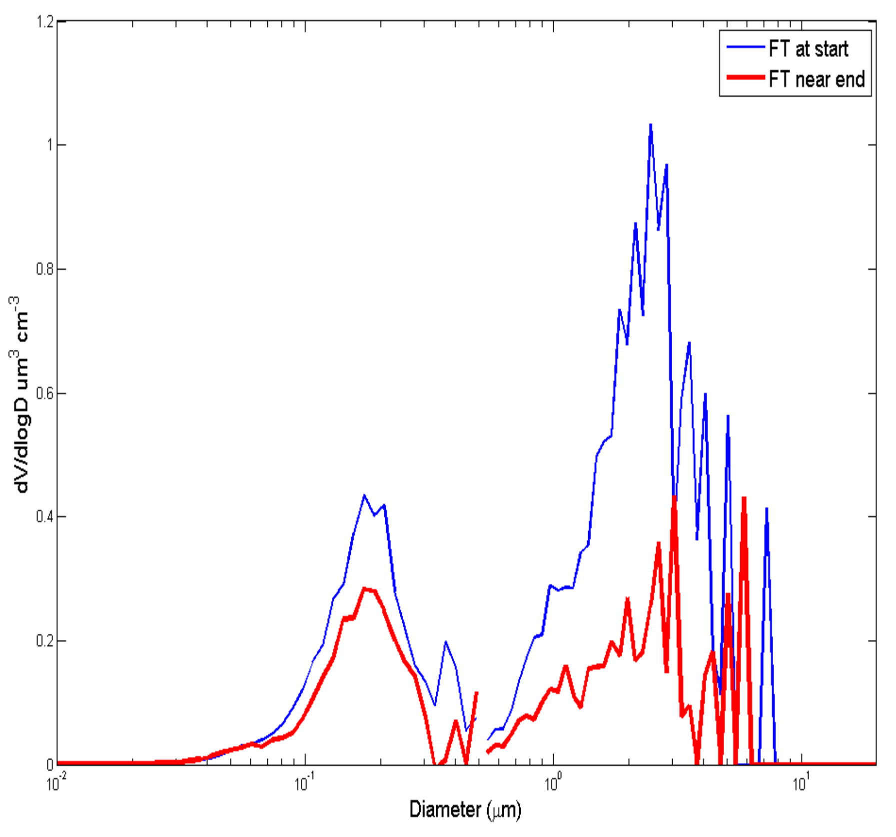


Free Troposphere Volume

RF12: Beginning of episode

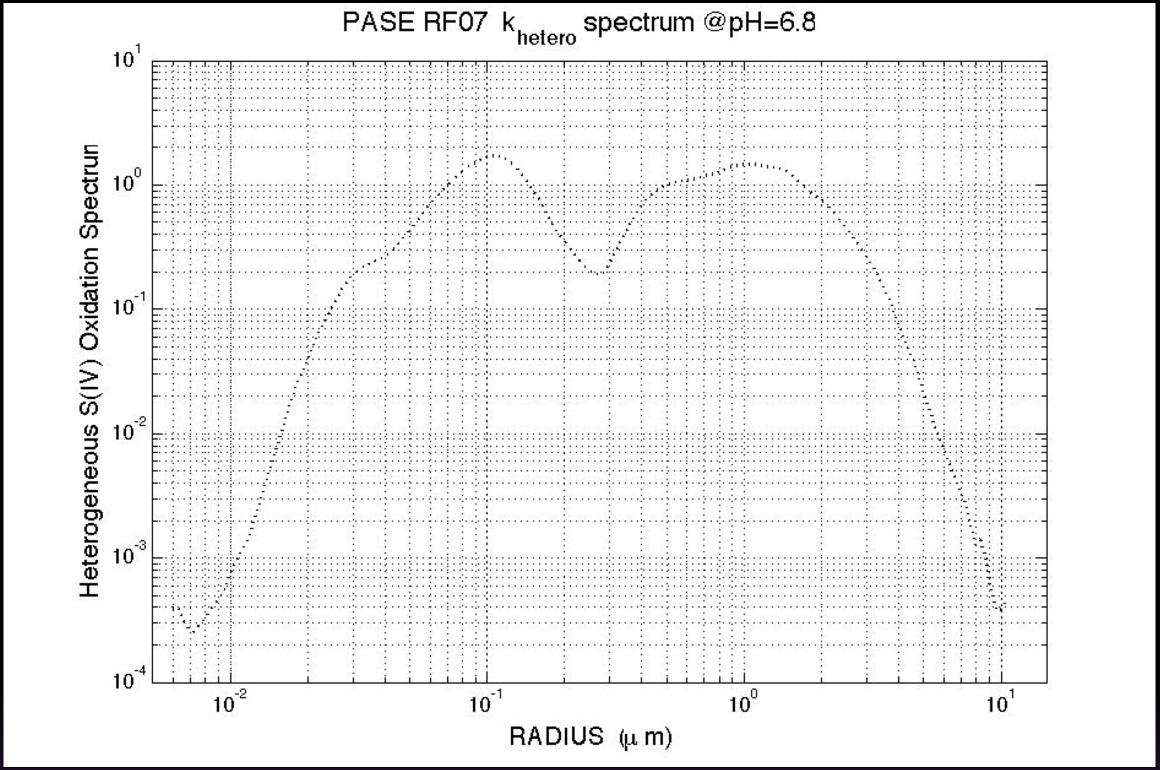


RF13: End of dust episode

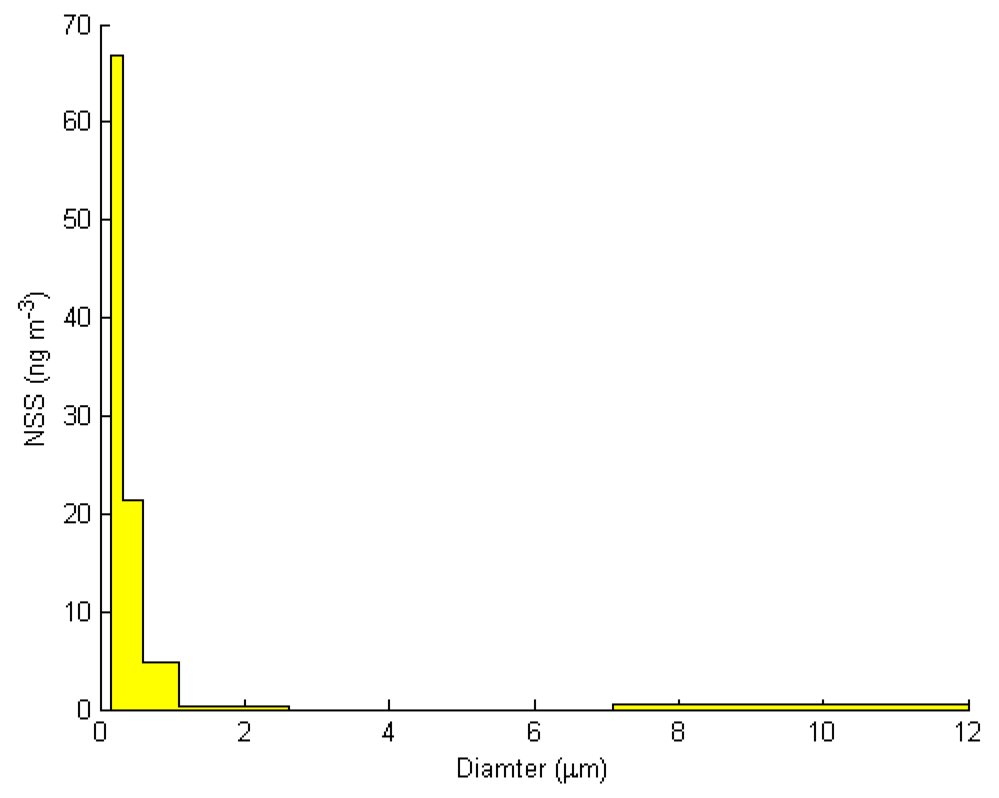


Summary

- Clouds are important
  - How many cloud cycles per air mass per day?
  - Can they grow coarse NSS particles?
  - What dynamical roles do they play?
- We cannot treat the BuL as entirely separate from the BL
  - Exchange of air between the two: how much?
- Significant non-local influence
  - What NSS or SO_2 fraction is local?


PASE RF07 k_{hetero} spectrum @pH=6.8
Heterogeneous S(IV) Oxidation Spectrun
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-2}
10^{-1}
10^{0}
10^{1}
RADIUS (μ m)

NSS Histogram



RF02 BL