PASE December 2009

Ship & Aircraft Plumes

Flights RF10 & 1st Stack RF09

Peroxide Budgets

I. Ship & Aircraft Plumes

- Unique opportunity … plume aerosol photochemistry … pristine bkg air.
- High NO_x … active halogens … DMS oxidation impact.
- Dawn to mid-morning transition.
- Transport and dilution.

Ship Plumes Roadmap

- State possible cases from 4 flights.
- Describe what we are using as plume criteria.
- Show VOS shiptracks and HYSPLIT[1] back trajectories.
- Plume dilution estimates.
- Photochemical expectation.
- Chemical interpretation.
- Outstanding issues in the chemistry & transport.

[1] *The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.html) used in this publication.*

I. Plume Case Identification

Two part process to identify cases

Type I - Observed chemistry and aerosol spikes;
Is there a VOS[1] ship consistent with trajectories?

Type II - From VOS ship tracks & trajectory estimates;
Are there missed chemical and aerosols plumes?

While it is relatively “easy” to see plumes in the chemistry, did we actually note/observe all we should have seen based upon VOSs.

[1] *VOS - volunteer observing ships*

Noted Plume Cases

Type I

RF13 - multiple encounters after 15:55 UTC

Highly likely, 3-day transport,

RF04 - ~20.53 UTC

Possible, 2-day transport but aloft, convective flight.

RF07 - ex. ~23.95 & ~24.21 UTC

Plausible from CN, SO_2 and O_3, but difficult match to VOS

Type II

RF01 - ~20.71, ~21.02, ~21.46, ~22.99 UTC

Probable from ship track, 1.5-day transport, mixed in with aircraft events.

Plume Phenomenon

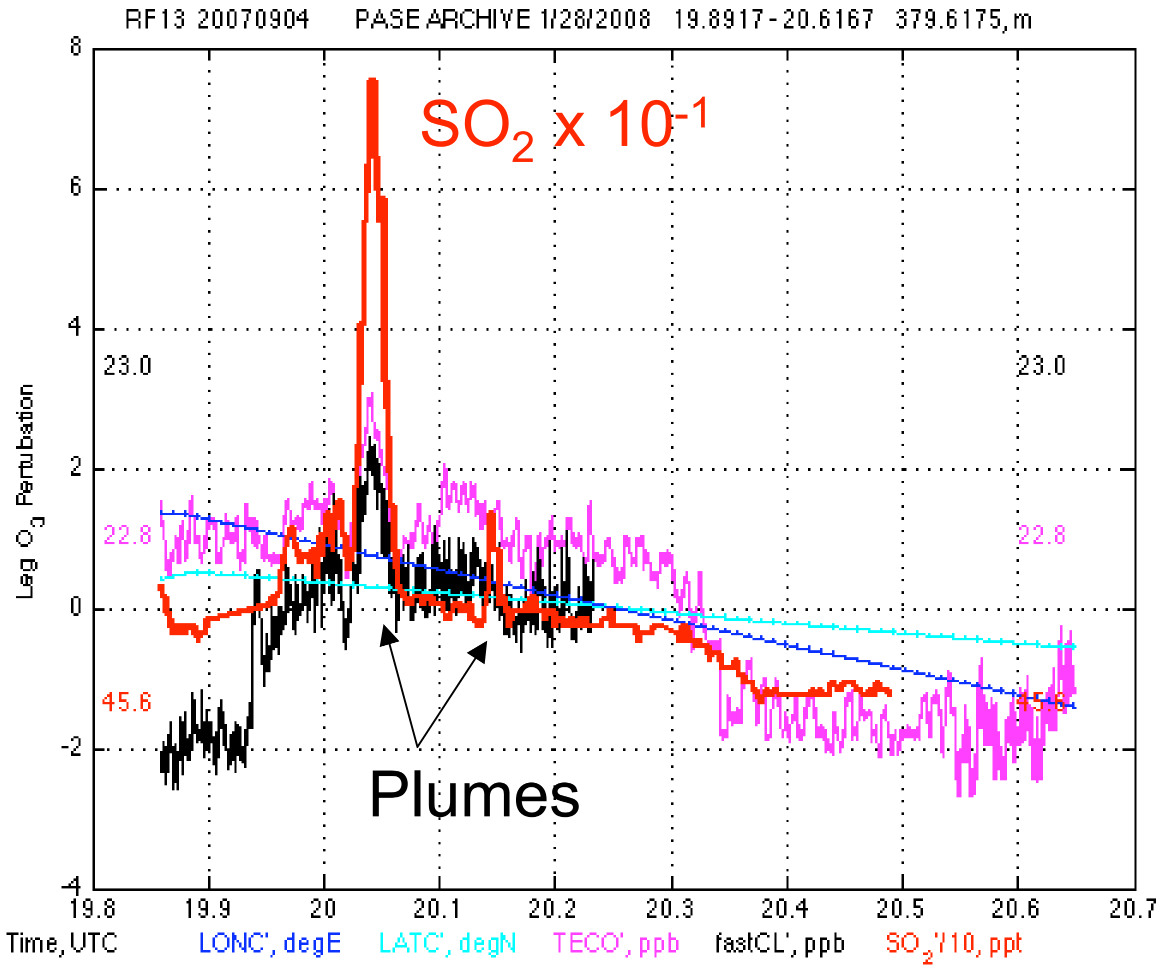
example: RF13 ~19:57-20:04, ~20:09

Perturbation Plots

ΔSO_2 ~75 ppt

ΔO_3(TECO) ~ 2 ppb

ΔO_3(fastCL) ~ 2 ppb



SO_2 x 10^{-1}

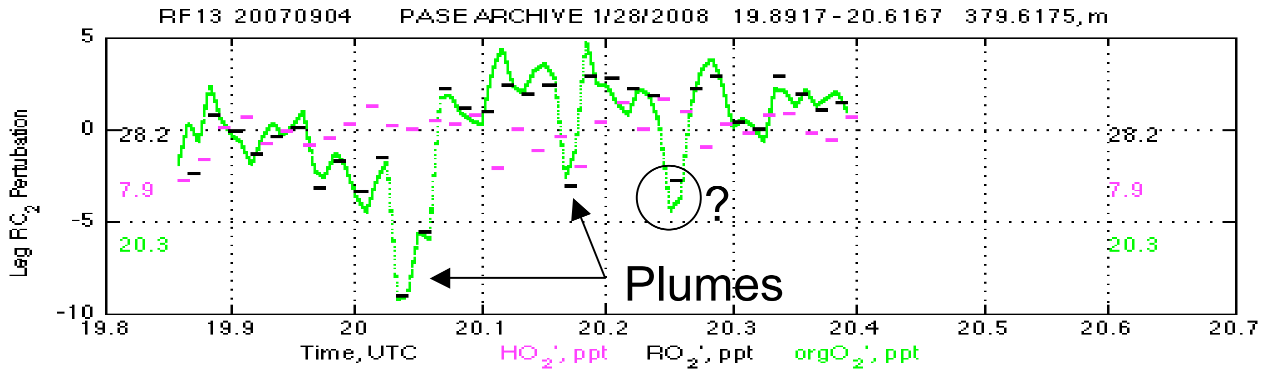
Plumes

Plume Phenomenon - 2

RO_2+HO_2

HO_2

Interp_orgO_2

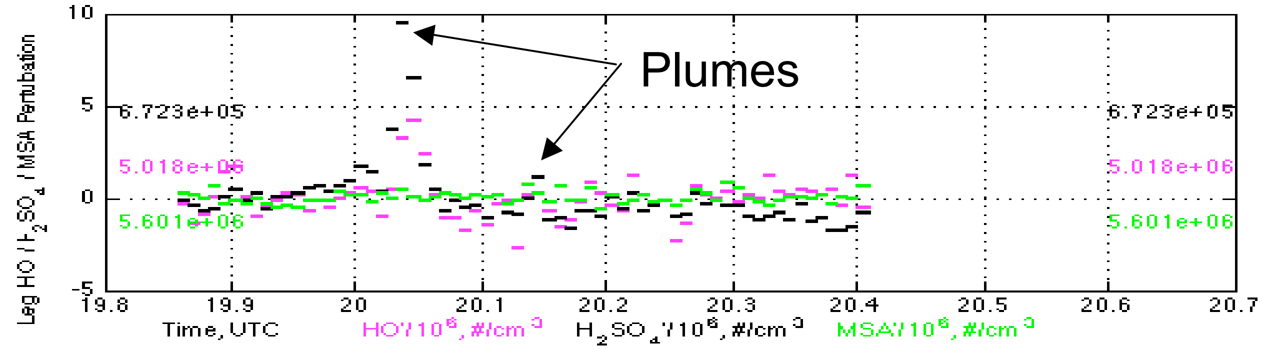


HO

H_2SO_4

MSA

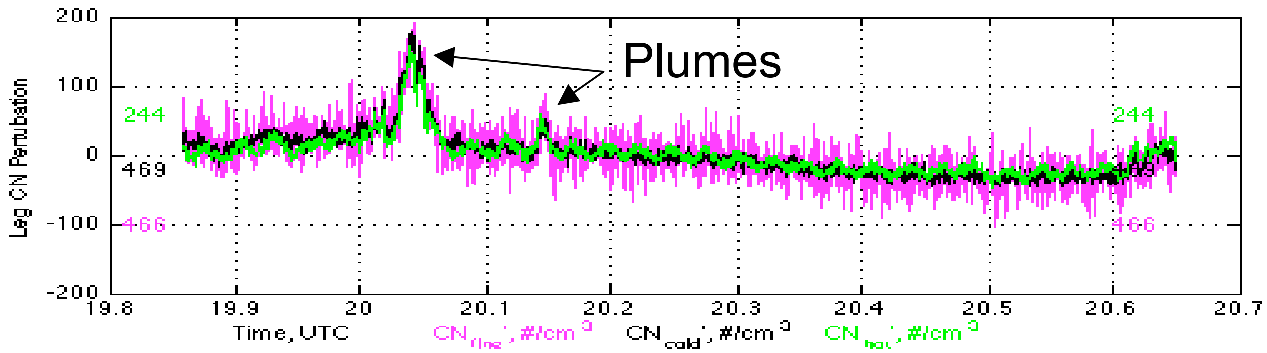
} x10^{-6}



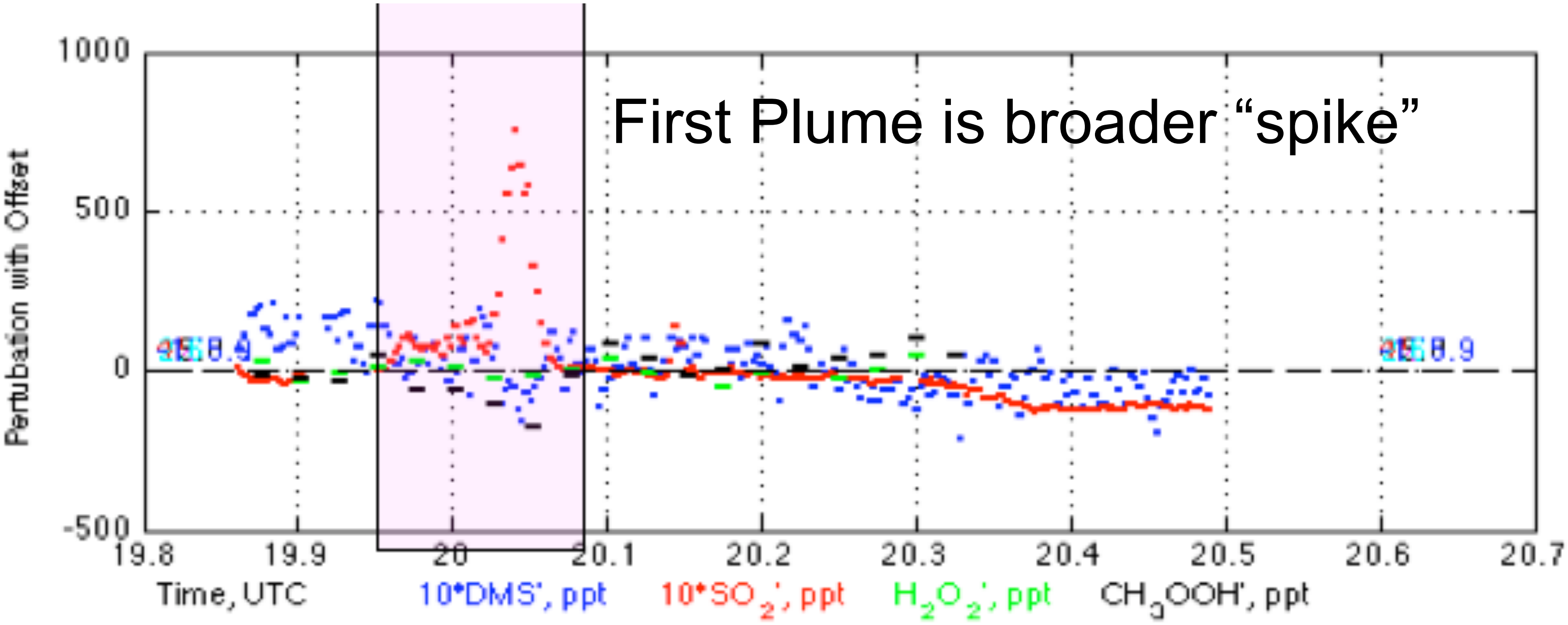
CN_{fine}

CN_{cold}

CN_{hot}



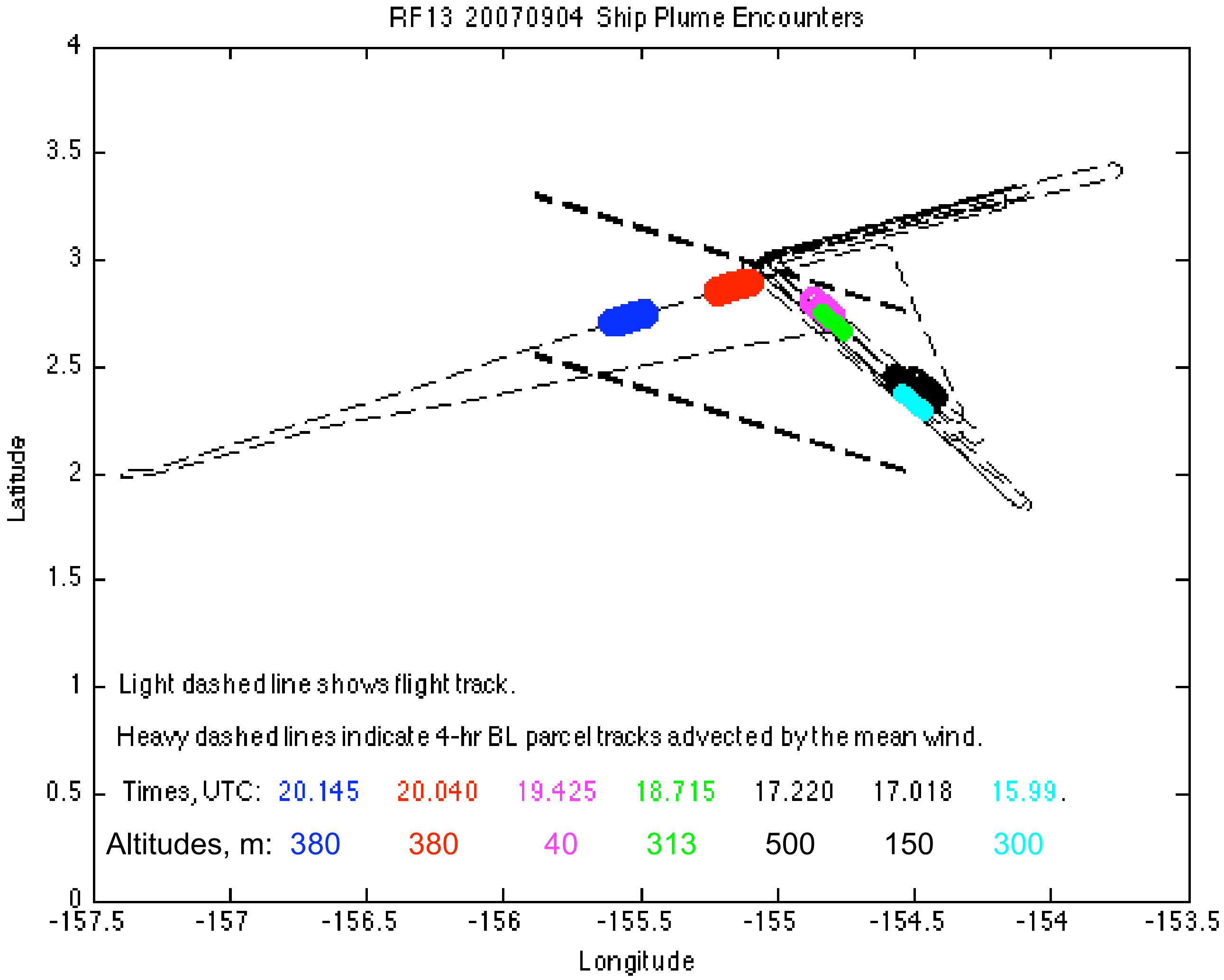
Plume Phenomenon - 3



First Plume is broader “spike”

$SO_2 \times 10^1$ $DMS \times 10^1$ H_2O_2 CH_3OOH

RF13 Plume Locations



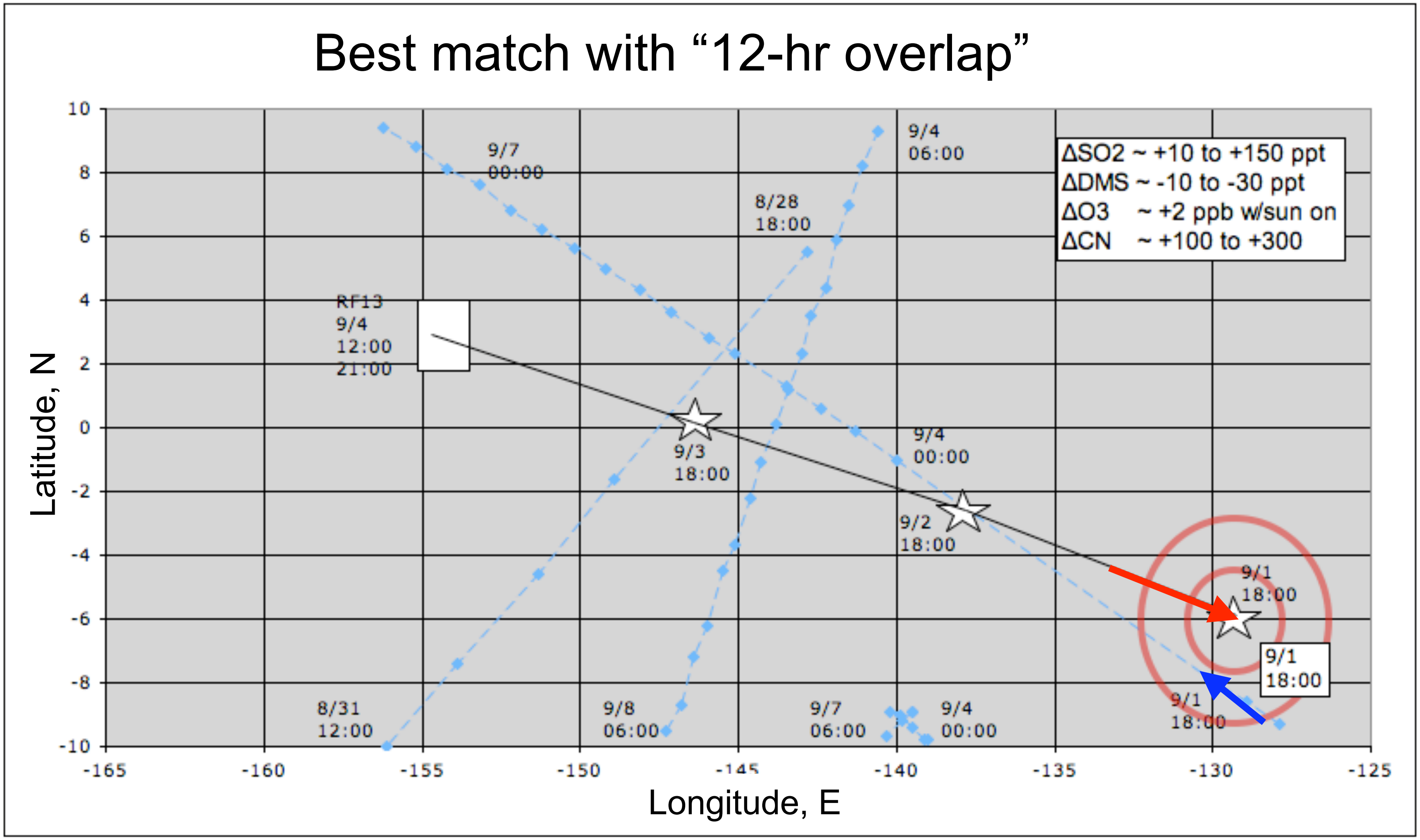
RF13 20070904 Ship Plume Encounters

Light dashed line shows flight track.

Heavy dashed lines indicate 4-hr BL parcel tracks advected by the mean wind.

Times, UTC:	20.145	20.040	19.425	18.715	17.220	17.018	15.99.
Altitudes, m:	380	380	40	313	500	150	300

RF13 Plume Trajectories & Tracks



Best match with “12-hr overlap”

ΔSO2 ~ +10 to +150 ppt
ΔDMS ~ -10 to -30 ppt
ΔO3 ~ +2 ppb w/sun on
ΔCN ~ +100 to +300

Is 3 days okay based upon plume dilution?

Dilution estimate Method A:

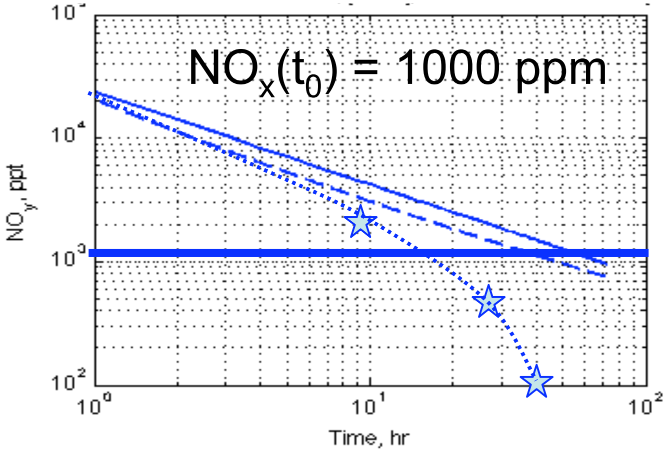
1. Simple power law relationship in Z and Y.
2. Coefficients from multiple ship track expts.
3. Added limit on Z; Z_{max} = 500 m.
4. Plume cross section area: A(t) = Z(t)Y(t).
5. from von Glassow et al. [2003].

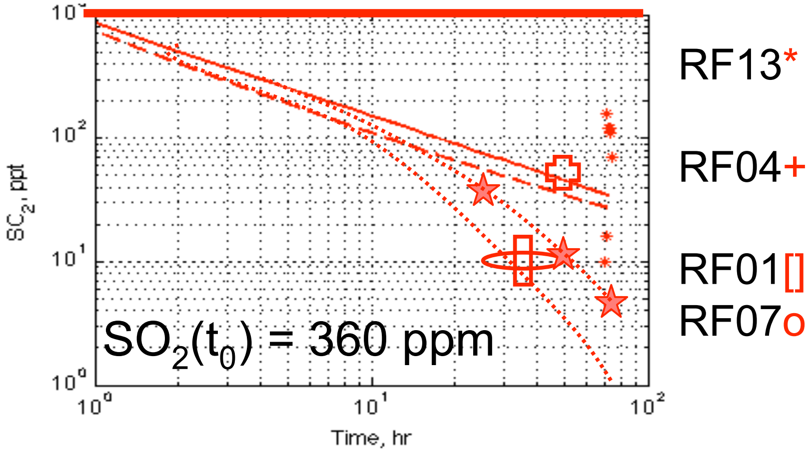
Dilution estimate Method B:

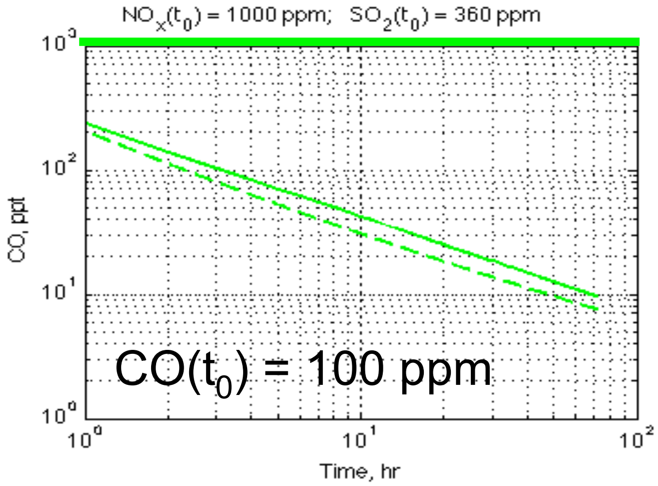
1. LES study using FIRE and BOMEX data.
2. Dilution rate scaled to convective turnover time t*; t* = Zi/w*; w*=f(integrated bouyancy flux).
3. $D(t) = a(t^*/t)^b = d\ln(A_{plume})/dt$.
4. from Chosson et al. [2008].

Ship Plume Dilution Δ Estimates

Method A - thin solid; Method B - dashed; 1 ppb - thick solid







Zi = 500, m

A = 0.046, min^{-1}

B = 1.07

t* = 20.9, min

CN(t_0)

O(10^8)

Added loss (chem. or dep.)

τ_{SO_2} ~ 0.8-1.5 day (z_i/w_d) ★

τ_{NO_x} ~ 1/2 day (24-hr HO) ☆

RF13 Plume Maximum “Deltas”

Time	Alt.	O3	SO2	DMS	CN	HO	H2SO4	CH3OOH	RO2
15.99	300	-1.00	15	na	500	0.7	0.0	na	
17.02	148		150	-40	350	1.5	3.0	na	-5.0
17.22	499	-0.75	115	-20	250	1.0	3.0	-75	-8.0
18.72	313	1.00	115	-25	225	2.6	15.0	-120	-10.0
19.43	37	2.00	115	-25	225	5.0	17.0	-100	-12.0
20.04	380	2.00	75	-15	160	5.0	10.0	-180	-9.0
20.15	380	0.25	10	0	40	0.5	2.0	-50	-6.0
possible									
17.62	499	-0.25	0	0	25	0.0	0.0	-50	-1.5

Plume Event Chemistry Summary

- Increased SO_2
- Increased CN; fine = cold = hot; non-volatile
- Increased O_3 often but not always
- Increased HO (day)
- Increased H_2SO_4 (day)
- Decreased RO_2 and interpolated $orgO_2$ (day)
- Decreased CH_3OOH (day)
- Decreased DMS often but not always
- HO_2 and H_2O_2 relatively unaffected
- MSA relatively unaffected

Plume Photochemical Expectation[1]

Ship emits NOx, SO_2, CO, VOCs, CH_2O, and "soot" and sulfate fine particles

Three stages of chemistry based on NOx

Daytime

stage one – early plume dispersion with NO_x >1000 ppb and $NO/NO_2/O_3$ photostationary state applies, O_3 depletion.

stage two – intermediate plume dispersion with $1 < NO_x < 1000$ ppb, O_3 recovery, enhanced HO and HNO_3 and H_2SO_4 production, and HO_2 and RO_2 are small, and hydroperoxide production is absent.

stage three – long-range plume dispersion with $NO_x < 1$ ppb, HO is maximized, HO_2 and RO_2 radicals return, VOC oxidation becomes important, net O_3 production and possible hydroperoxide formation.

[1] *Chen et al. [2005]; von Glasow et al. [2003]; Song et al. [2003a&b]; Karamchandani and Seigneur [1999]; Karamchandani et al. [1998; 2000];*

Plume Photochemical Expectation cont.

Nighttime

stage one – early plume dispersion with NO_x >1000 ppb and O3 titration as NO converted to NO_2,

stage two – intermediate plume dispersion with 1 < NO_x < 1000 ppb, NO, NO_2, NO_3 and N_2O_5 chemistries are effective, and

stage three – long-range plume dispersion with NO_x < 1 ppb, NO_2 dominates NO_x, some NO_3 and negligible N_2O_5.

Power Plant and Ship Plume

- Expected photochemistry of ship plumes as they dilute is consistent with our observed changes in SO_2, HO, H_2SO_4 and O_3. CN?
- In stage 2 and 3, dilution with background air should set peroxide levels to background values, ΔROOH=0.
- HO_2 and RO_2 should both decrease which in turn leads to decreased peroxide production.

Karamchandani et al. [1998, 1999, 2000], *Karamchandani and Seigneur,* [1999], *von Glasow et al.* [2003], *Chen et al.* [2005], and *Song et al.* [2003a&b]

Unresolved “Howevers”:

Q1: How is CH_3OOH reduced in ship plume impacted ambient air relative to H_2O_2, which does not appear to change?

Plume chemistry is enriched in NO_x, and depleted in HO_2 and CH_3OO and RO_2 in general. From the standpoint of hydroperoxide production there should be little production of either H_2O_2 or CH_3OOH within a plume. Hence, the H_2O_2 or CH_3OOH concentrations should be that of the diluent air.

Q2: How does HO_2 remain constant while RO_2 is reduced as expected in plume air?

Do Loss Rxns in Plume Ans. Q1?

HO or other speculative reactant, e.g. Cl from $NO_3/N_2O_5/HNO_3$

$$CH_3OOH + HO \longrightarrow H_2O + CH_3OO$$

$$CH_3OOH + HO \xrightarrow{O_2} H_2O + CH_2O + HO_2$$

$$CH_3OOH + Cl \longrightarrow HCl + CH_3OO$$

$$CH_3OOH + Cl \xrightarrow{O_2} HCl + CH_2O + HO_2$$

$$H_2O_2 + HO \longrightarrow H_2O + HO_2$$

$$H_2O_2 + Cl \longrightarrow HCl + HO_2$$

Table: *k*s for ROOH reactions with HO and Cl, $cm^3\ molec^{-1}\ s^{-1}$

	HO	Cl
H_2O_2	1.7×10^{-12}	4.1×10^{-13} (4x slower than HO)
CH_3OOH	$7.4(5.5) \times 10^{-12}$	$5.7(5.9) \times 10^{-11}$ (7x faster)

Simple Loss Example

$[H_2O_2]_0 = 1000$

$[CH_3OOH]_0 = 1000$

$[HO]_p = 2x\ [HO]_{bkg} \sim 10^7$

$k_1=1.7x10^{-12}$

$k_2=7.4x10^{-12}$

$$[CH_3OOH]_t:[H_2O_2]_t = \exp(-\{k_2 - k_1\}\ [HO]t)$$

From HO loss alone, it would take ~1 hr after mixing to deplete CH_3OOH relative to H_2O_2 by 100 to 200 ppt.

Does CH_3OO cycling to HO_2 by NO_x in Plume Ans. Q2?

~~$CH_3OO + HO_2 \longrightarrow CH_3OOH + O_2$~~

$CH_3OO + NO \longrightarrow CH_3ONO_2$

$CH_3OO + NO \xrightarrow{O_2} CH_2O + NO_2 + HO_2$

$CH_3OO + NO_2 \longrightarrow CH_3OONO_2$

$CH_3OO + NO_3 \longrightarrow CH_2O + HO_2 + NO_2$

~~$CH_3OO + RO_2 \longrightarrow CH_2O + RO + O_2$~~

~~$CH_3OO + RO_2 \longrightarrow CH_2O + ROH + O_2$~~

~~$CH_3OO + RO_2 \longrightarrow CH_3OH + RO + O_2$~~

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net: $CH_3OO + NO_x \rightarrow\rightarrow CH_2O + RNO_x + HO_2$

and with

$CH_2O + h\nu \rightarrow\rightarrow CO + HO_2 + H_2$

Could Halogen Chemistry Ans Q1 and Q2 As Well?

- Plumes are active high NO_x environments with HNO_3 NO_3 and N_2O_5.
- RF13 plumes cross dawn to mid-morning sun.
- Q3: Is there evidence of halogen and NOx chemistries in CH_3OOH, DMS or other species?

Plume “Punch” List

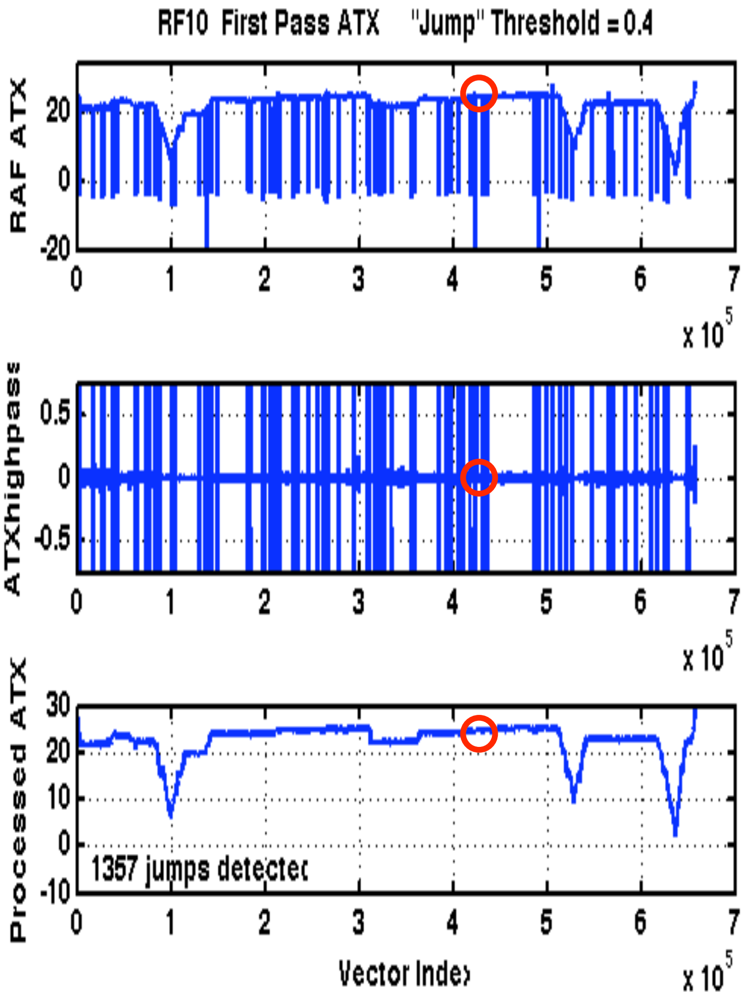
- Aerosol evolution piece of story.
- Directed plume photochemical simulations.
- Evidence for a halogen story.

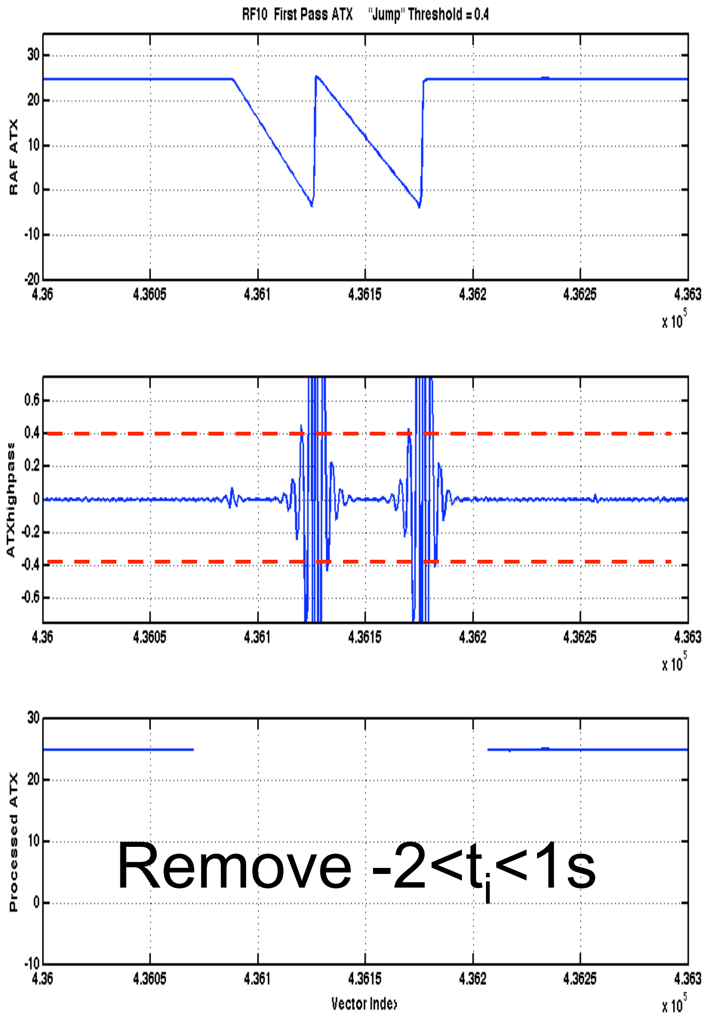
II. Recover Flights RF10 & RF09

- Regain Fluxes for 2 of 13 flights.
- Spikes in some RAF data channels.
- Detect and eliminate ramps and jumps.
  - High pass filter.
  - Threshold defined for each variable.
- Strategy for data fill-in going forward.
- Ex. Spectra & Flux results using a simple fill strategy.

ATX Spike Example:

index~436150 (25 hz)

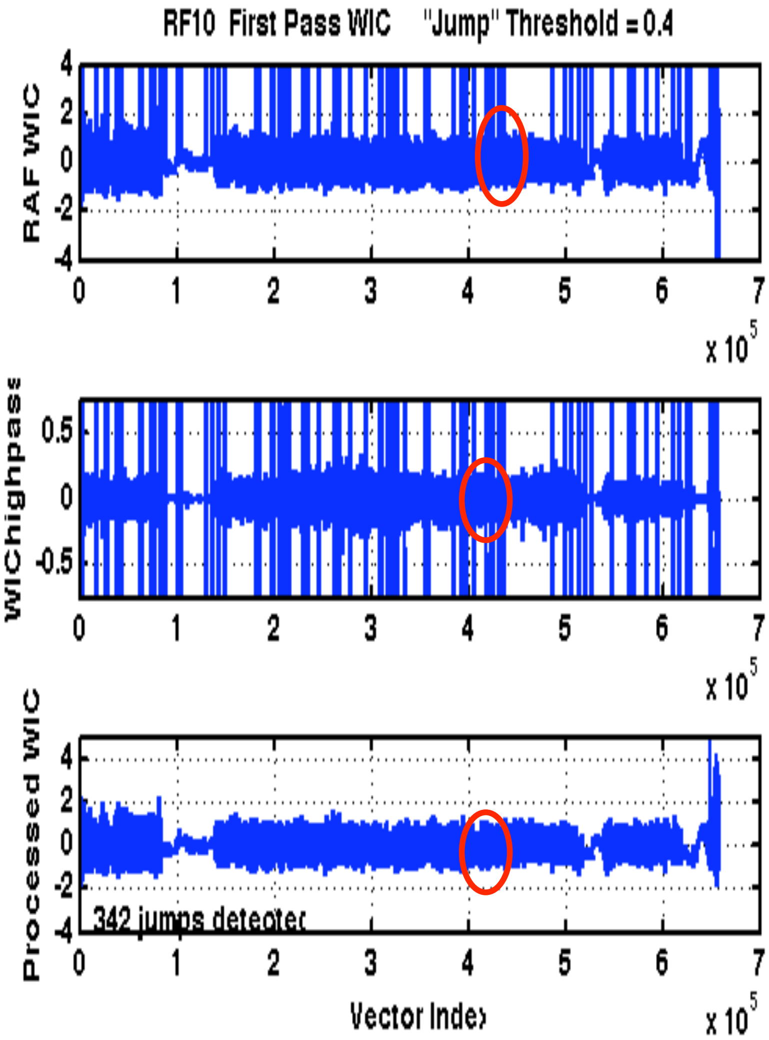


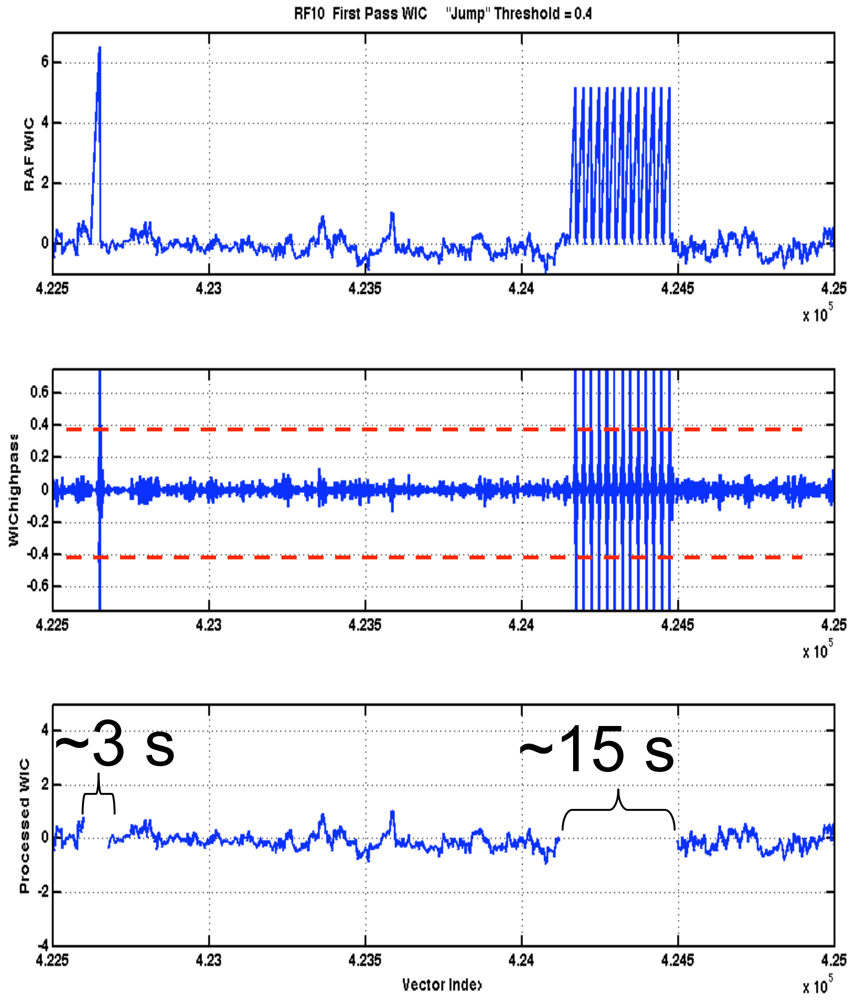


Remove $-2<t_i<1$s

WIC “Spike Train” Example:

index ~ 424250 (25Hz)





Simple Fill Strategy

- Applies to removed Spikes & Plumes:
  - RF01, RF02, RF09, RF10, RF12, & RF13

- Procedure

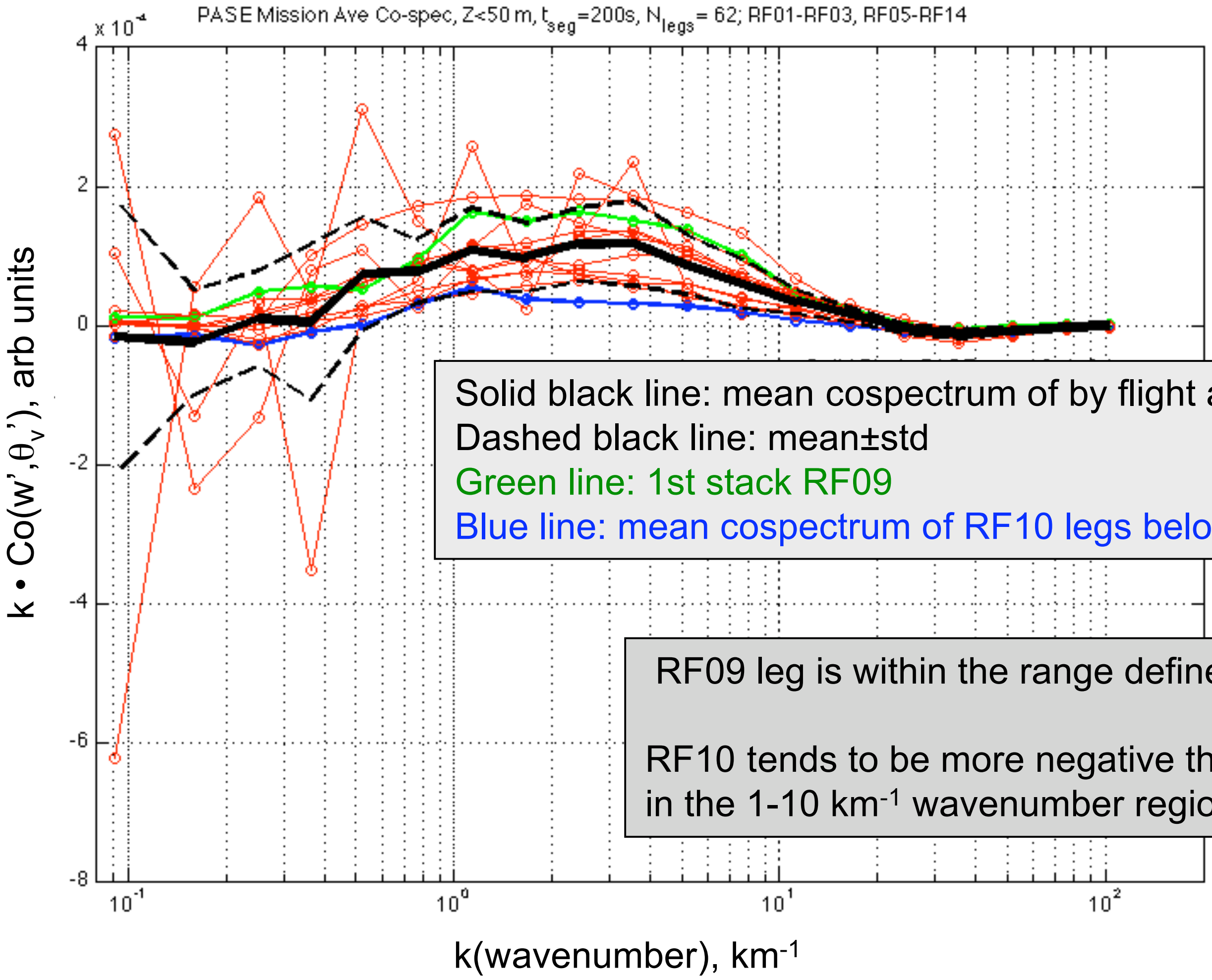
1) 75% data coverage within 200 s segment.
2) Determine perturbations; demean and detrend segment.
3) Linear interpolation of perturbation across gap (no discernable difference with zero perturbation fill).

Vertical Cospectra & Flux Comparisons

- By flight, by time, by altitude
- By Variable
  - Temperature, potential temperature (T,P)
  - Water, virtual potential temperature (T,P,q)
  - Speed (momentum: $[U^2+V^2]^{1/2}$)
  - Chemical: DMS, SO_2, and O_3
- kCo(w'S') & ∑Co(w'S')

Virtual Potential Temperature

Recalculated using MRLA with fill procedure



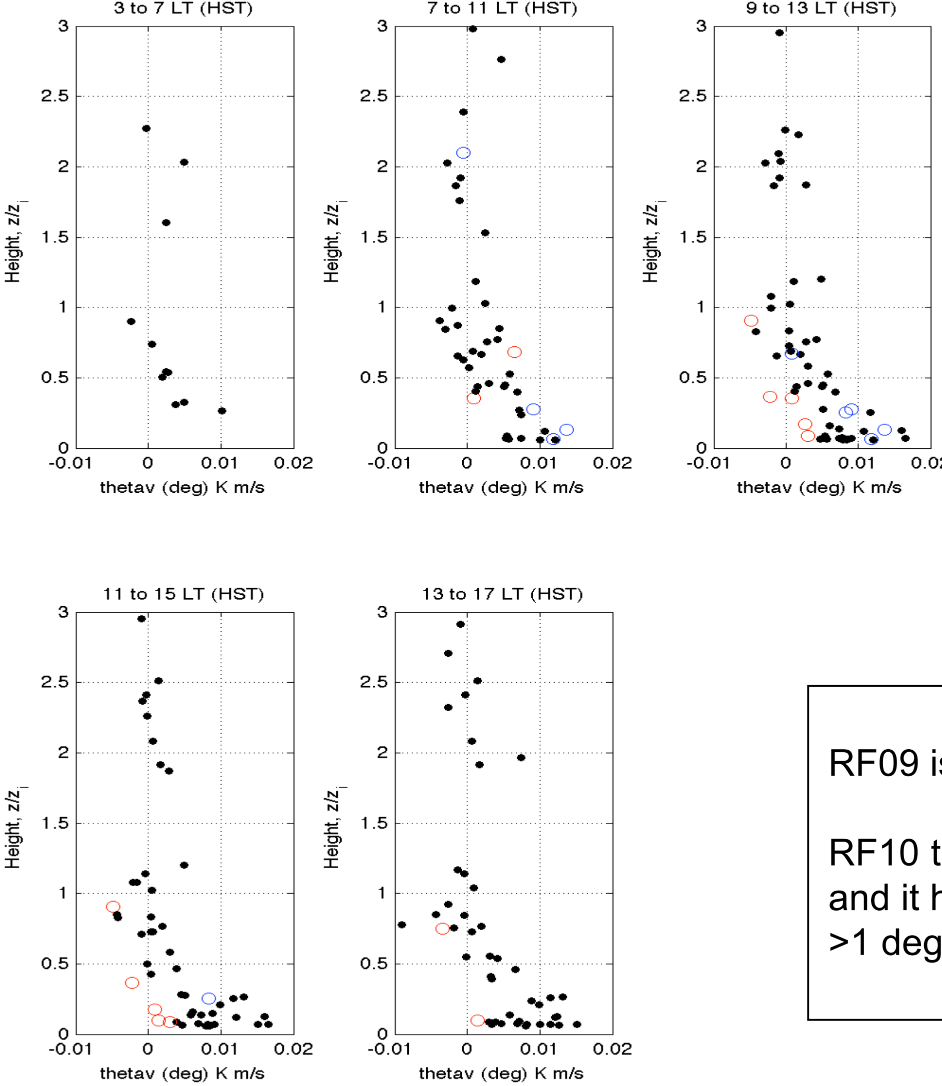
Solid black line: mean cospectrum of by flight averages for legs below 50 m.
Dashed black line: mean±std
Green line: 1st stack RF09
Blue line: mean cospectrum of RF10 legs below 50 m

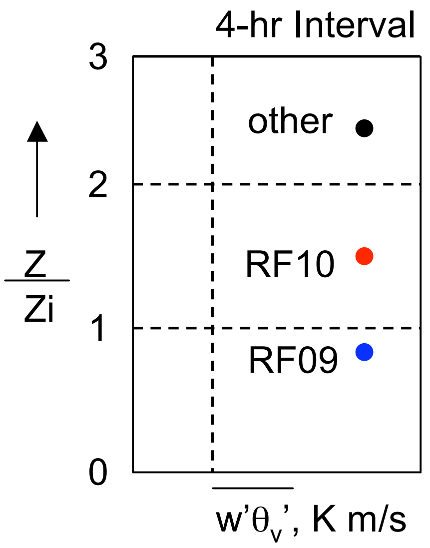
RF09 leg is within the range defined by other flights.

RF10 tends to be more negative than the other flights in the 1-10 km^{-1} wavenumber region.

Virtual Pot. Temp. Flux

Recalculated using MRLA, unfilled EC



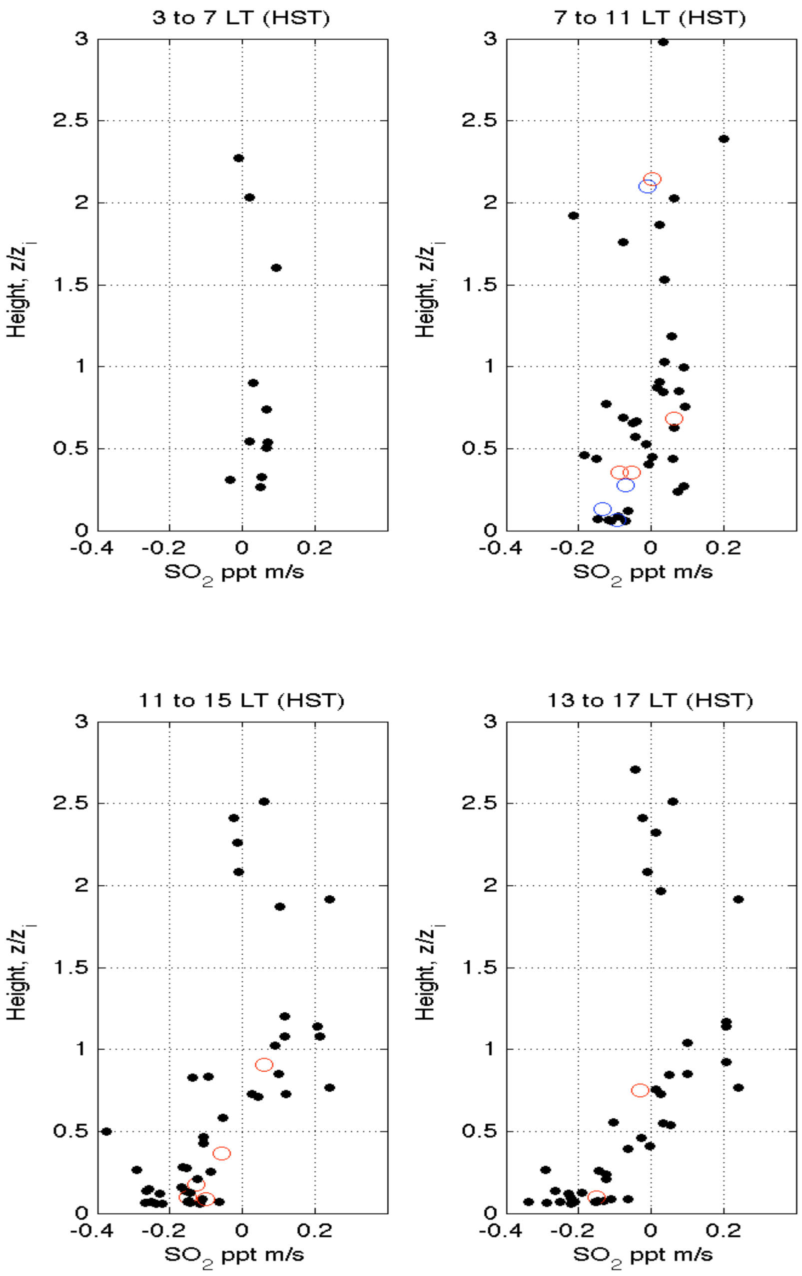


RF09 is within the range defined by other flights.

RF10 tends to be more negative than the other flights and it has the coldest surface temperature (T_{surf}) by >1 deg K.

$\overline{w'SO_2'}$

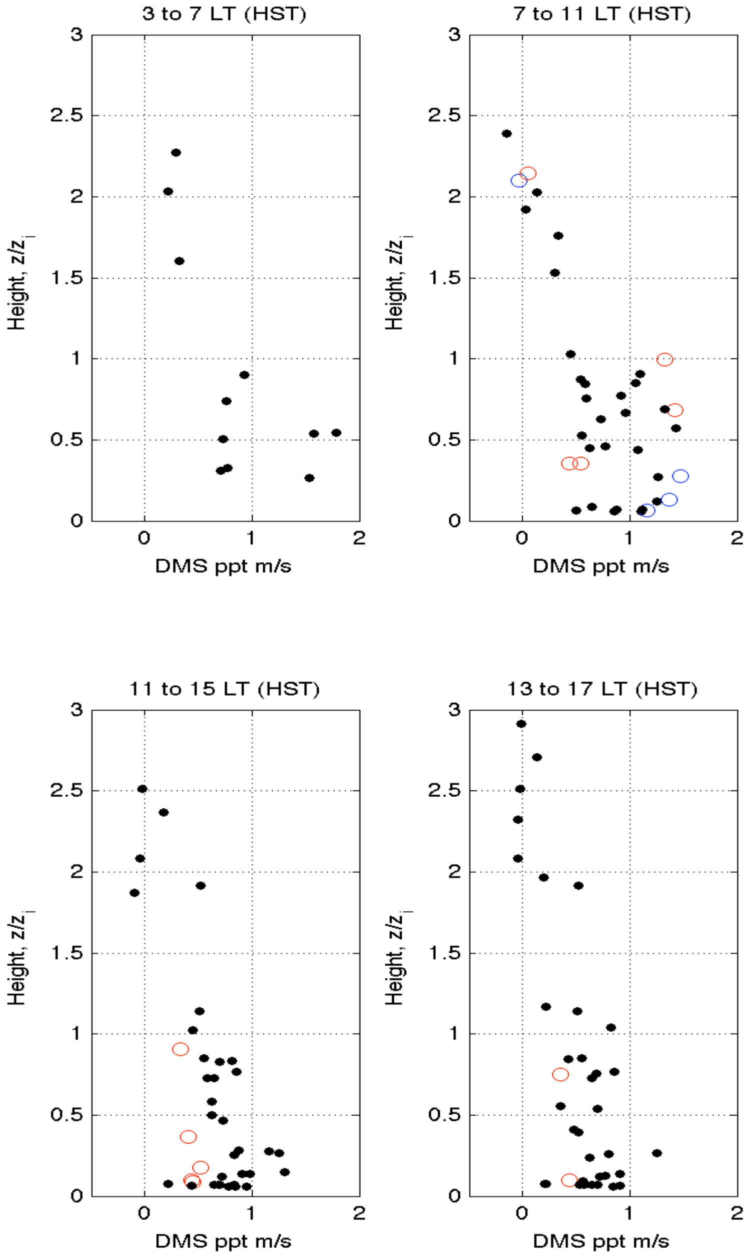
no fill
EC



● RF09 ● RF10

RF09 is central within the range defined by other flights.

RF10 is central within the range defined by other flights.



$\overline{w'DMS'}$

no fill EC

● RF09

● RF10

RF09 is on the positive edge of the range defined by other flights.

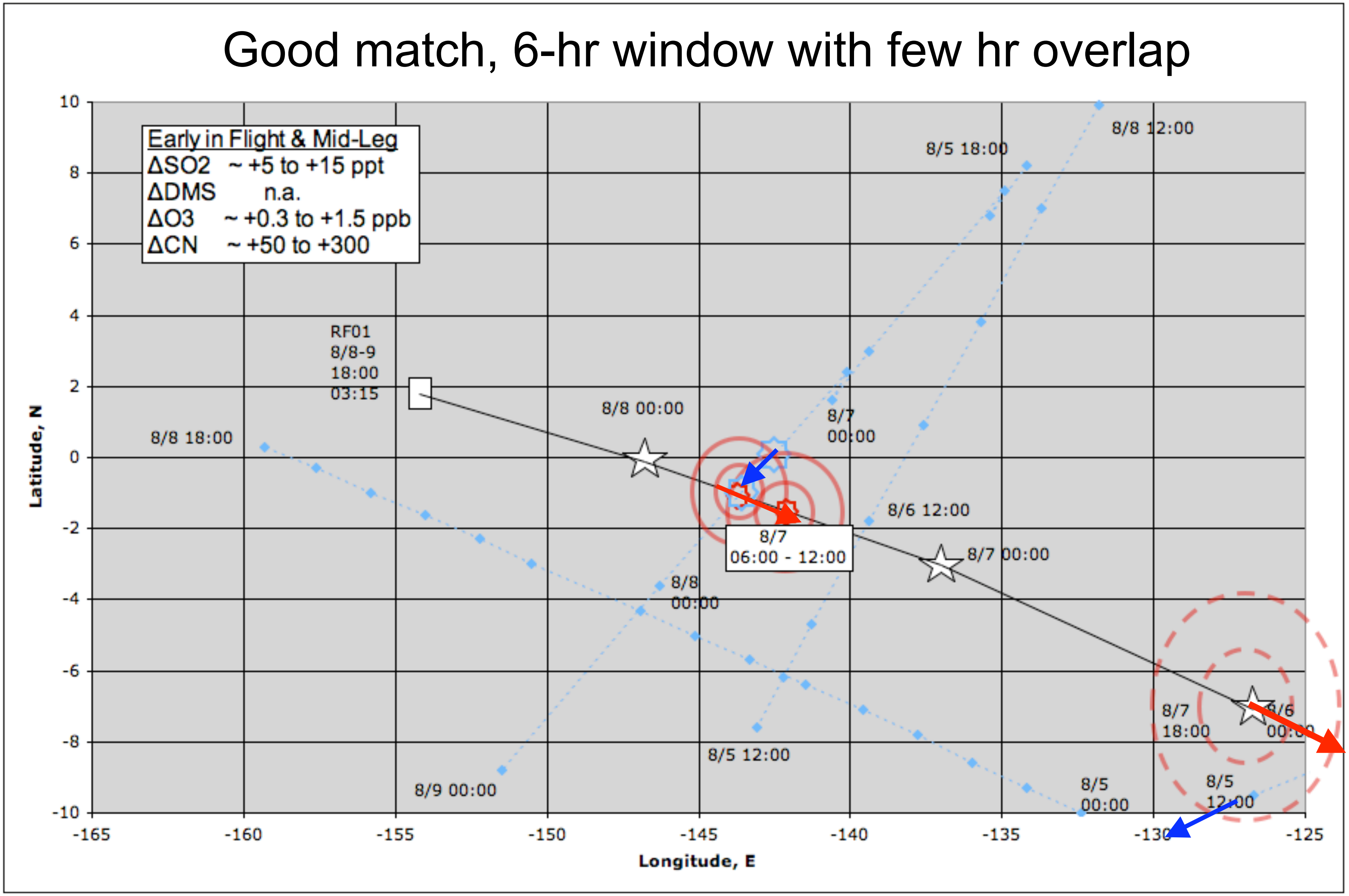
RF10 is on the negative edge of the range defined by other flights.

Going Forward on Fill Strategies

- ☑ 1) zero fill
- ☑ 2) linearly interpolated values
- ☒ 3) singular spectrum analysis (Schoellhamer, 2001; Kondrashov and Ghil, 2006)
- ☒ 4) Lomb-Scargle periodogram (Hocke and Kämpfer, 2009)
- ☐ 5) ARMA automated method (Broersen, 2006)

Backup Slides

RF01 Plume Study

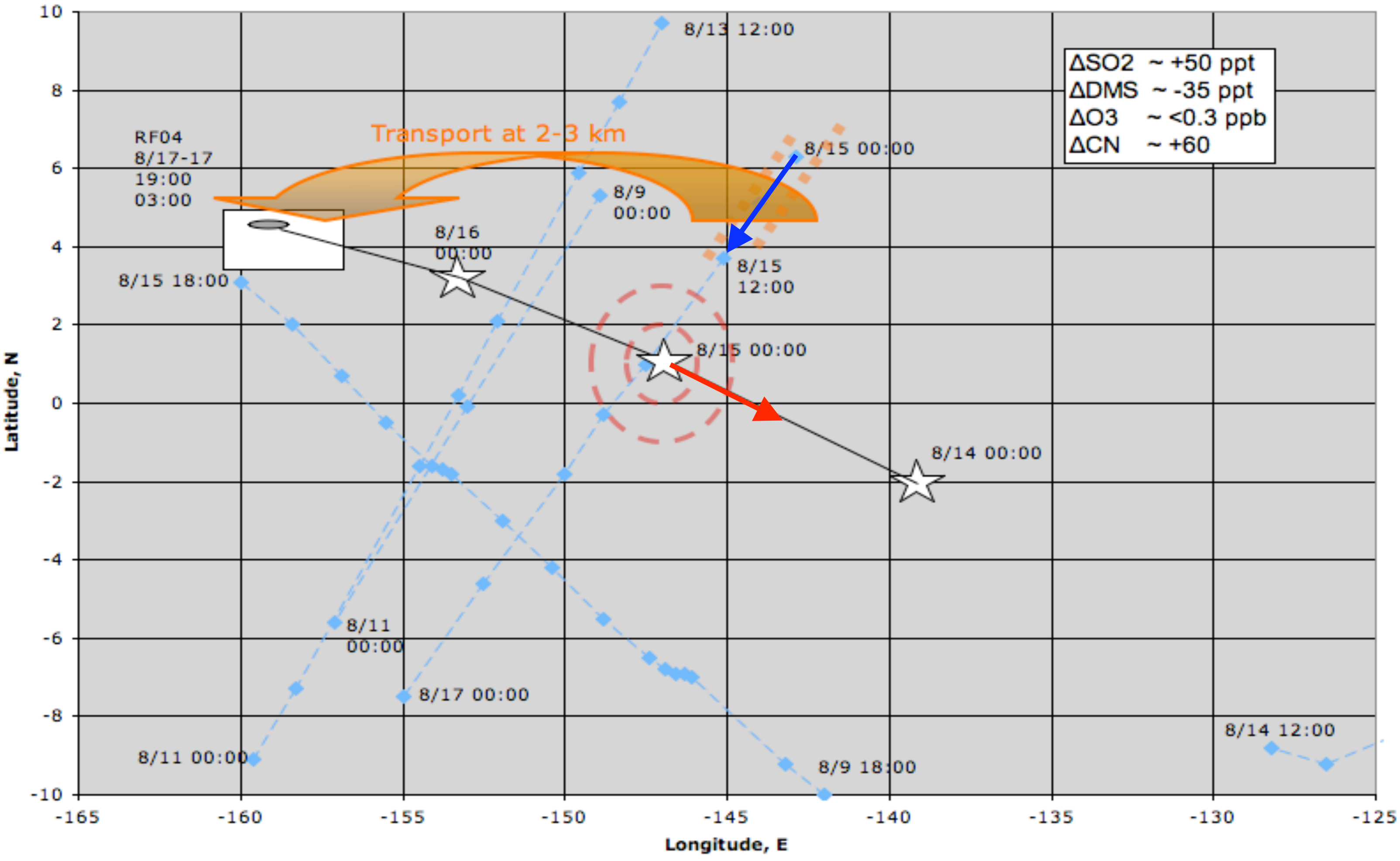


Good match, 6-hr window with few hr overlap

Early in Flight & Mid-Leg
ΔSO2 ~ +5 to +15 ppt
ΔDMS n.a.
ΔO3 ~ +0.3 to +1.5 ppb
ΔCN ~ +50 to +300

RF04 Plume Study

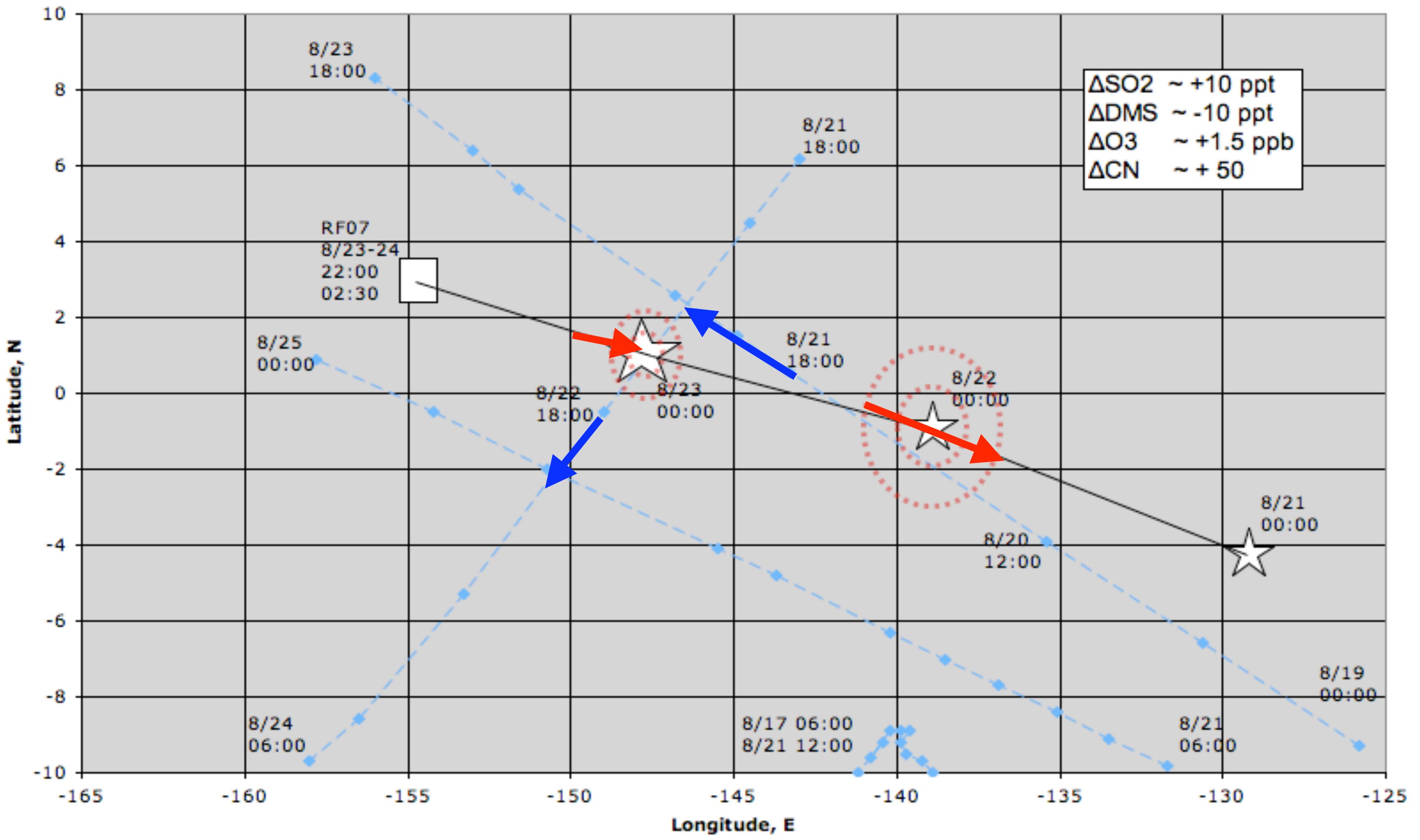
BL no; 2-3 km transport path possible given convection



ΔSO_2 ~ +50 ppt
ΔDMS ~ -35 ppt
ΔO_3 ~ <0.3 ppb
ΔCN ~ +60

RF07 Plume Study

Two ships: 6-hr and 12 hr mis-matches



Plume Halogen Radical Activation

e.g., *Finlayson-Pitts* [2003]; *Aldener et al*. [2006]:

$$ClONO_{2(g)} + NaCl_{(aq)} \longrightarrow Cl_{2(g)} + NaNO_{3(aq)}$$

$$NO_{3(g)} + NaCl_{(aq)} \longrightarrow Cl_{(g)} + NaNO_{3(aq)}$$

$$N_2O_5 + NaCl_{(aq)} \longrightarrow ClNO_{2(g)} + NaNO_{3(aq)}$$

e.g., *Finlayson-Pitts* [2003]; *Finlay and Saltzman* [2008]:

$$O_3 + Br^-_{(aerosol)} \xrightarrow{bulk, hetero}$$

$$BrONO_2 + Br^-_{(aerosol)} \longrightarrow$$

$$BrNO_2 + Br^-_{(aerosol)} \longrightarrow$$

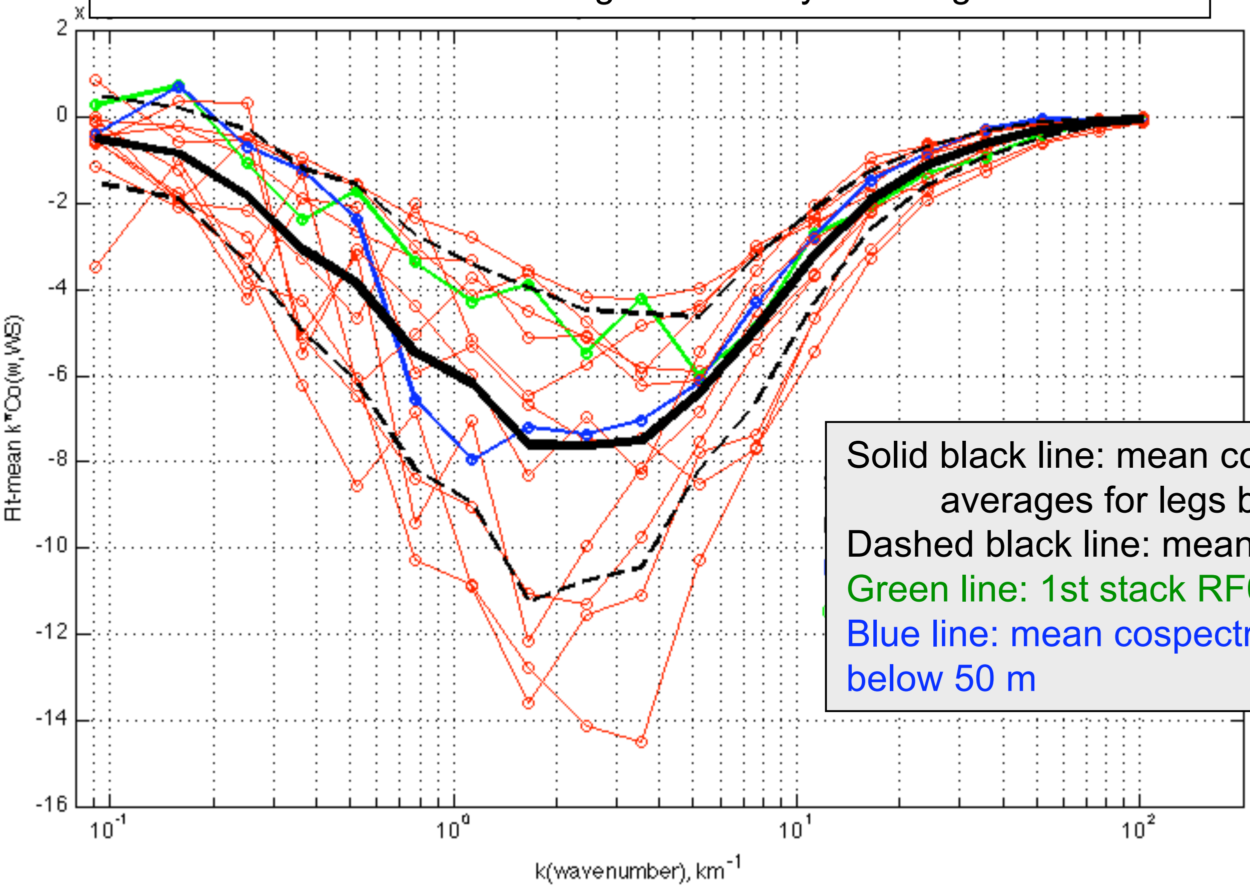
e.g., *Nissenson et al.* [2008]:

$$HO_{(g)} + Cl^-{}_{(aq,sfc)} \longrightarrow 0.5Cl_{2(g)} + HO^-{}_{(aq)}$$

w, Speed Cospectrum

RF09 is central within the range defined by other flights.

RF10 is central within the range defined by other flights.



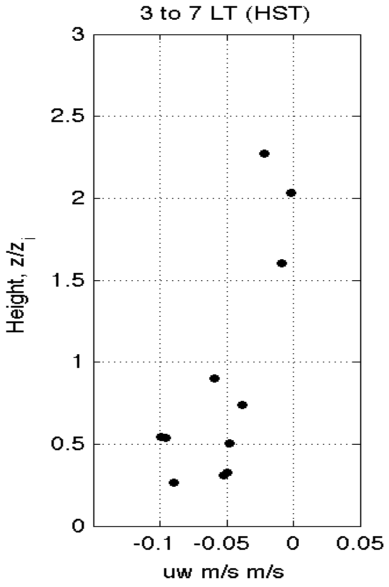
Solid black line: mean cospectrum of by flight averages for legs below 50 m.

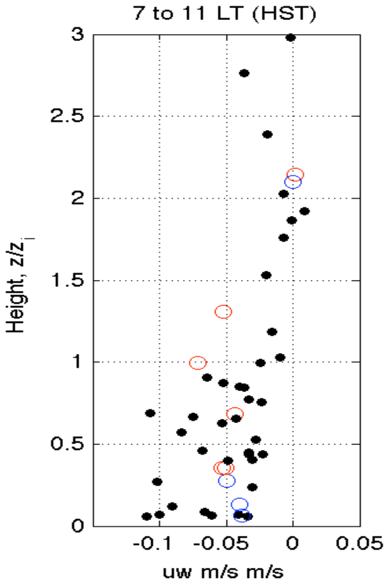
Dashed black line: mean±std

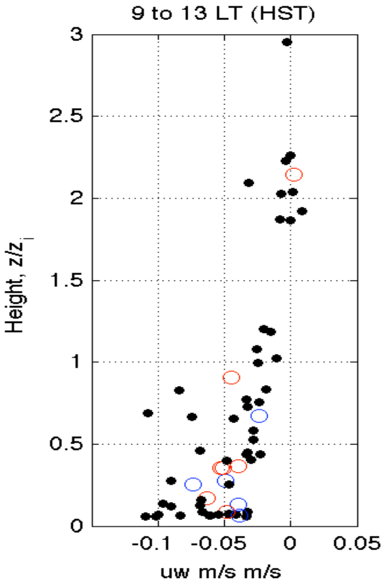
Green line: 1st stack RF09

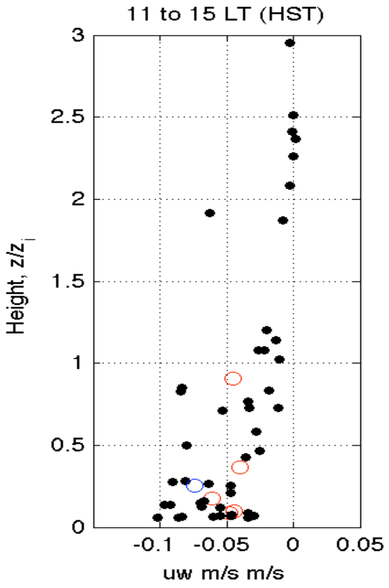
Blue line: mean cospectrum of RF10 legs below 50 m

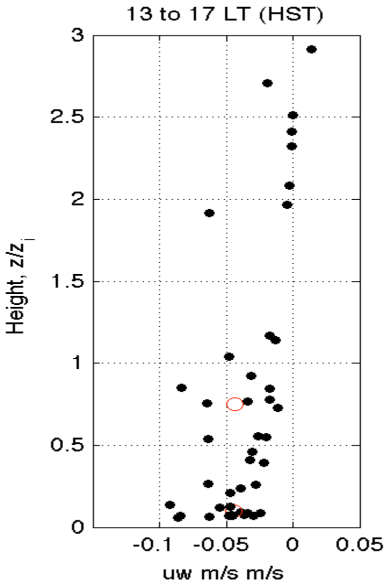
Speed


3 to 7 LT (HST)


7 to 11 LT (HST)


9 to 13 LT (HST)

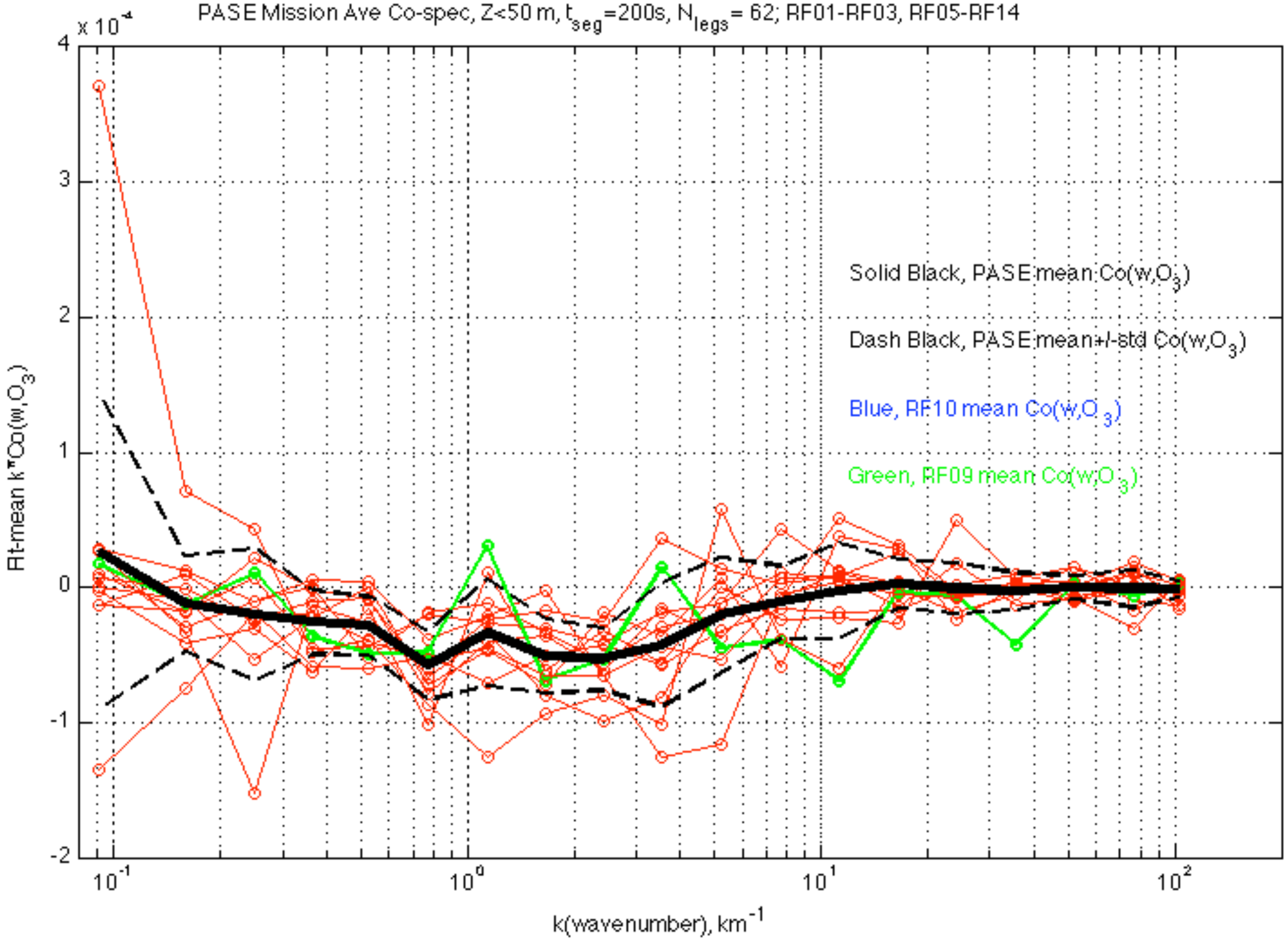

11 to 15 LT (HST)


13 to 17 LT (HST)

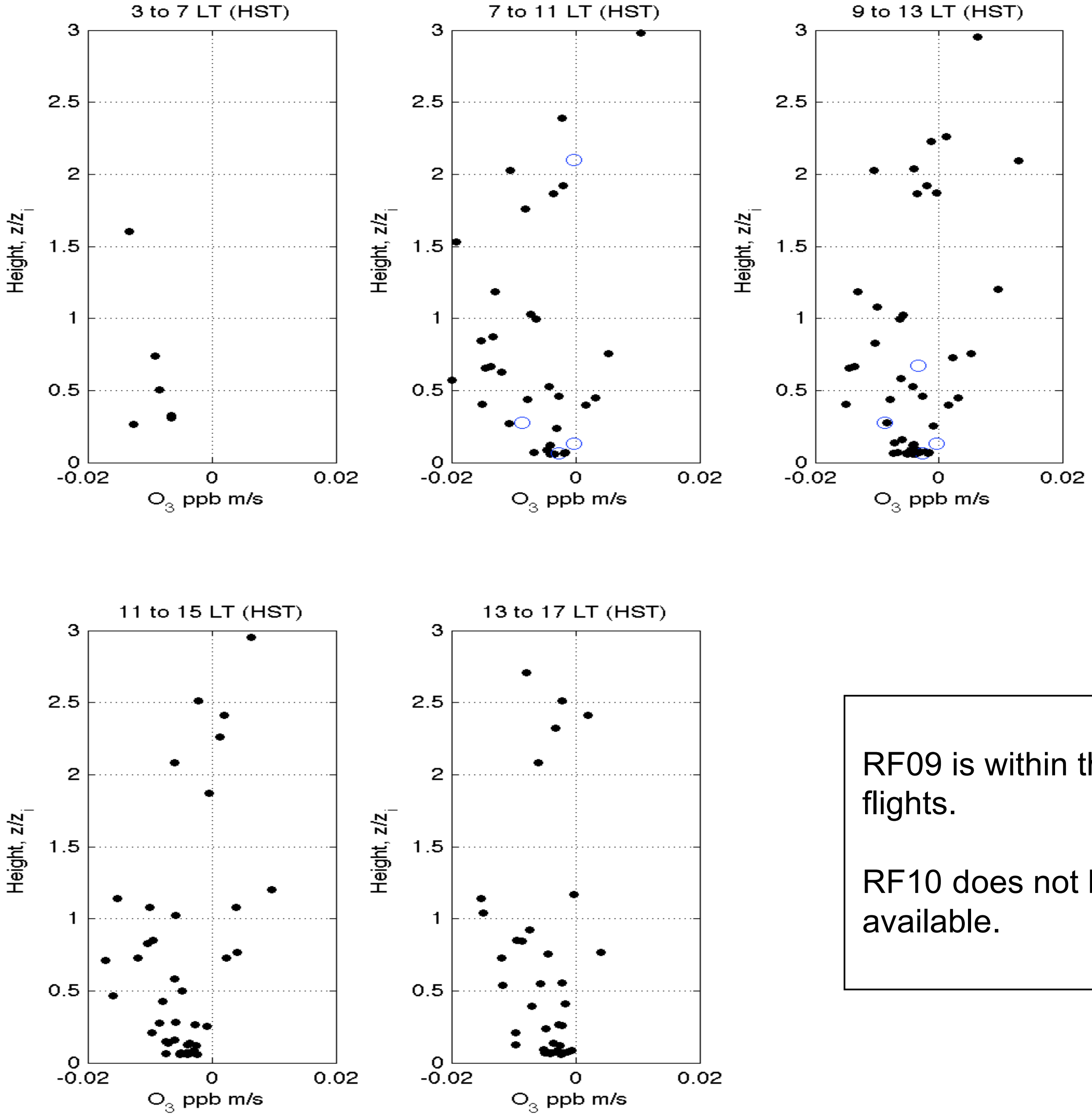
RF09 is central within the range defined by other flights.

RF10 is central within the range defined by other flights.

w Ozone Cospectrum



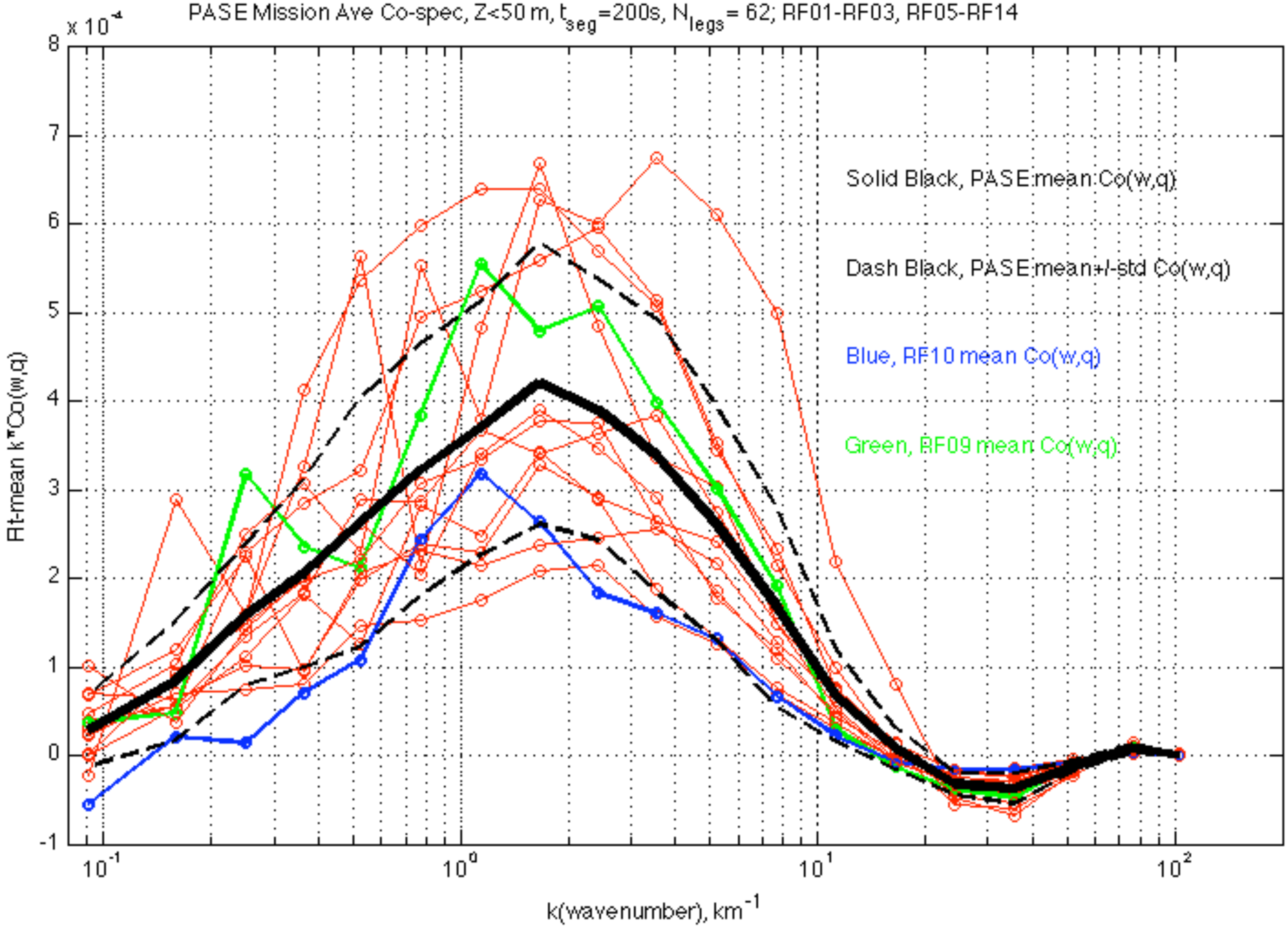
Ozone



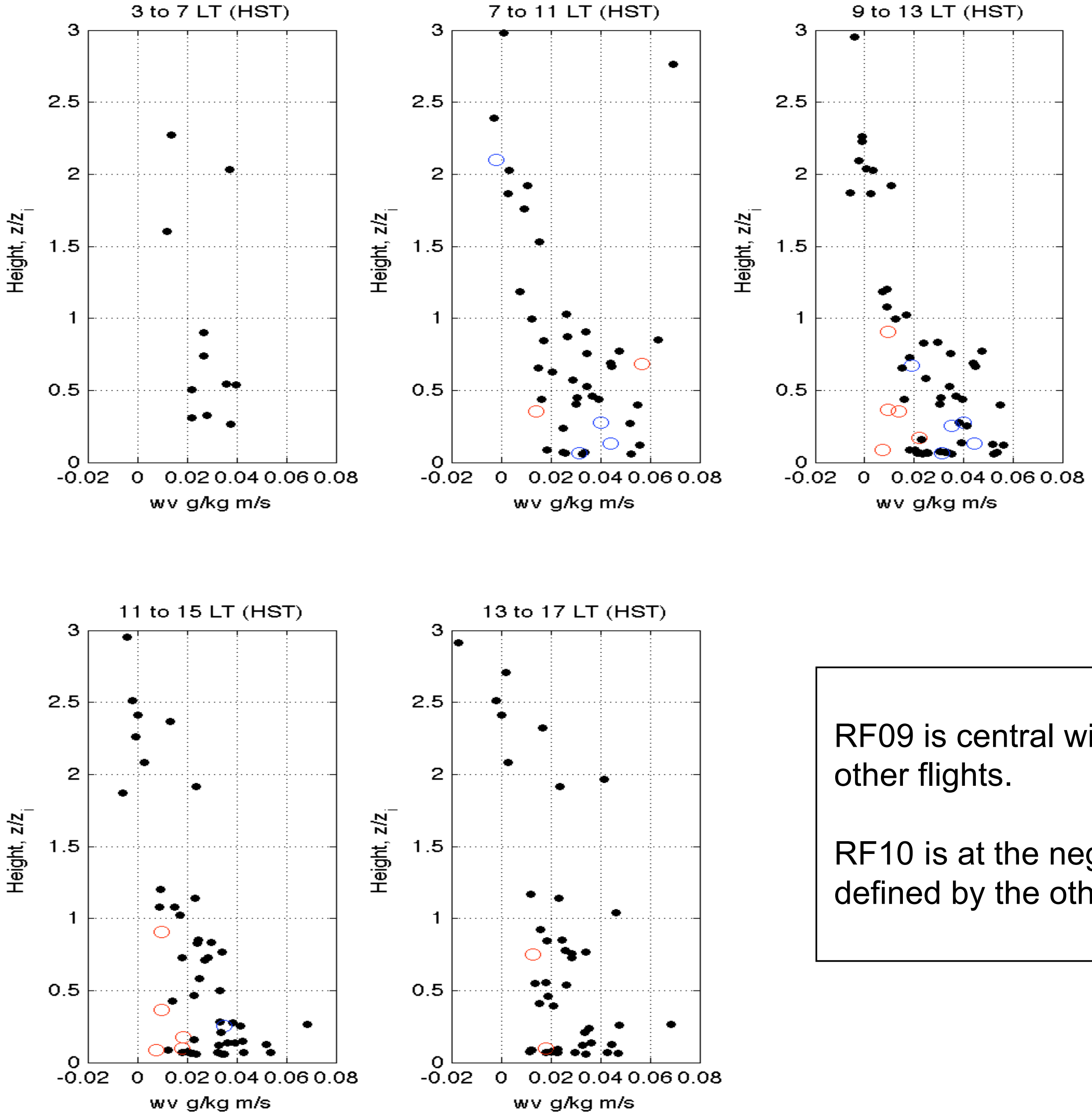
RF09 is within the range defined by other flights.

RF10 does not have fast ozone data available.

w,H_2O Cospectrum



H_2O



RF09 is central within the range defined by other flights.

RF10 is at the negative edge of the range defined by the other flights.

w,SO_2 Cospectrum