LTADS – UCD Overview

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Part 1:

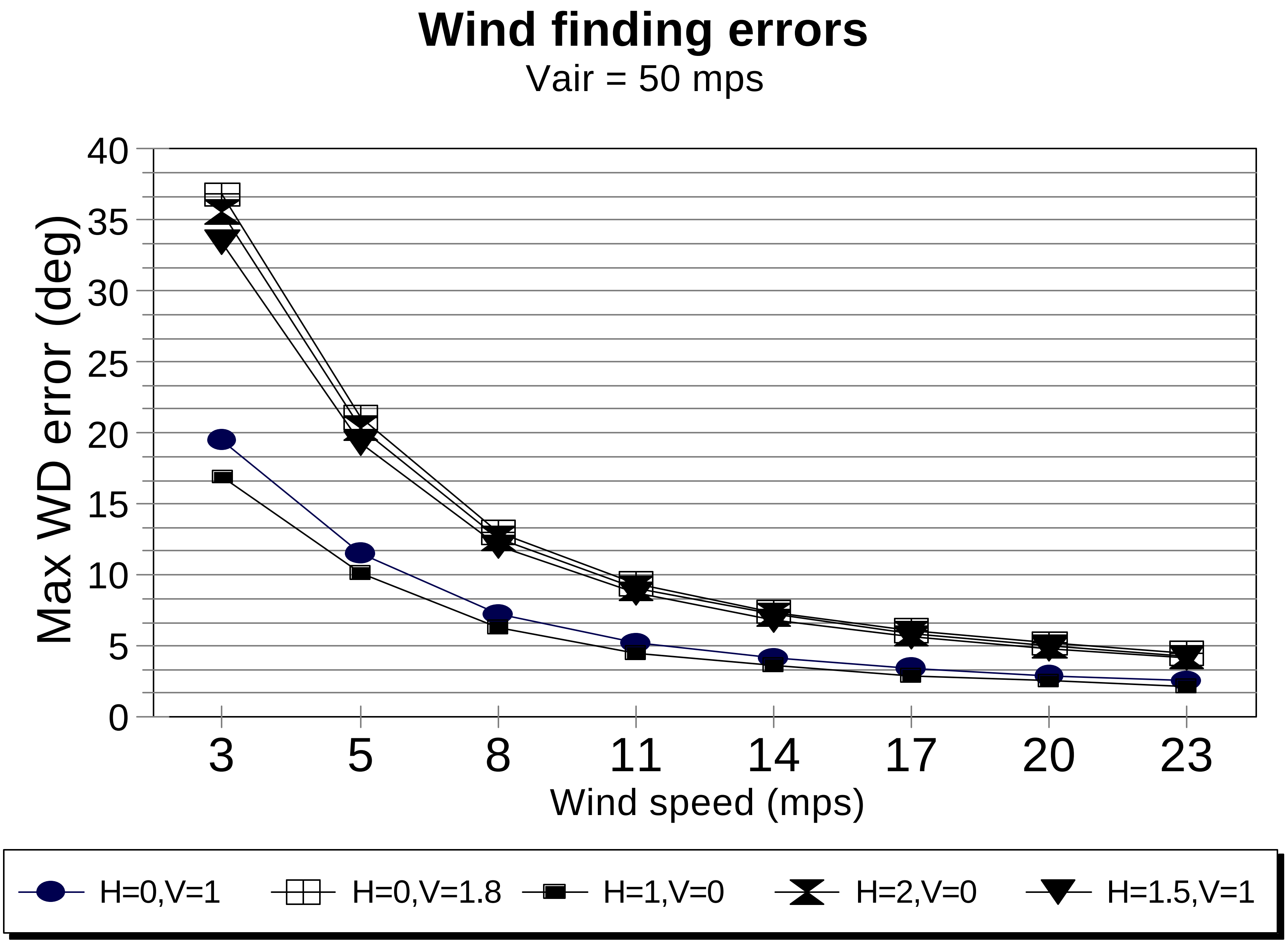
Aircraft & Real-time Sampling Instruments for Meteorology and Pollutants (NO_y, O_3, PM)

Cessna 182 Used for Sampling

Ozone, NO_y and Particle Instruments in Rear of Aircraft

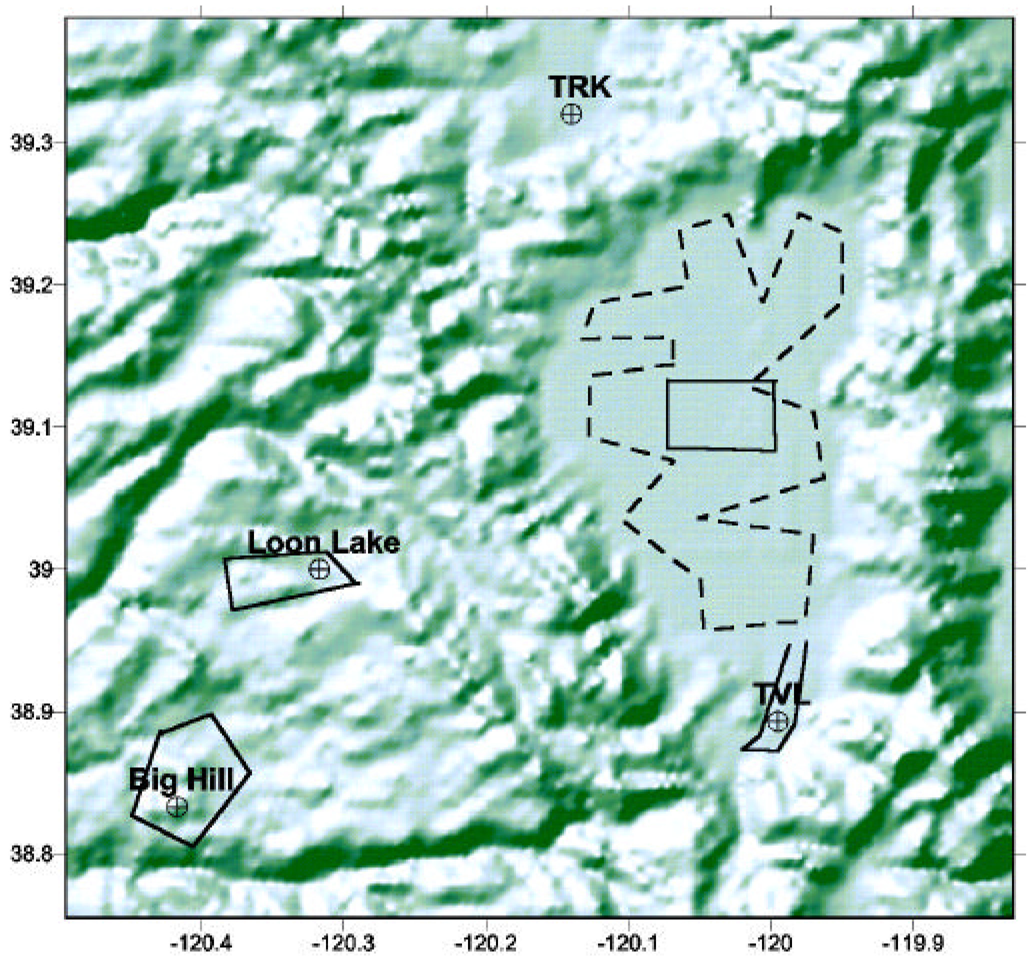
View of Cockpit Instrumentation

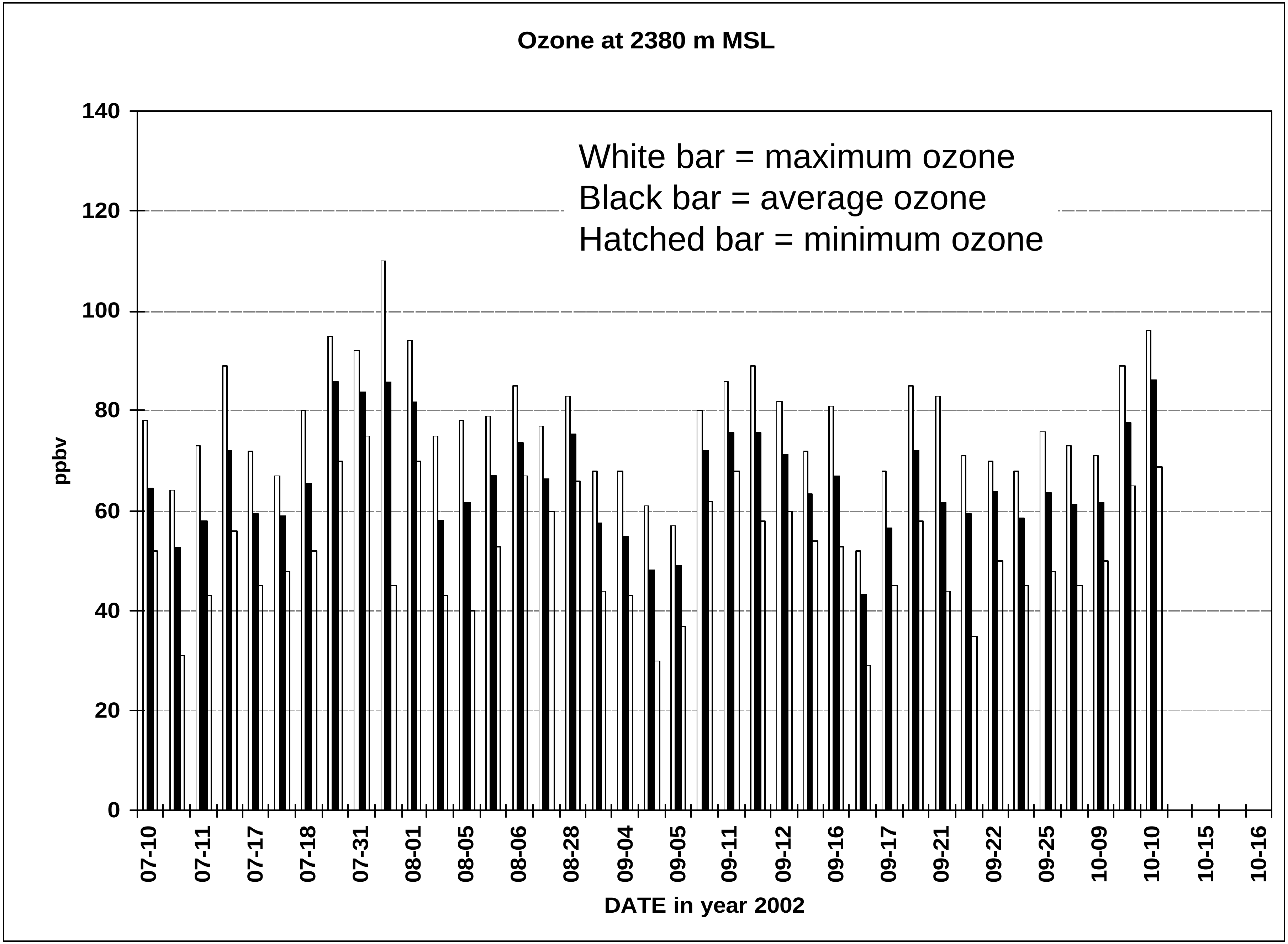
AIMMS-10 Unit Beneath Wing



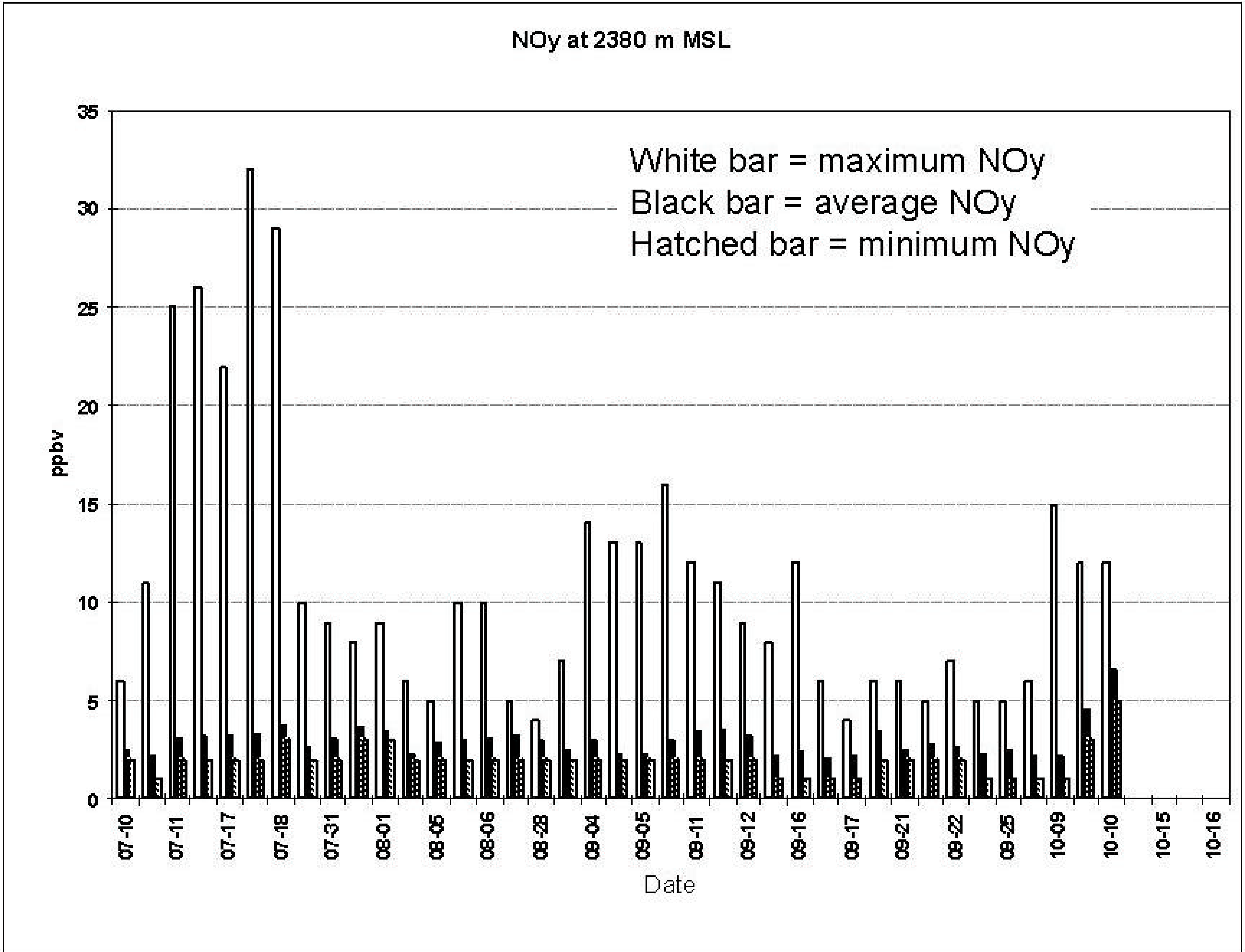
Wind finding errors
Vair = 50 mps
Max WD error (deg)
40
35
30
25
20
15
10
5
0
3
5
8
11
14
17
20
23
Wind speed (mps)
H=0,V=1
H=0,V=1.8
H=1,V=0
H=2,V=0
H=1.5,V=1

Air Sampling Areas at Lake Tahoe

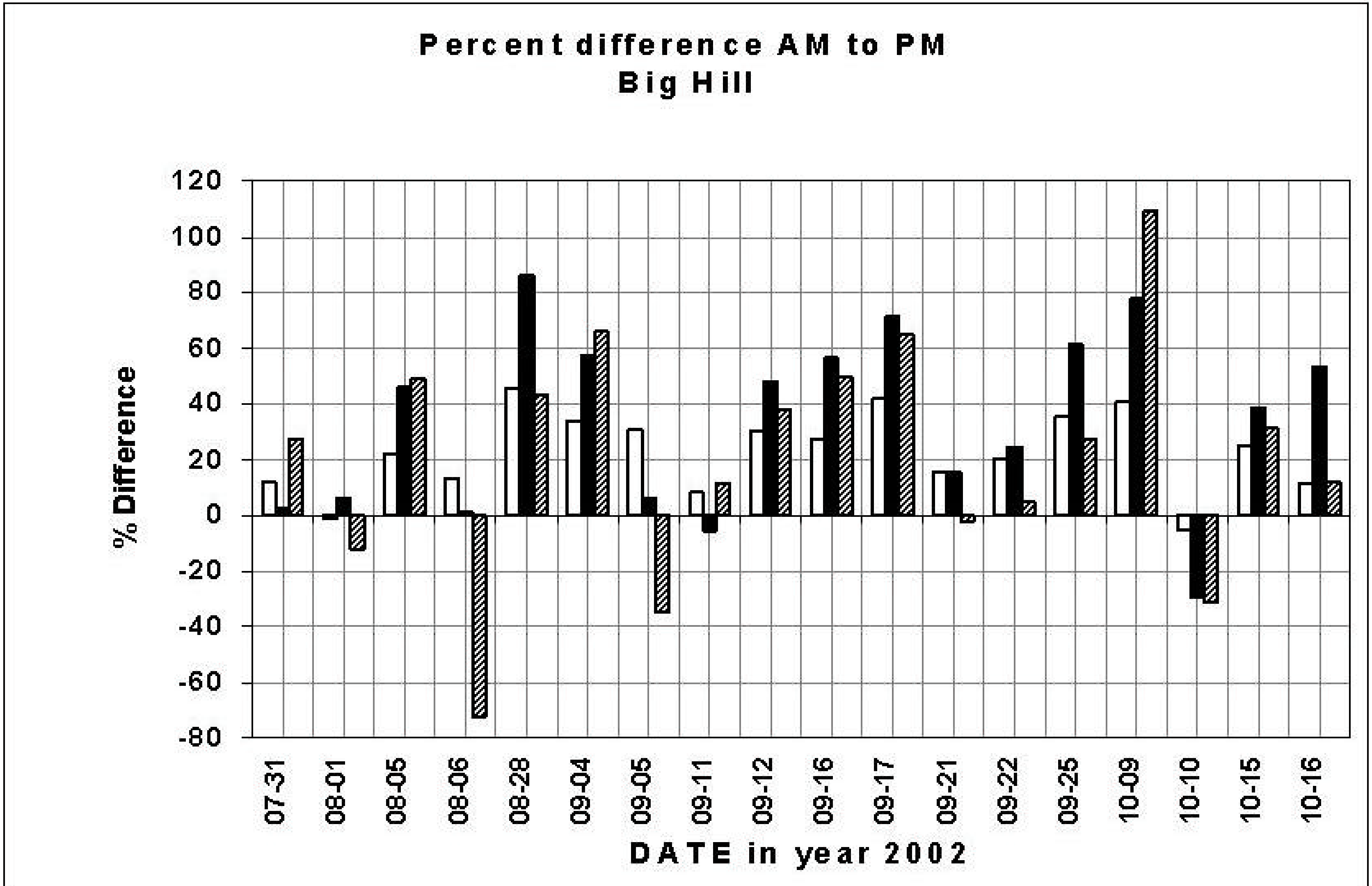




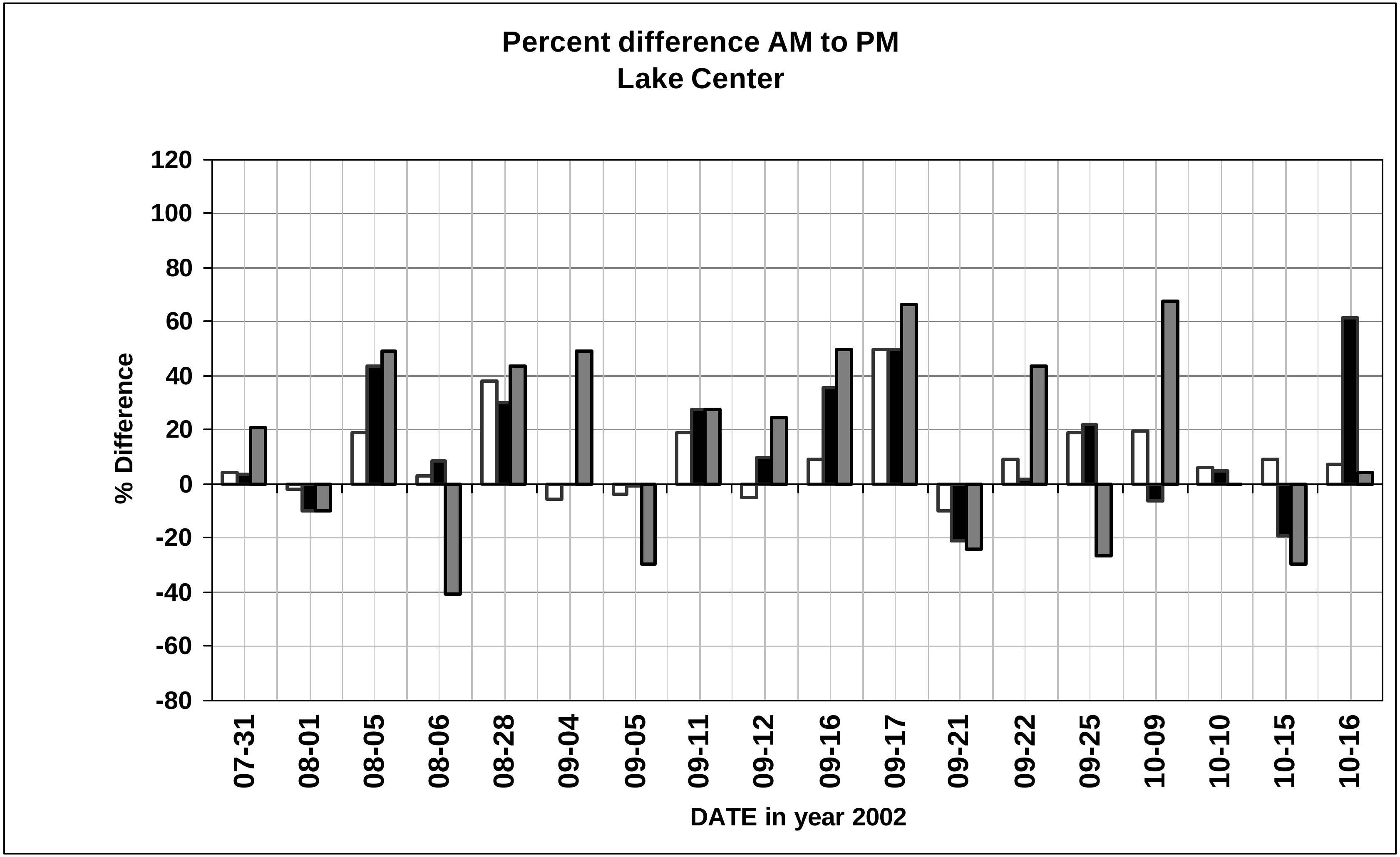
Ozone at 2380 m MSL
White bar = maximum ozone
Black bar = average ozone
Hatched bar = minimum ozone
140
120
100
80
60
40
20
0
ppbv
07-10
07-11
07-17
07-18
07-31
08-01
08-05
08-06
08-28
09-04
09-05
09-11
09-12
09-16
09-17
09-21
09-22
09-25
10-09
10-10
10-15
10-16
DATE in year 2002


NOy at 2380 m MSL
White bar = maximum NOy
Black bar = average NOy
Hatched bar = minimum NOy
ppbv
0
5
10
15
20
25
30
35
07-10
07-11
07-17
07-18
07-31
08-01
08-05
08-06
08-28
09-04
09-05
09-11
09-12
09-16
09-17
09-21
09-22
09-25
10-09
10-10
10-15
10-16
Date

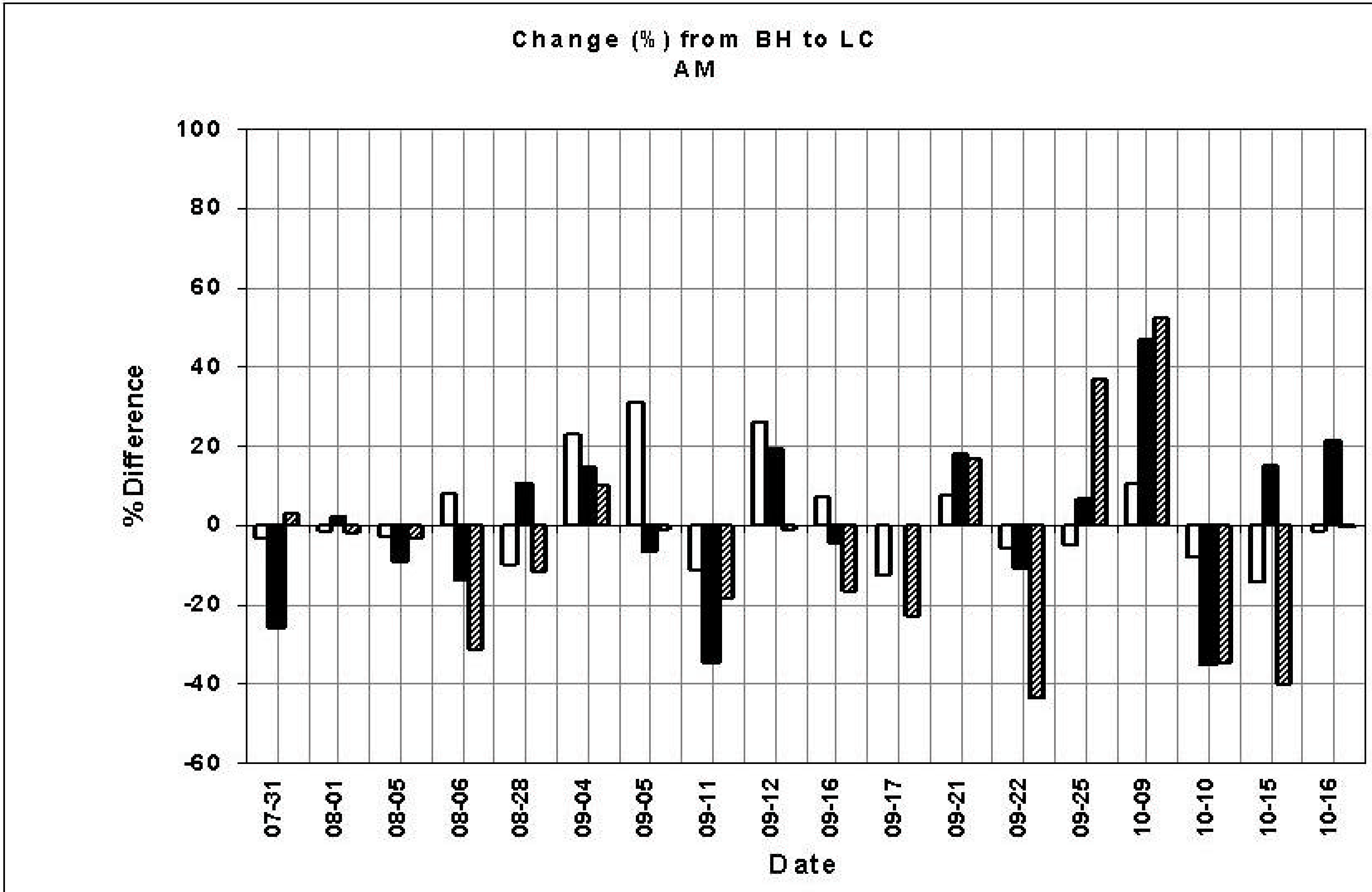
White = Ozone, Black = NOy, Hatched = PC1



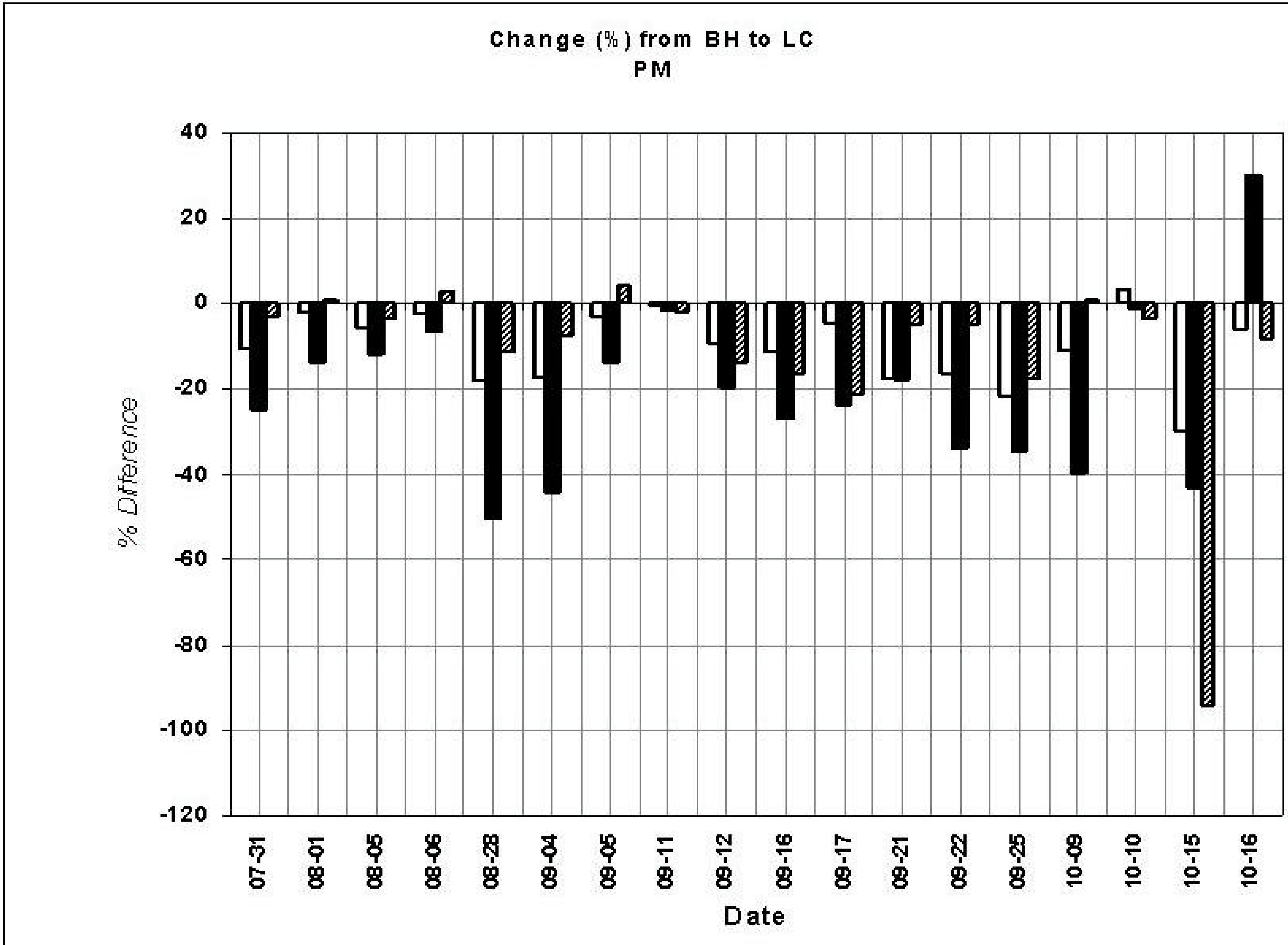
White = Ozone, Black = NOy, Hatched = PC1



White = Ozone, Black = NOy, Hatched = PC1



White = Ozone, Black = NOy, Hatched = PC1

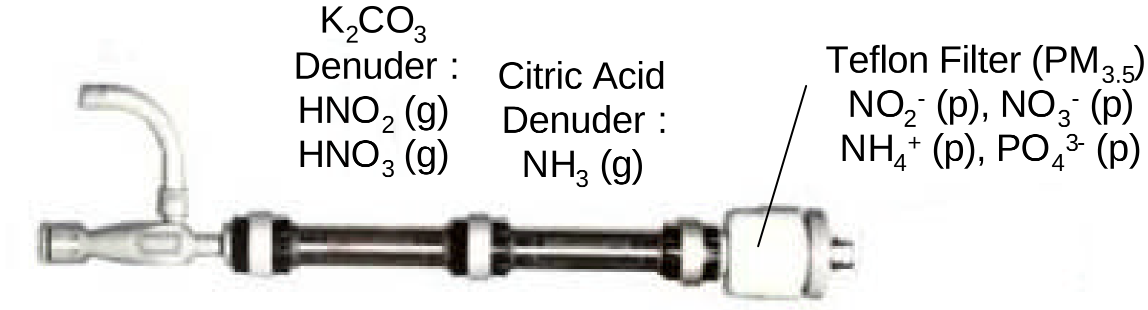


Part 2:

Denuder – Filter Pack (DFP) Measurements of Gaseous and Particulate Nitrogen

Aircraft Denuder / Filter Pack (DFP)

- DFP Apparatus and Analytes

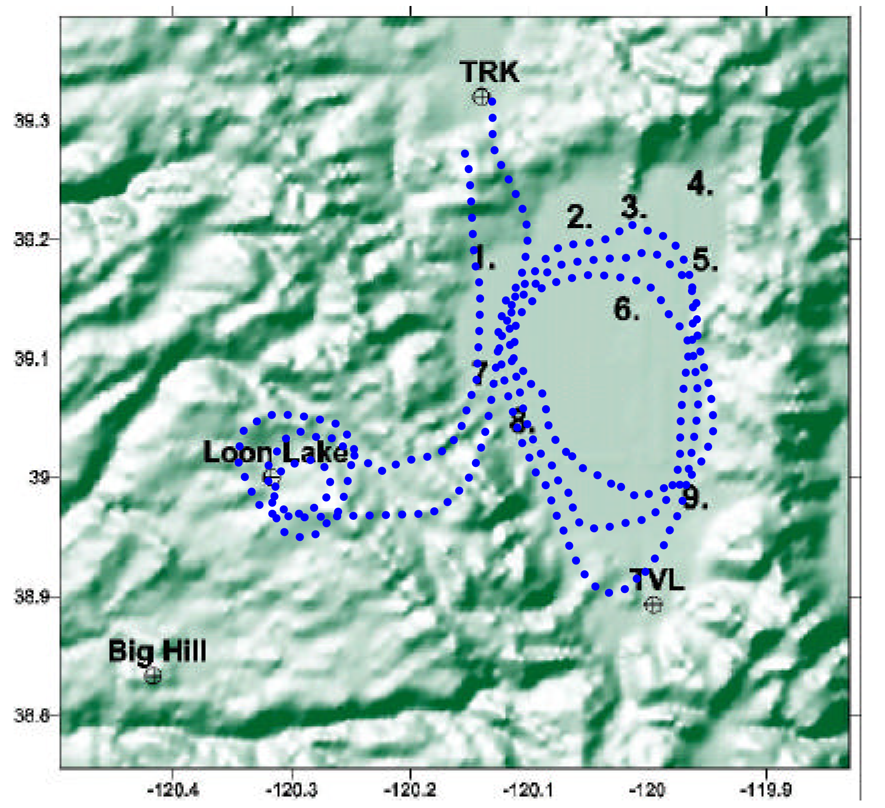


- Extraction and Analysis
  - Samples taken to UCD lab at end of 2nd sampling day
  - Denuders and filters extracted w/ purified water (Milli-Q)
  - Analyzed for inorganic N (IN) with ion chromatography
  - Organic nitrogen (ON) determined by photolysis of extracts

    ON = IN (after photolysis) – IN (before photolysis)

    More difficult to quantify ON compared to IN because of multiple steps and because it is determined by difference

DFP Sampling



- For Each Flight
  - Sampled at 7800’ (2380 m)
  - Sampled at 6800’ (2070 m)
  - Air volume sampled =
    1.00 ± 0.16 m^3
  - Took sounding at Loon Lake
- Sampling Schedule
  - 2 DFP samples for each flight (one each at 2380 and 2070 m)
  - One flight in morning & one in afternoon on each sampling day
  - Usually sampled on two consecutive days
  - Samples taken from July 10th – October 16th, 2002
  - Total of 22 days of sampling and 86 samples

DFP Blanks and Blank Corrections

- Blanks
  - A blank DFP was collected on nearly every sample day
  - Blanks extracted and analyzed in the same way as samples
  - For each analyte, the average and standard deviation of the blanks were calculated for the entire sampling campaign

- Blank Corrections
  - The average blank value was subtracted from each sample value for a given analyte
  - For uncertainty calculations, the relative standard deviation of the blank values (RSD = σ/average) for a given analyte was used as an approximation of the sample RSD

Sample and Blank Statistics

Blank-Subtracted Sample Values (nmol N m^{-3}-air)

	Gaseous Species (n = 86)				Particulate Species (n = 52)				Gas + Particle [a]	
	HNO_2 (g)	HNO_3 (g)	NH_3 (g)	ON (g)	NO_2^- (p)	NO_3^- (p)	NH_4^+ (p)	ON (p)	TIN	TN
Min	0.1	0.6	2.4	0.0	< LOD	0.8	0.2	0.4	21.7	32.5
Max	11.5	59.9	312.7	102.9	< LOD	13.2	33.6	33.0	342.7	362.1
Median	0.8	25.8	45.3	5.9	< LOD	1.8	10.0	3.0	85.7	106.4
Mean	1.4	25.1	65.3	13.3	< LOD	2.2	12.1	6.0	107.4	124.3
Std Dev	1.9	11.7	58.4	21.8	< LOD	2.8	9.4	7.9	69.5	75.9

Field Blank Values (nmol per denuder or filter)

	Denuders (n = 22)				Filters (n = 13)				Denuder + Filter	
	HNO_2 (g)	HNO_3 (g)	NH_3 (g)	ON (g)	NO_2^- (p)	NO_3^- (p)	NH_4^+ (p)	ON (p)	TIN	TN
Mean	0.9	10.1	25.9	21.6	0.0	0.8	3.3	19.5	37.2	82.1
Std Dev	1.1	4.9	12.7	15.2	0.1	0.7	2.4	14.3	10.8	14.7

Ratio of Sample Mean/Blank Mean (assuming 1 m^3 of air for each sample)

Gaseous Species				Particulate Species				Gas + Particle	
HNO_2 (g)	HNO_3 (g)	NH_3 (g)	ON (g)	NO_2^- (p)	NO_3^- (p)	NH_4^+ (p)	ON (p)	TIN	TN
1.5	2.5	2.5	0.6	na	2.8	3.7	0.3	2.9	1.5

[a] TIN = Total Inorganic Nitrogen; TN = Total Nitrogen = TIN + ON(g) + ON(p)

- For major species (HNO_3, NH_3, NO_3^-, NH_4^+) samples levels are typically ~ 3 times greater than in blanks: good quantification
- For minor species (HNO_2, NO_2^-, ON) sample values are typically too low to distinguish significantly from blanks: sample values are only qualitative

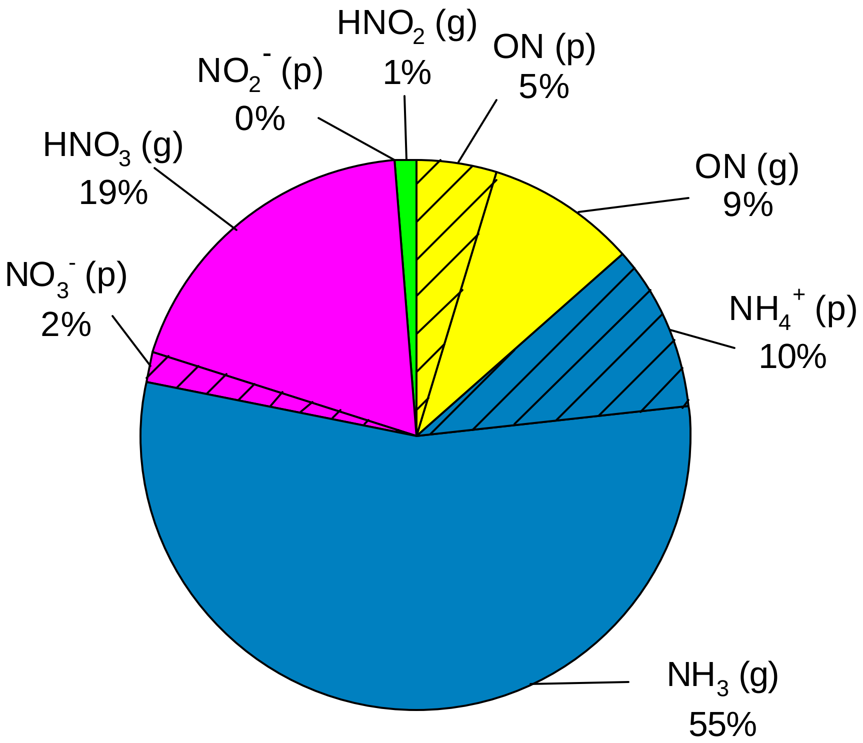
DFP Data Limitations and Problems

- Phosphorus (P)
  - Because of high and variable blank levels of P on the filters, values of P are not reported
  - For P levels measured in the summer of 2001, see Zhang et al. (Environ. Sci. Technol., 2002, 36, 4981-4989; copy is on this CD)
- Missing PM Data
  - Because of filter blank problems, we do not report particle data during July 7th – Sept. 5th
  - However, PM was typically a small component of the N budget
- Boat Samples
  - Because of high blank levels for all N species, we do not report values from the boat samples taken in winter/spring 2003.

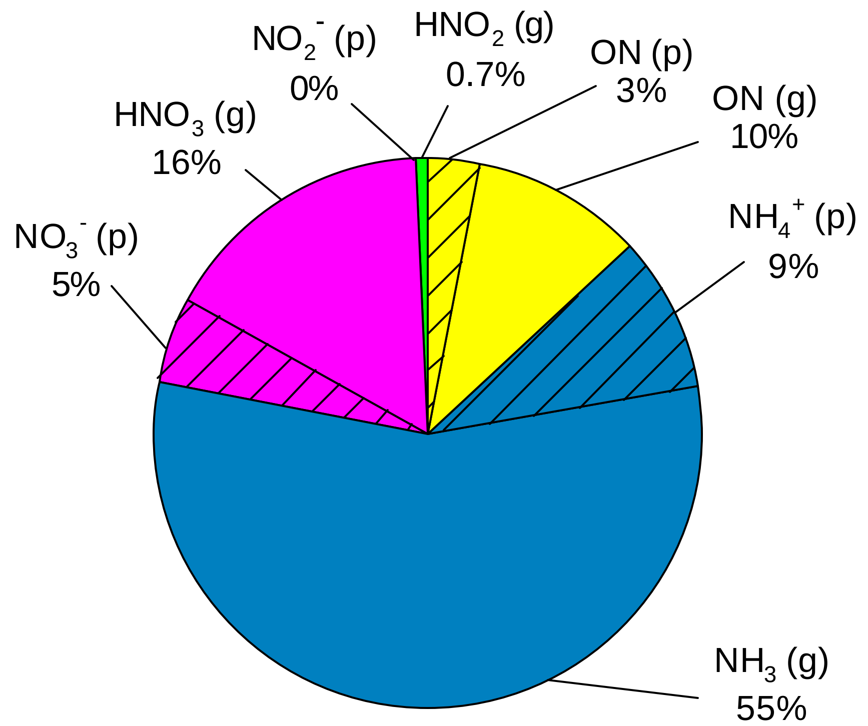
Nitrogen Distributions: 2002 vs. 2001

(Summer 2001 data from Zhang et al., 2002)

2002 Average *(N = 52)*
(Avg. $TN_{(g+p)}$ = 124 ± 76 nmol N m^{-3}-air)

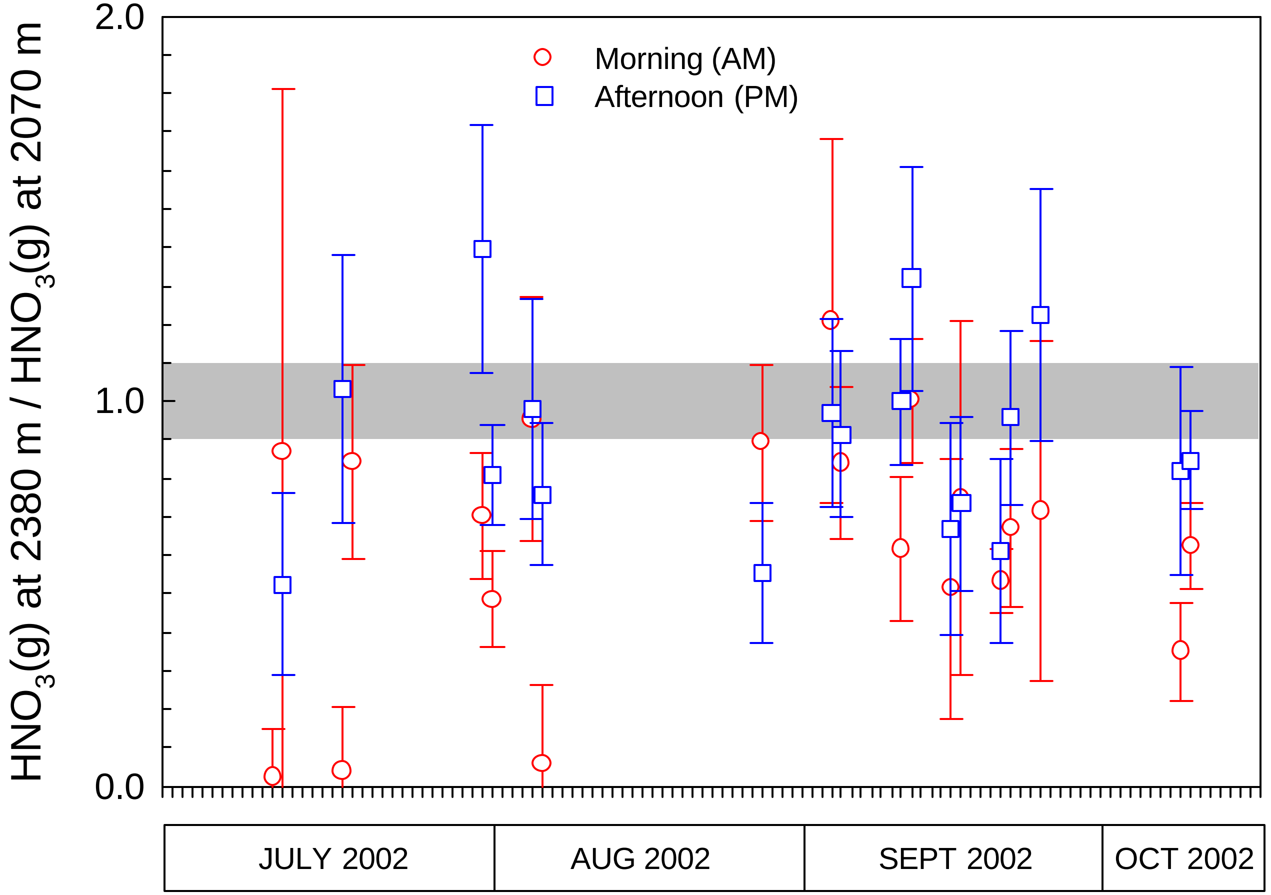


2001 Average *(N = 8)*
(Avg. $TN_{(g+p)}$ = 140 ± 33 nmol N m^{-3}-air)



- Very similar distributions and TN levels between the two years
- Approx 65% NH_3/NH_4^+, 20% HNO_3/NO_3^-, 14% ON, 1% HNO_2

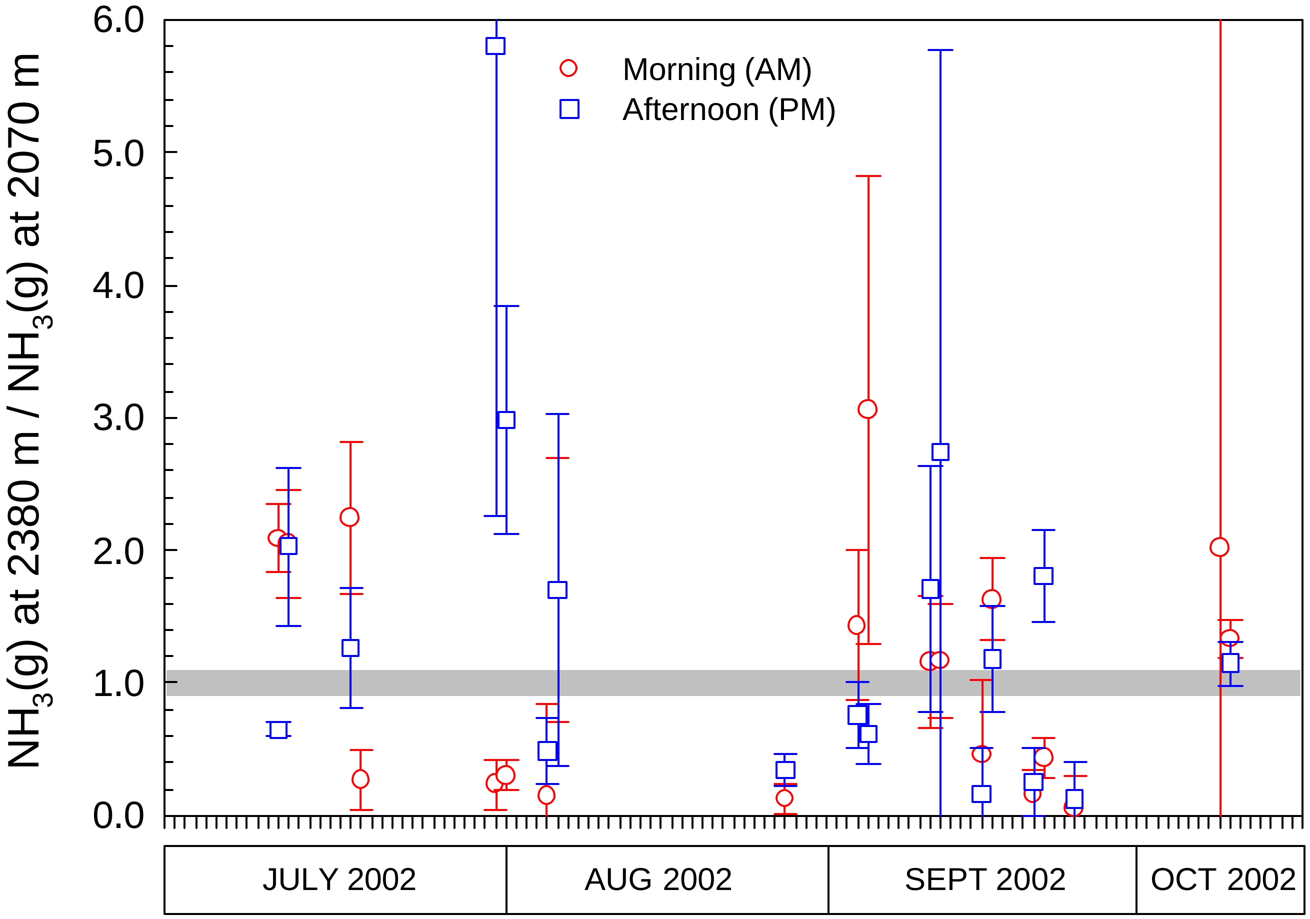
Vertical Distribution of $HNO_3(g)$



- Each point represents a single flight
- Average Ratio in Morning ($\pm\sigma$):
  0.63 ± 0.32
  (90% are < 1)
- Average Ratio in Afternoon:
  0.90 ± 0.25
  (72% are < 1)

- HNO_3 is typically higher at 2070 m compared to 2380 m, especially in AM
- Suggests a significant in-basin source for nitric acid (likely via NO_x)

Vertical Distribution of NH_3(g)

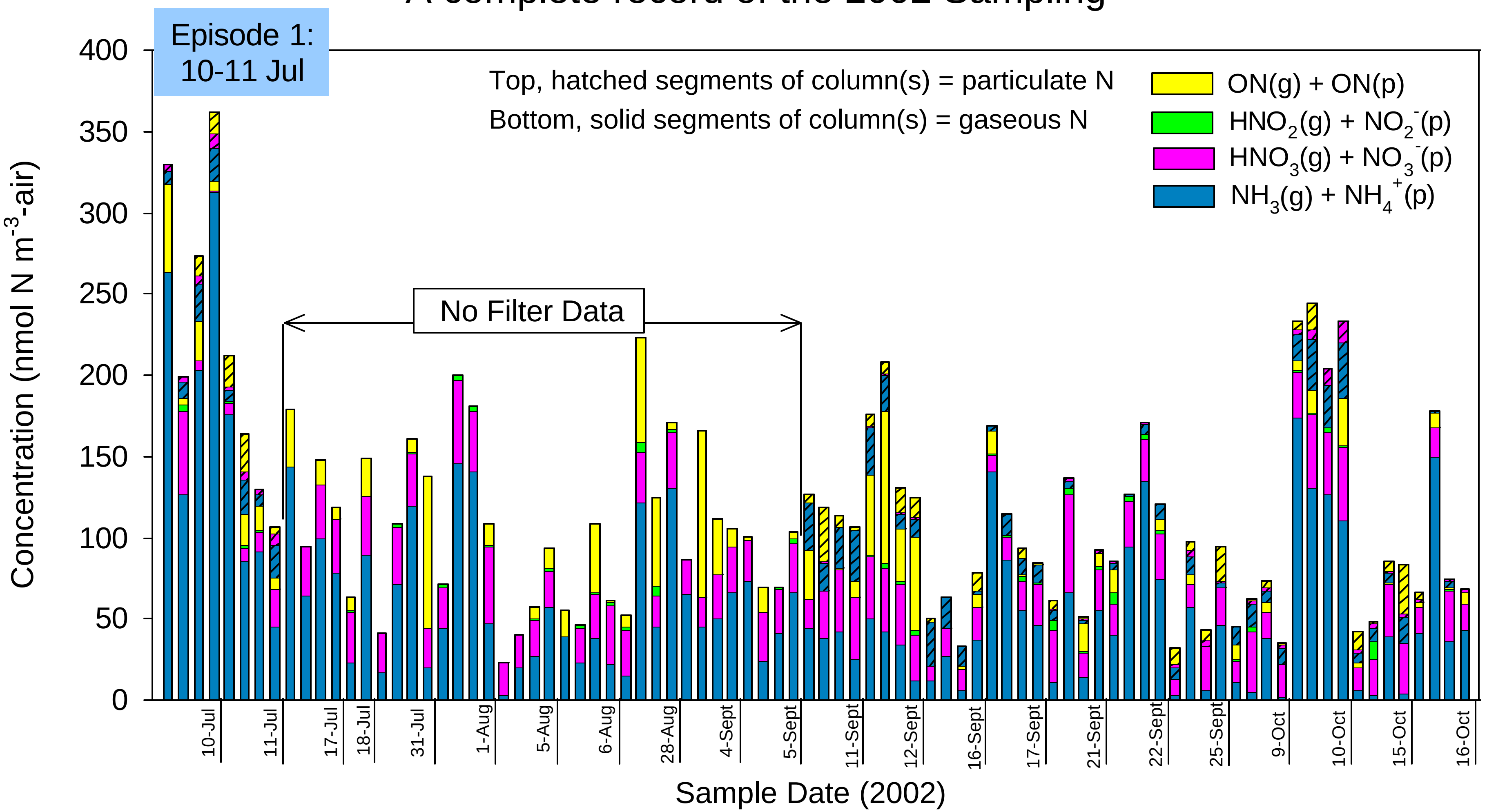


- Each point represents a single flight
- Average Ratio in Morning ($\pm \sigma$):
  1.10 $\pm$ 0.90
  (45% are < 1)
- Average Ratio in Afternoon :
  1.43 $\pm$ 1.38
  (44% are < 1)

- NH_3 is slightly higher at higher altitude (2380 m), but not significantly so
- Vertical gradient is more significant if lowest conc. samples are omitted (e.g., as in UCD presentation from October 2002)

Variability in N Amounts and Speciation

A complete record of the 2002 Sampling

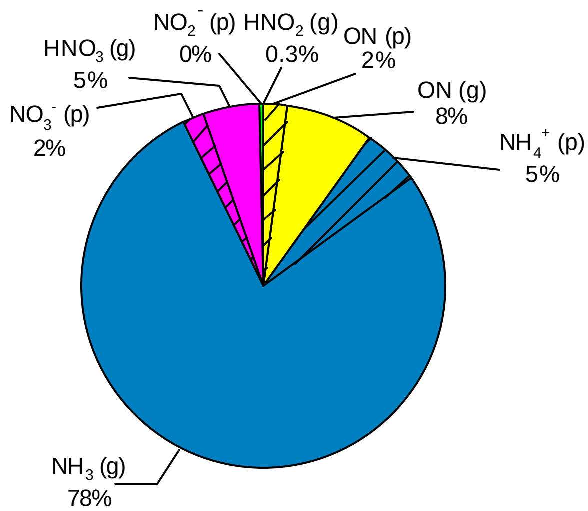


- High variability suggests very complicated & variable sources & transport
- Examine three episodes (pairs of sampling days) as examples

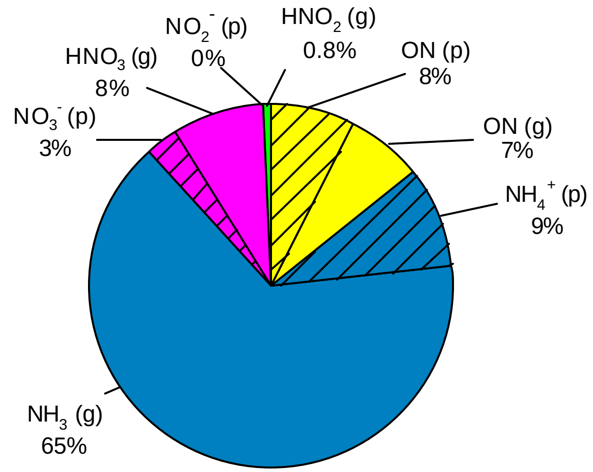
Episode 1: 10 – 11 July, 2002

- 10 July 2002 had some of highest TN concentrations we measured
- Average TN level on 11 July was ½ of the 10 July average
- NH3(g) & NH_4^+(p) were dominant species on both days, accounting for 70-80% of N

10 - July - 02
(Avg. $TN_{(g+p)}$ = 291 ± 71 nmol N m^{-3}-air)

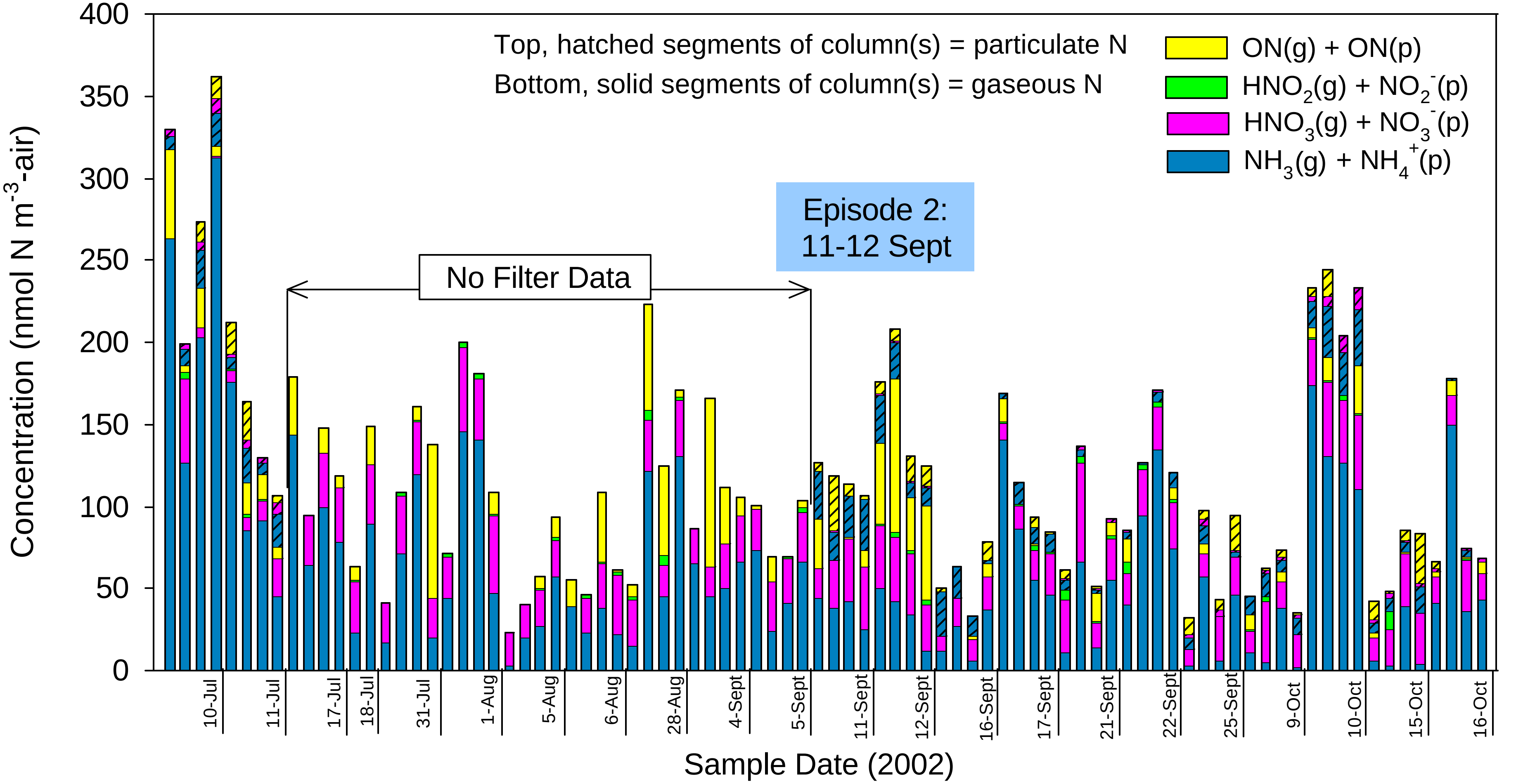


11 - July - 02
(Avg. $TN_{(g+p)}$ = 153 ± 46 nmol N m^{-3}-air)



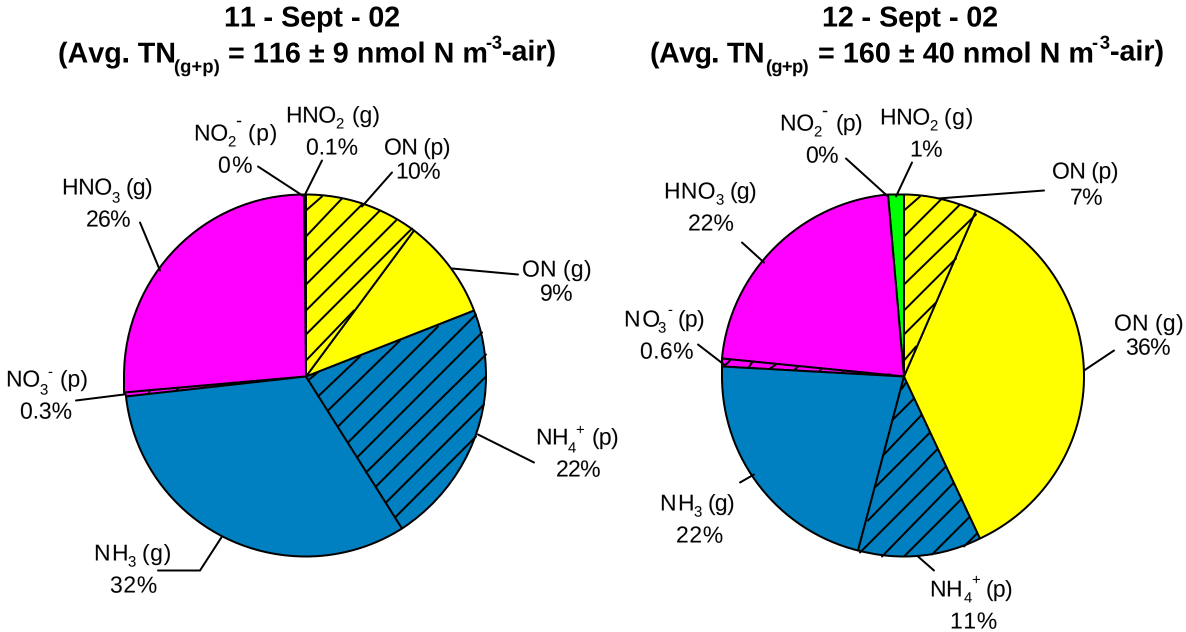
- Temperatures high both days (24 – 30 °C when sampling)
- HYSPLIT trajectories suggest regional pollution episode of somewhat stagnant air from 08 – 10 July, being diluted with flow from NE on 11 July
- Emissions from a small fire observed inside the basin (SSE of the lake) could have also contributed to high pollutant levels

Episode 2: 11 – 12 September, 2002



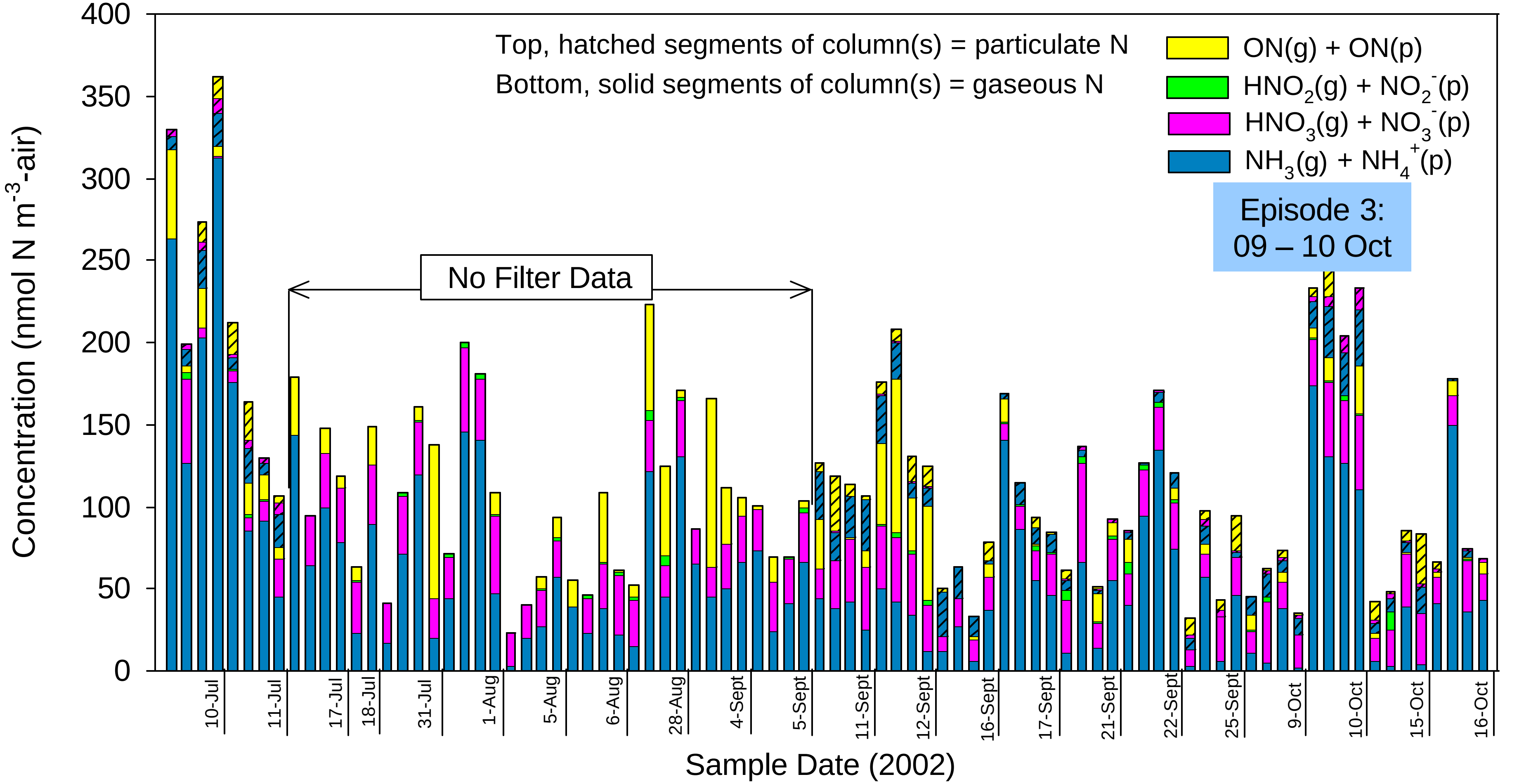
Episode 2: 11 – 12 September, 2002

- Moderate TN levels, increasing by ~ 40% from 11th to 12th
- Large shift in N speciation, with ON fraction approximately doubling between 11th and 12th
- HYSPLIT back trajectories indicate air on these 2 days was from SW Oregon, with stronger influence on 2nd day.



- Massive Biscuit fire in SW Oregon burned from 13 July (started) to 05 Sept (contained) to 09 Nov (extinguished), 2002. Burned 500,000 acres.
- Our 2001 samples suggested ON is a marker for aged forest fire smoke
- 2002 results suggest that OR forest fire emissions affected Lake Tahoe during this episode, especially on 2nd day.

Episode 3: 09 – 10 October, 2002



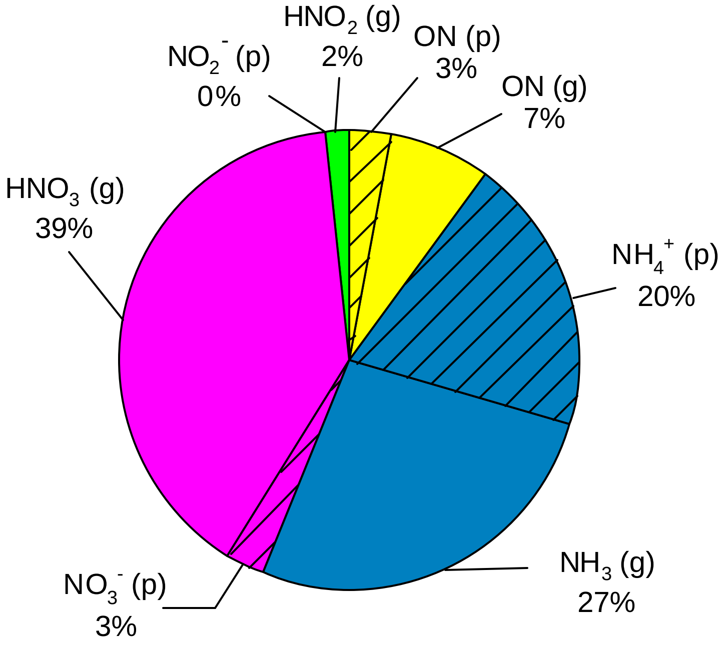
Episode 3: 09 – 10 October, 2002

Chemical Measurements

- Dramatic shift in levels of N between two days of episode
  Very low N on 9th, but TN concentration quadruples by 10th
- Large shift in N speciation occurred simultaneously
  Clean day (9th) has roughly equal amounts of HNO_3 and NH_3/NH_4^+
  Dirty day (10th) is dominated by NH_3(g) & NH_4^+(p)

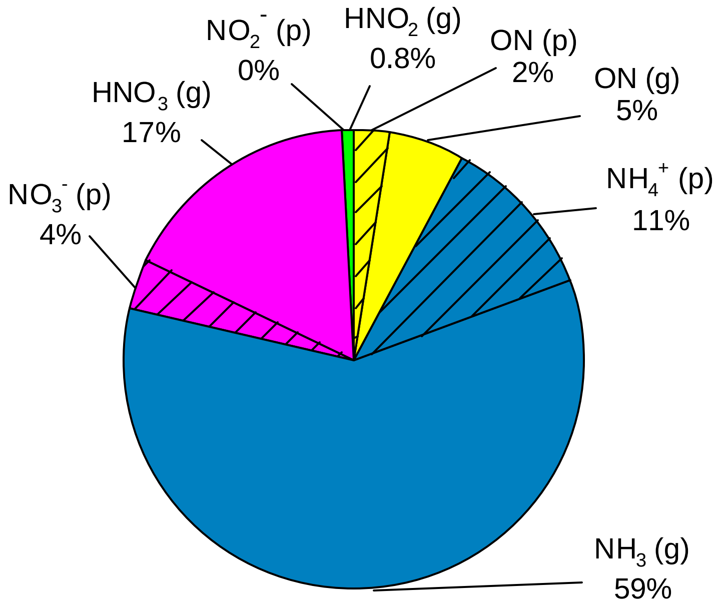
09 - Oct - 02

(Avg. $TN_{(g+p)}$ = 54 ± 17 nmol N m^{-3}-air)



10 - Oct - 02

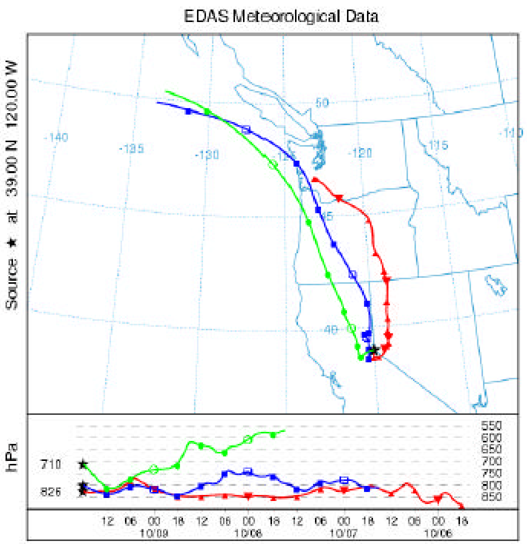
(Avg. $TN_{(g+p)}$ = 229 ± 17 nmol N m^{-3}-air)

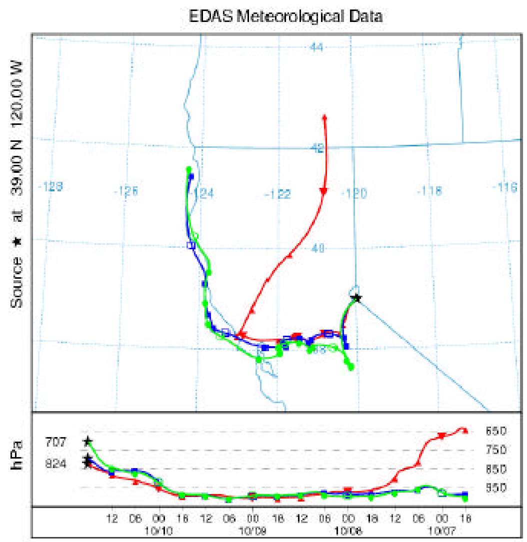


Episode 3: 09 – 10 October, 2002

Meteorology

- Local winds (e.g., from Tahoe City Coast Guard pier)
  Show strong SW winds on 10th, consistent with…
- HYSPLIT back trajectories ending at Tahoe
  Oct 9th: Marine air that had passed over central OR
  Oct 10th: Air that had crawled through the Central Valley for ~ 2 days and then pushed up to Tahoe





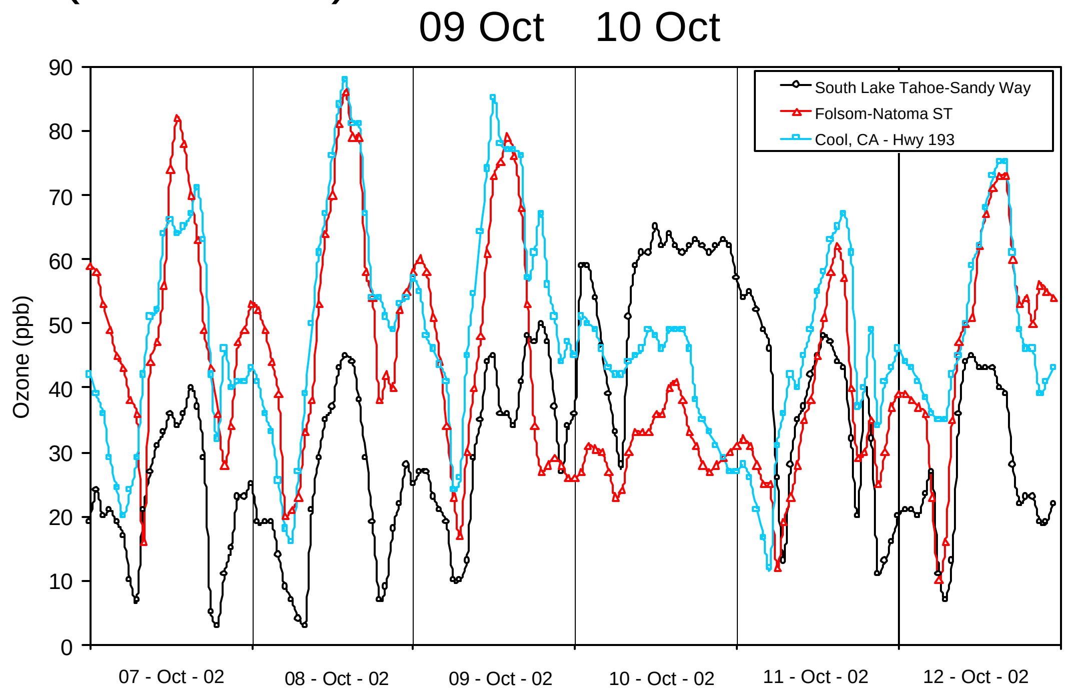
NOAA HYSPLIT, 4-day back trajectories ending at Tahoe at 10 am PST on 09 Oct (left) and 10 Oct (right).

Ending heights: red = 2070 m, blue = 2380 m, green = 3070 m.

Episode 3: 09 – 10 October, 2002

Interpretation and corroborating O_3 data

- Previous data suggest that this episode is a “Valley washout”, where pollutants from the CV are pushed into the Tahoe Basin
- ARB ozone data is consistent with this interpretation
  - 07 – early 09 October: relatively high ozone (peaks of 80 – 85 ppbv) in Valley (Folsom; red line) and Foothills (Cool; blue), but low (< 45 ppbv) at South Lake Tahoe (SLT; black)
  - 09 Oct (late) – 10 Oct: O_3 in Folsom and Cool falls as SLT O_3 rises, exceeding Valley levels
  - By the morning of 11 Oct all 3 sites have very low ozone (~ 15 ppbv), suggesting pollution has been mostly pushed through Tahoe Basin



Summary of DFP Data

- N concentrations were highly variable, ranging from ~ 30 to 360 nmol N m^{-3}-air
- Ammonia and ammonium were typically the dominant N species, accounting for approximately 2/3 of N, on average
- Atmospheric levels of N in the Tahoe air basin appear to be affected by a wide variety of “sources”, including
  - Regional background pollutant levels
  - In-basin emissions
  - Local and distant forest fires
  - The Central Valley
- Limitations of our DFP data
  - Only provides “snapshots” of certain days, not a continuous record or climatology of atmospheric N.
  - Source identification is limited by a number of factors, including lack of meteorological data inside and upwind of Tahoe Basin

- Annular Denuder / Filter Pack System