

Measurements of NO_y and HNO₃ at a Rural-Forested Site in the Southern Appalachians

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NADP Fall Science Meeting

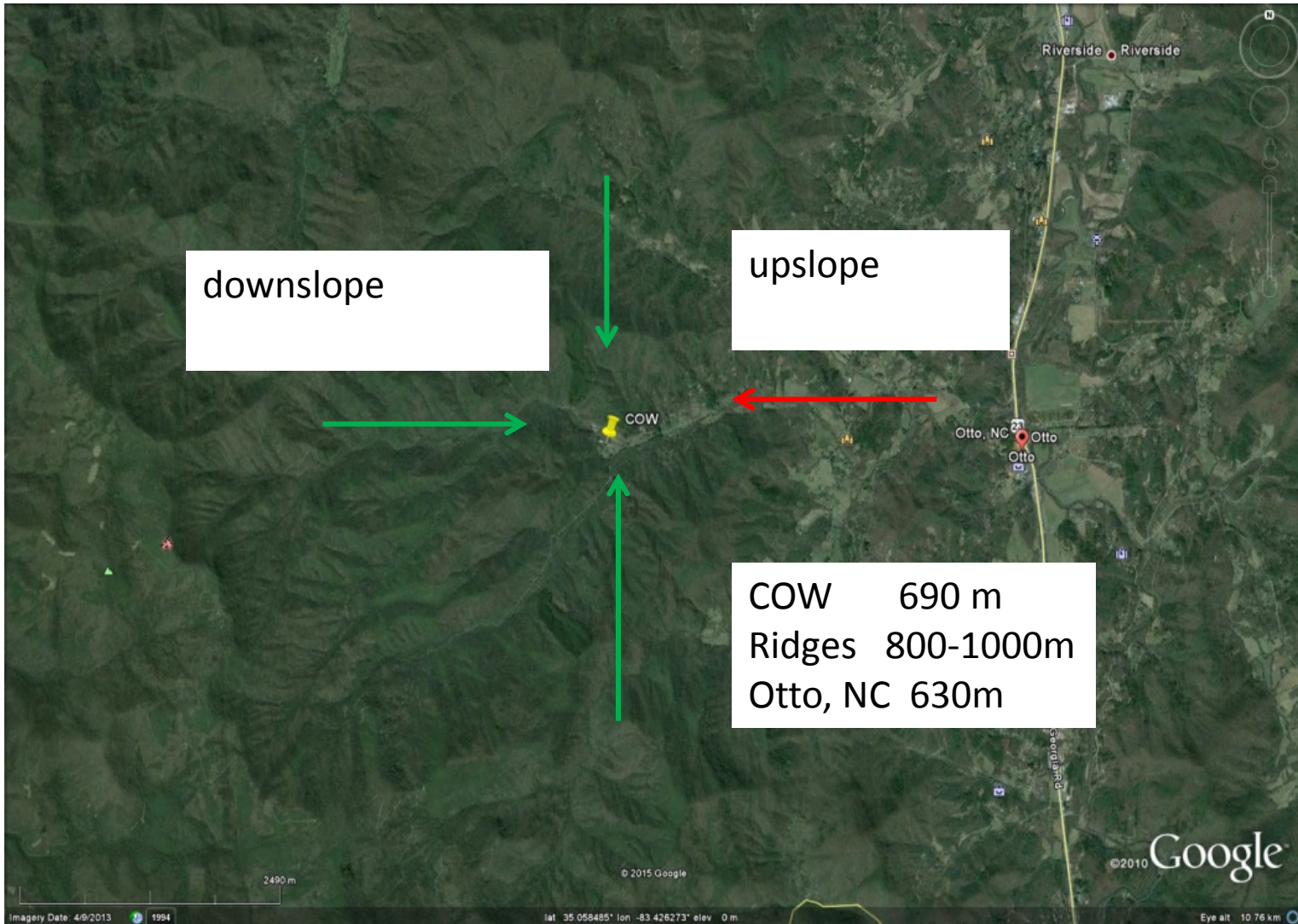
Santa Fe, NM

11/03/16

SEARCH Participation in Coweeta Experiments

- Overall Objective
 - Assist USEPA Development/Improvement of SO_x/NO_x transfer functions for Southern Appalachians (complex terrain; acidity and nitrogen deposition vs. CLs)
- SEARCH Contribution
 - Provide NO_y/HNO₃/PANs/ANs to help close the NO_y budget
- USEPA Campaign Schedule
 - Summer 2015 (Aug 4-Aug 22)
 - Fall 2015 (Oct 8-Oct 22)
 - Spring 2015 (Apr 21-May 12)
 - Summer 2016 (Jul13-Aug 3)
- Near-continuous operations August 2015-August 2016

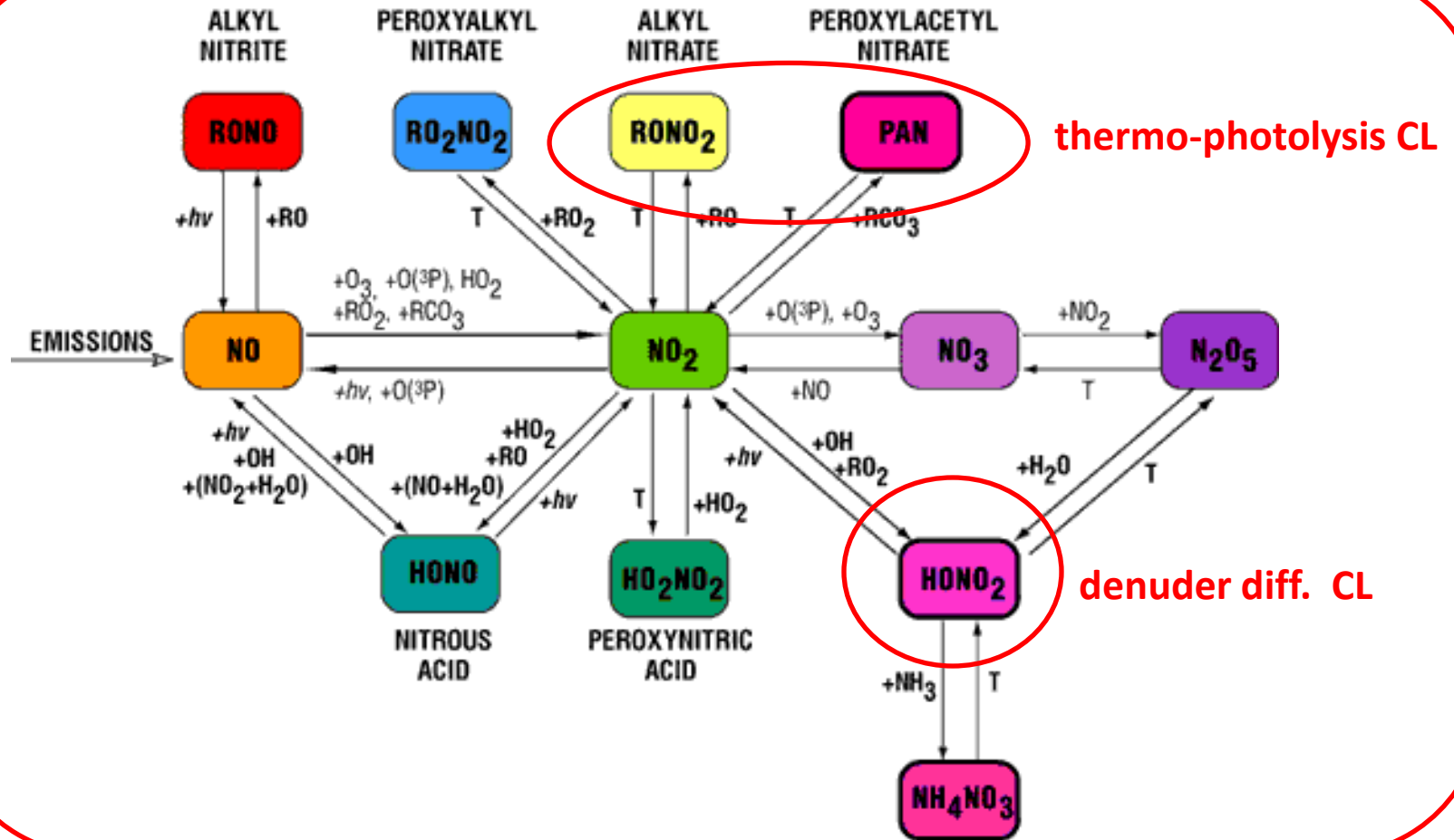
General Environs



Measurement Locations



SEARCH NO_y Composition Measurements at Coweeta



NO_y catalytic reduction CL

SEARCH NO_y/NO_y* (HNO₃) Analyzer

- Continuous 2-Channel Denuder Difference Method
- NO_y Channel (undenuded) measures gaseous and particulate NO_y (340C Mo converter)
- NO_y* channel measures residual NO_y downstream of a KCl-coated annular denuder (340C Mo converter)
- $\text{HNO}_3 = \text{NO}_y - \text{NO}_y^*$
- Assumes all KCl-reactive NO_y is HNO₃
 - Tested for NO, NO₂, PAN and simple alkyl nitrates
 - Potentially untrue for HONO, N₂O₅, NO₃; pernitric acid; however daytime concentrations in the low ppt range due to photolysis, so contamination most likely at night and daybreak

Monitor for Aerosols and Gases in Ambient Air (MARGA)

Metrohm Applikon

- **Online ion chromatography**
 - Gases – wet rotating denuder
 - Aerosols – steam jet aerosol collector
- **Hourly concentrations**
 - NH_3 , HNO_3 , SO_2 , HONO , HCl , NH_4^+ , NO_3^- , SO_4^{2-} , Na^+ , Cl^- , base cations
- **Internal liquid (LiBr) standard**
- **External multipoint liquid standards**
- **Inlet 1/2" O.D. PFA - 45 cm**
- **Two sample boxes operated at different heights above canopy**

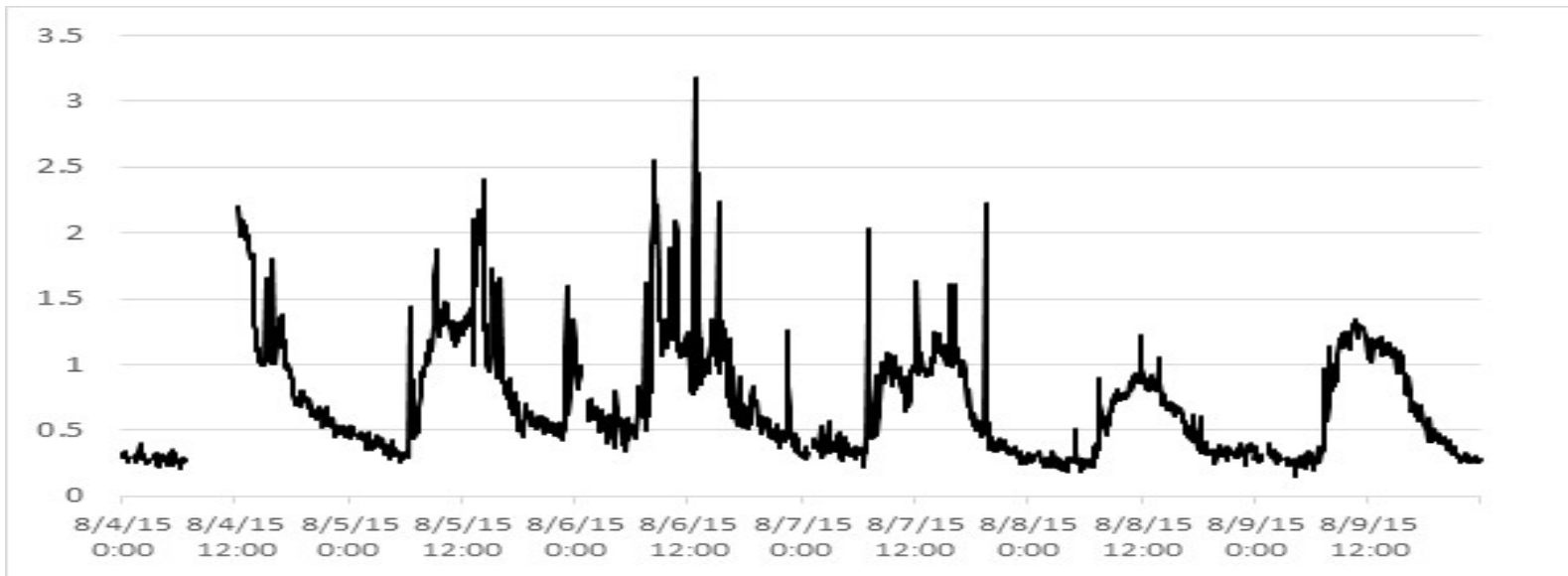


MARGA sample box above forest
Coweeta Hydrologic Laboratory

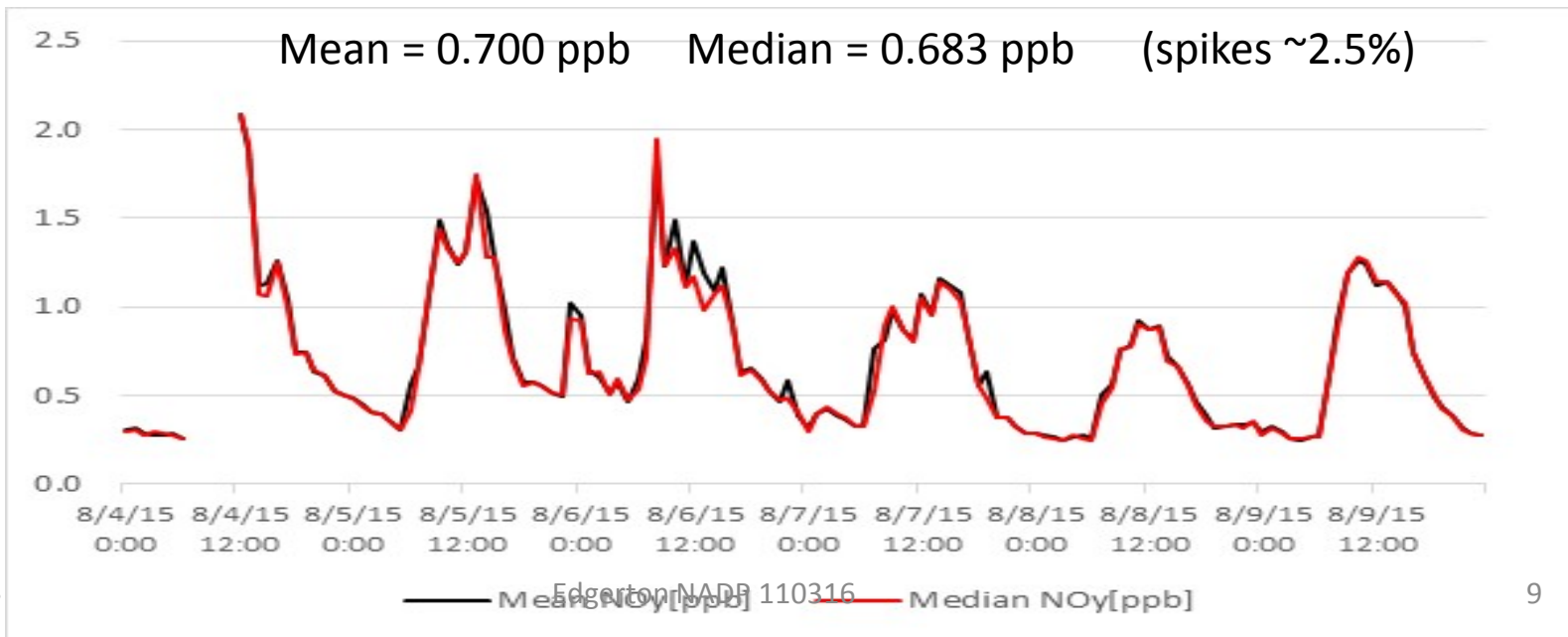
Results

First-Blush NOy at Coweeta-Summer 2015

5-min NOy (ppb)

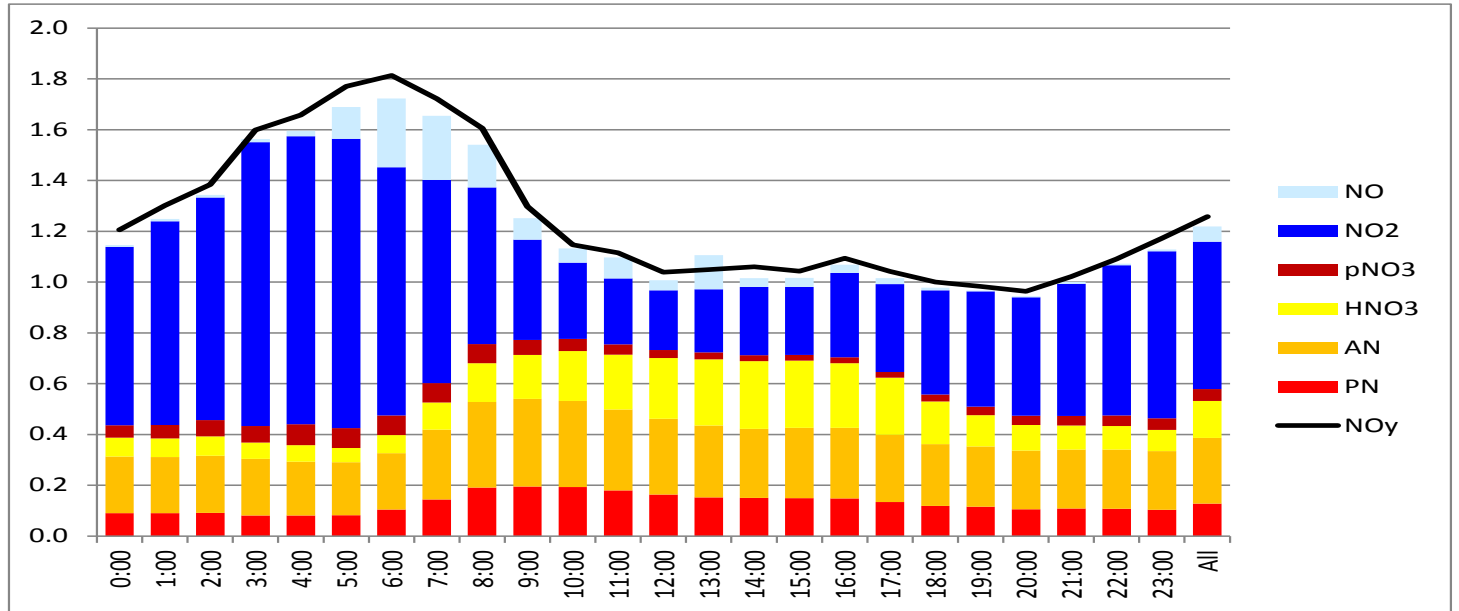


1-hr NOy (ppb)

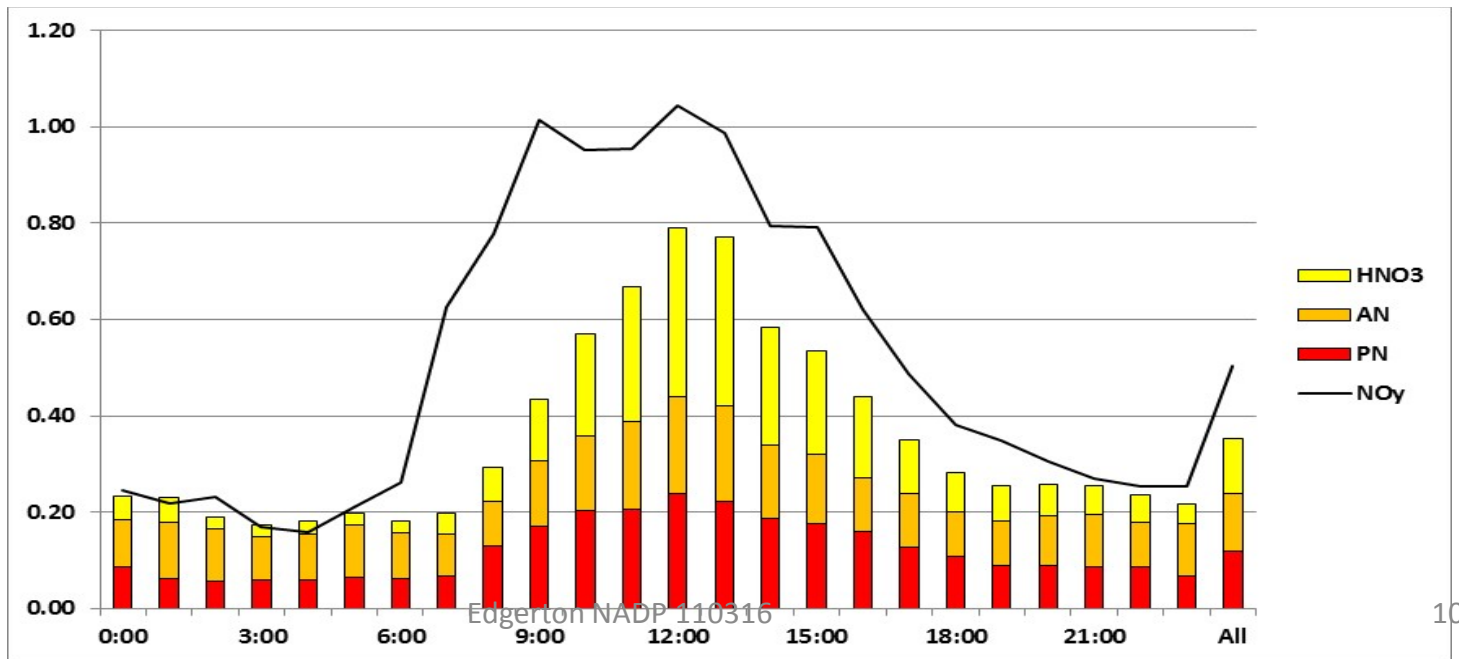


NO_y Composition-Measured and Inferred

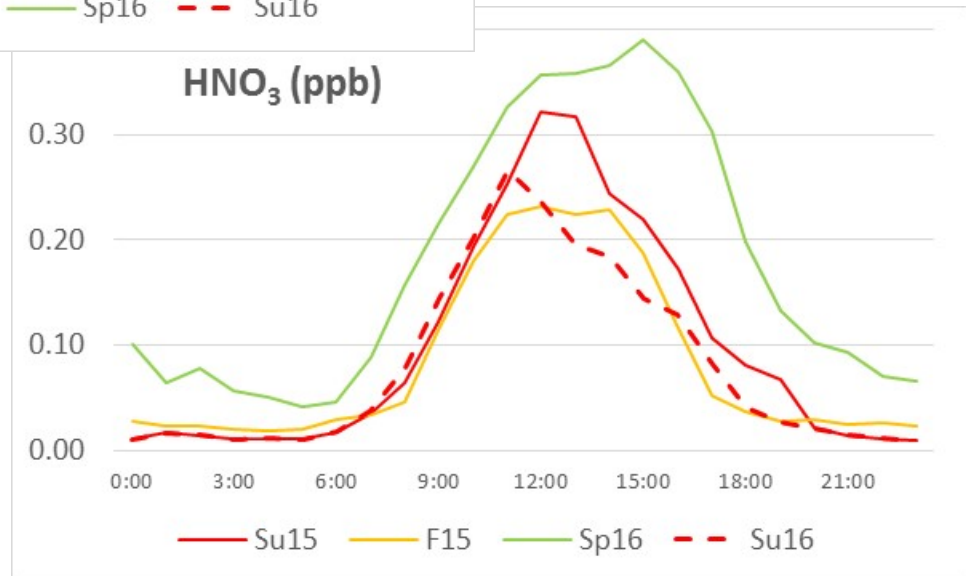
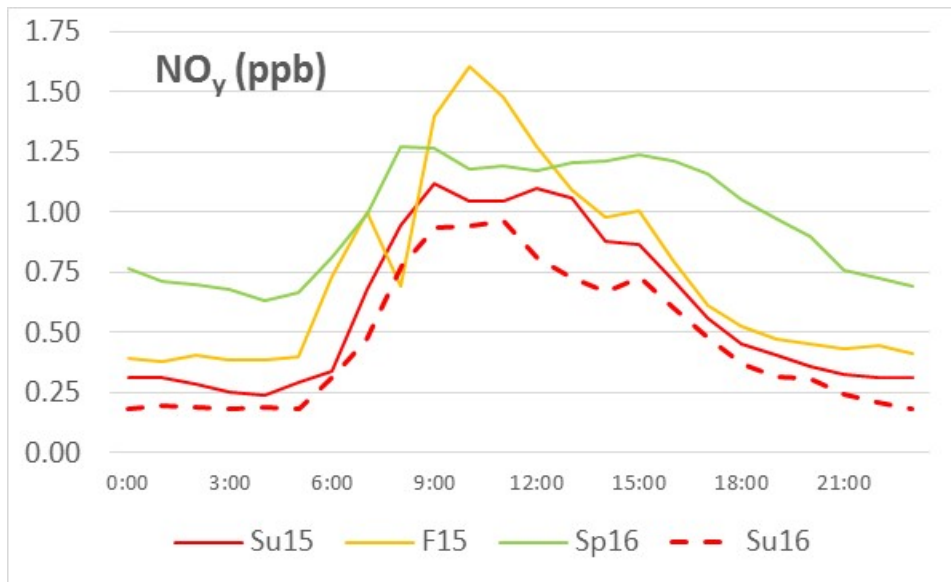
**CTR, AL
Su 2013
(SOAS)**



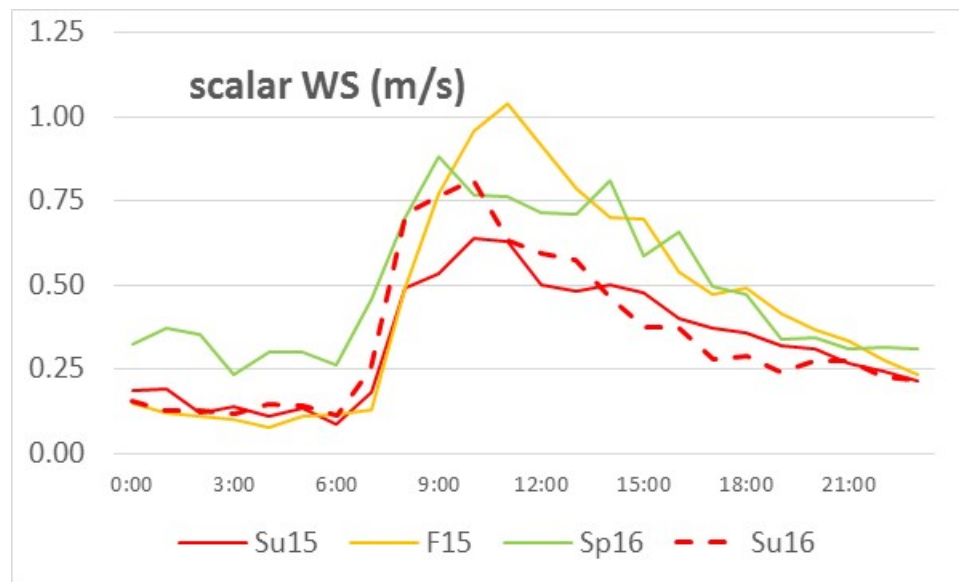
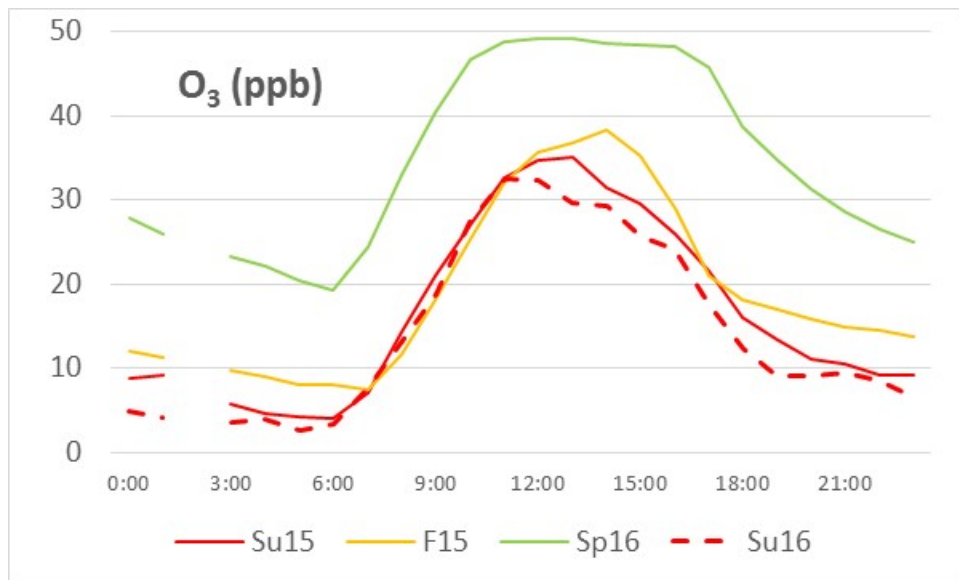
**COW, NC
Su 2015**



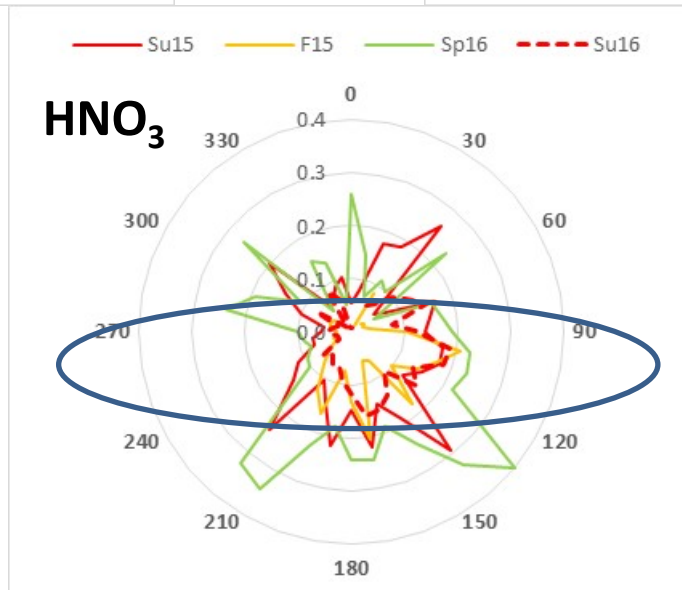
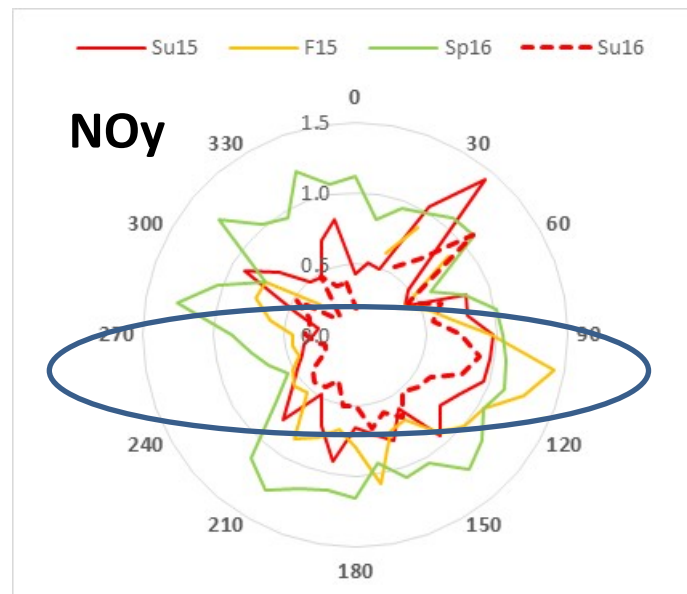
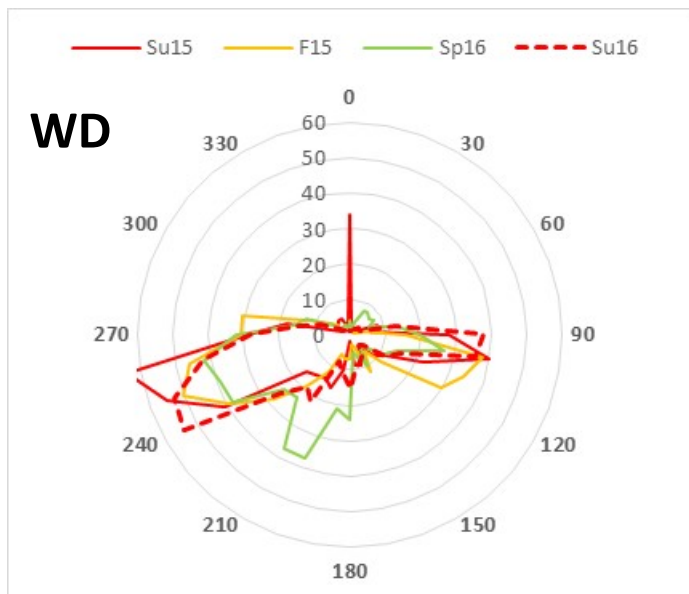
Diurnal Profiles for NO_y and HNO₃



Diurnal Profiles for O₃ and WS



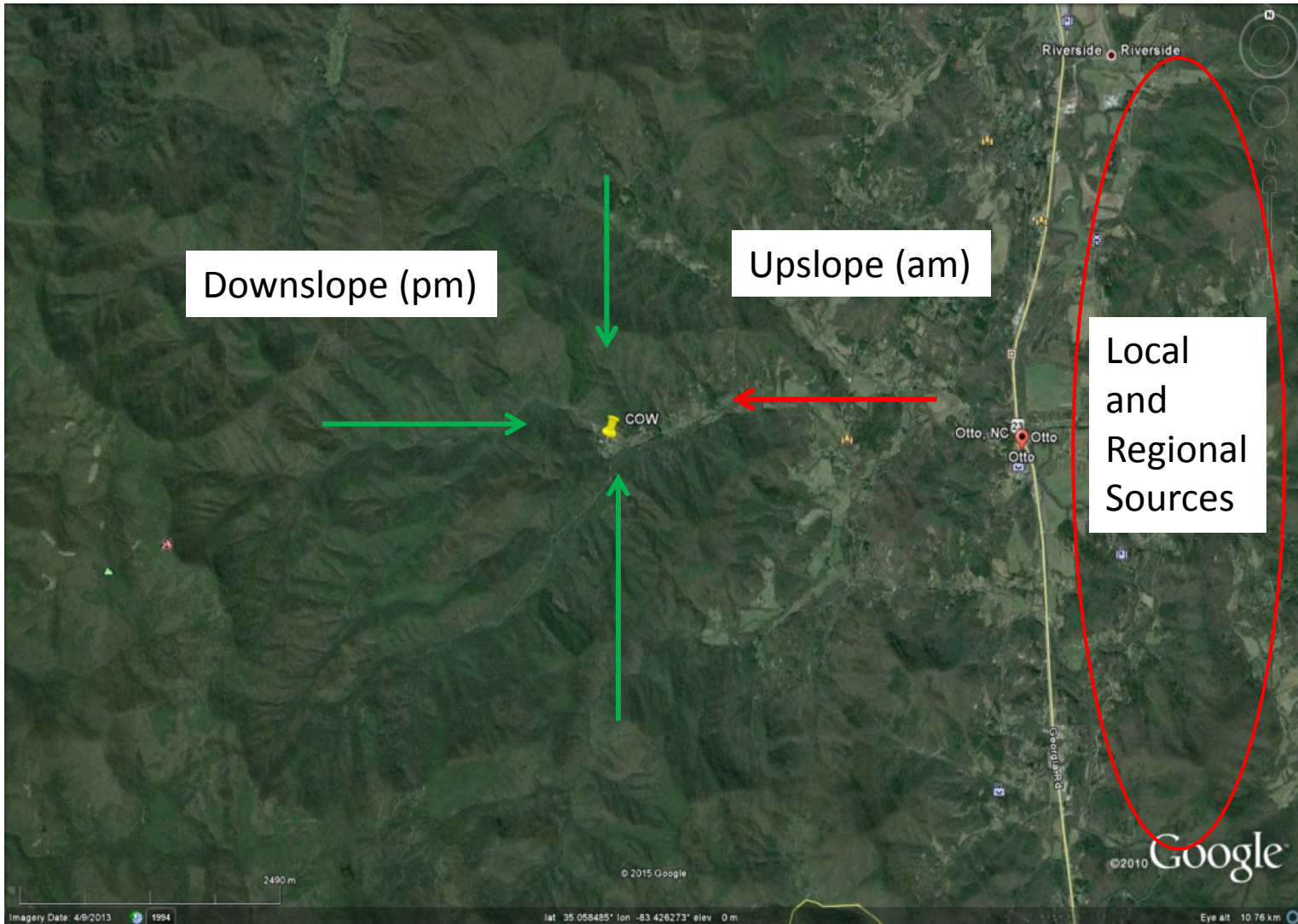
Directionality



NO_y and HNO₃ Summary by Campaign

Time Period	NO _y			HNO ₃			% HNO ₃
	mean [ppb]	CV (%)	n (hours)	mean [ppb]	CV (%)	n (hours)	
Su15	0.592	68	470	0.118	109	414	20
F15	0.728	71	458	0.079	125	444	11
Jan16	1.487	64	727	0.146	75	686	10
Sp16	0.966	51	519	0.182	109	500	19
Su16	0.462	69	472	0.080	118	449	17
Other	1.027	68	5089	0.165	114	4821	16
Aug15- Aug16	0.988	72	7735	0.151	114	7314	15

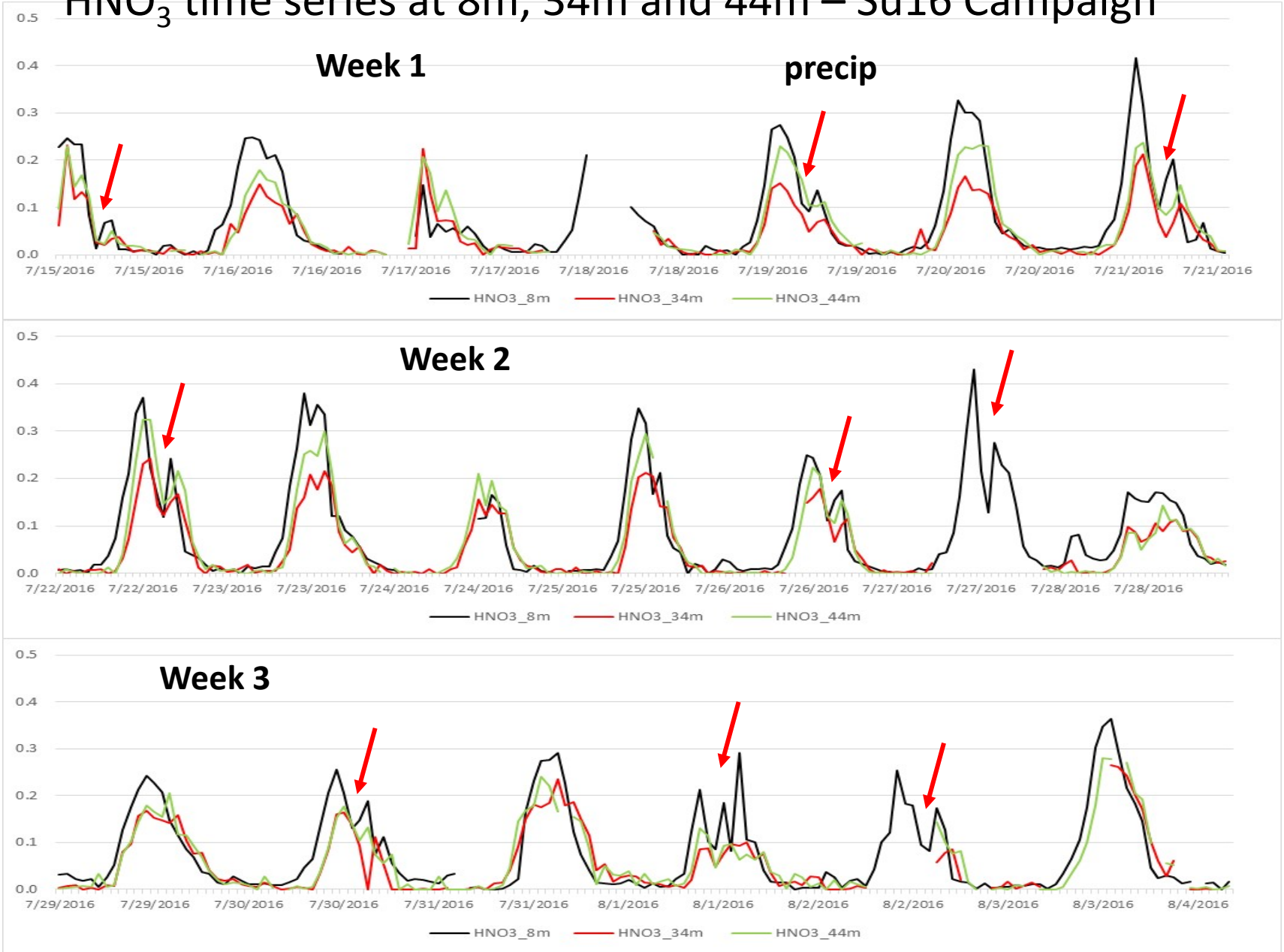
General Environs



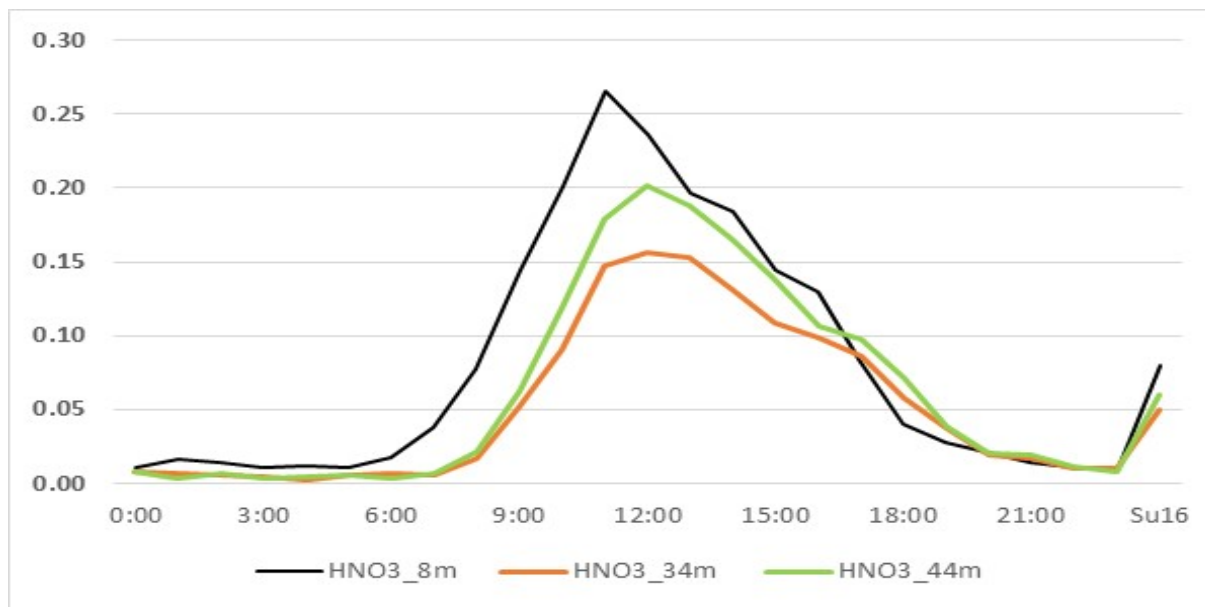
Surface vs. Flux Tower Data

- Horizontal separation (300-400 m)
- Vertical separation (26-36 m)
- Instrumental differences (MARGA vs. CL)

HNO₃ time series at 8m, 34m and 44m – Su16 Campaign



HNO₃ Summary for 3 Locations-Su16 Campaign



stat/Z	HNO ₃ (ppb)						8m/34m	8m/44m
	8m	34m	44m	8m	34m	44m		
mean	0.080	0.050	0.060	0.076	0.052	0.063	1.5	1.2
s.d.	0.094	0.061	0.075	0.092	0.061	0.076		
min.	0.001	0.002	0.002	0.002	0.002	0.002		
max.	0.431	0.265	0.324	0.417	0.265	0.324	1.6	1.3
n	449	424	422	392	392	392		

Conclusions

- NO_y concentrations average ~1 ppb and range from ~0.5 ppb summer to ~1.5 ppb winter
- Diurnal variation shows midday peak and overnight minimum (interplay of met and chemistry)
- NO_z dominated much of the time in summer
- HNO₃ concentrations average 0.08 ppb, with midday peak (0.2-0.5 ppb) and overnight minimum (near-zero)
- Interesting variability in space during summer 2016 (8m>44m>34m).

Acknowledgements

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