Contribution of HONO to New Radical Formation in Los Angeles

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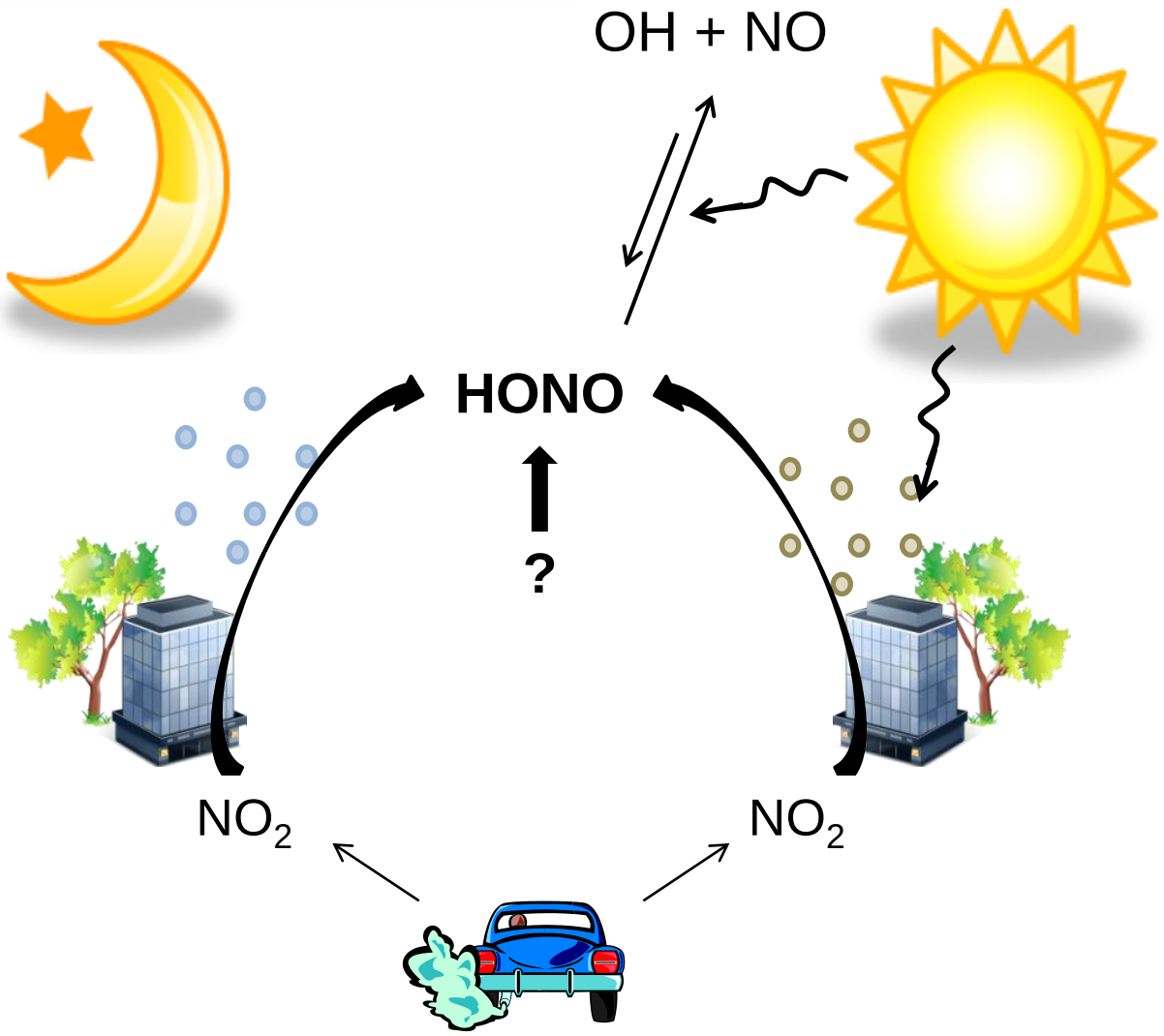
Nitrous Acid (HONO)

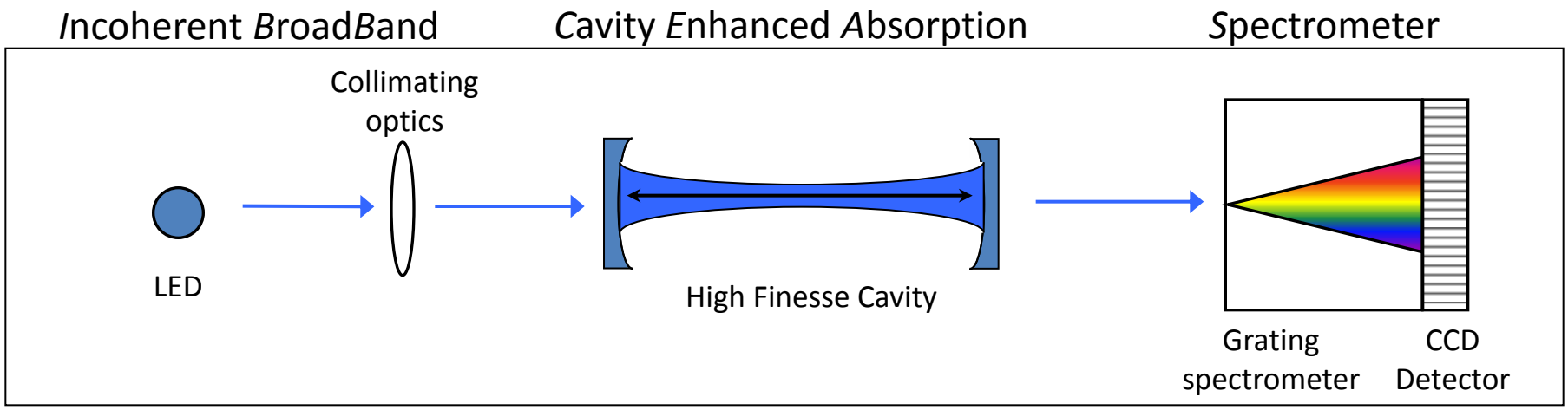


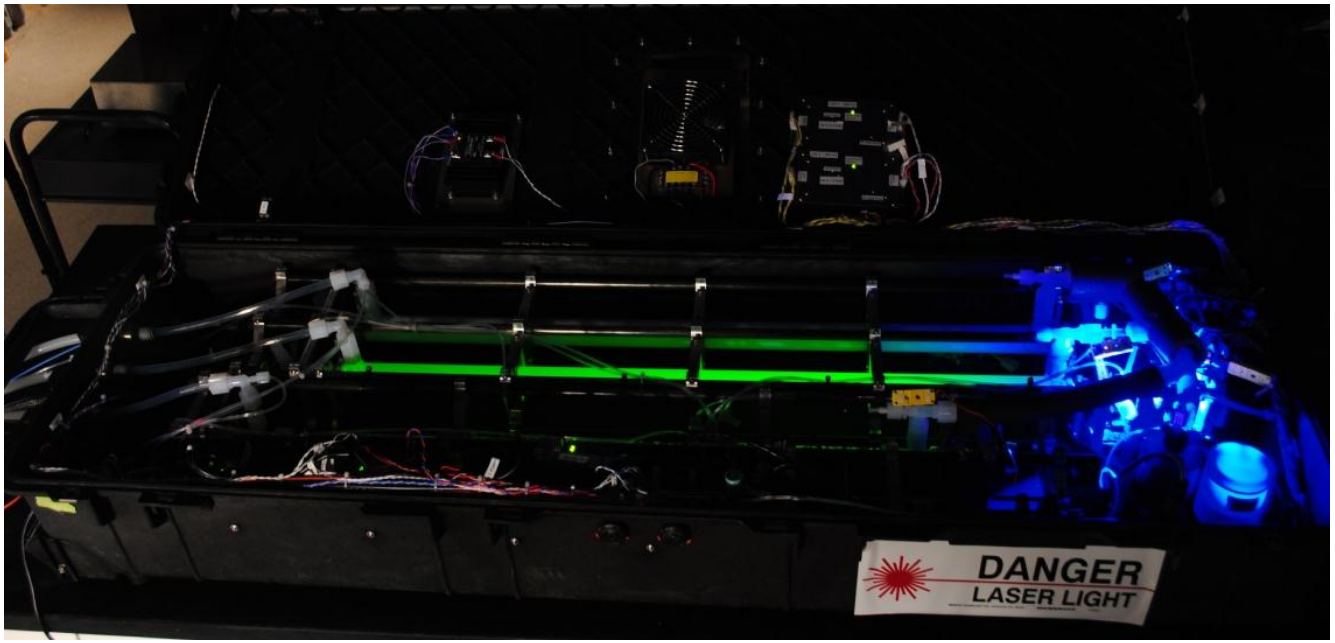
• Daytime levels and sources of HONO, and their impact on the oxidative capacity of the atmosphere, remain uncertain.

HONO Measurements at Pasadena

- **DOAS** (UCLA)
  - Used to measure HONO in many field campaigns and intercomparisons.
  - Light source on library, ~200m from site.
  - Lowest path length ~10km long, 30-40m above the ground surface.
- **NitroMAC** (Paris)
  - Denuder, followed by derivitization of NO_2^- and analysis by HPLC.
  - Similar to LOPAP technique.
  - Participated in intercomparison at Euphore chamber.
- **Acid CIMS** (NOAA)
  - Newly developed field instrument.
  - Acetate ionization of NO_2^- provides a measurement of HONO.
  - Used in fire lab study and successfully compared to FTIR.
- **IBBCEAS** (NOAA)
  - Incoherent BroadBand Cavity-Enhanced Absorption Spectoscopy.
  - Newly developed field instrument.
  - Conceptually proven in laboratory studies.
  - No published field results to date.

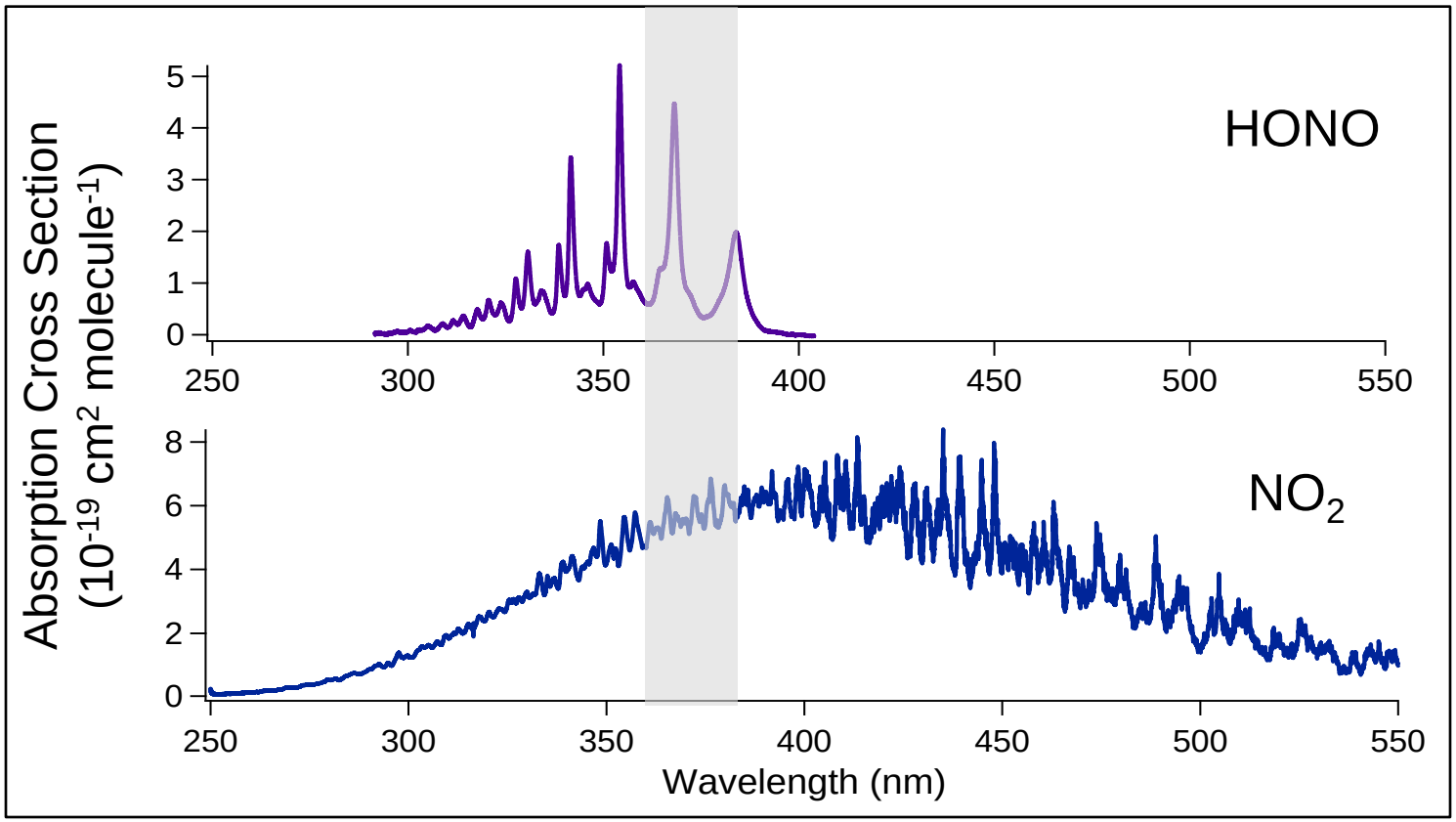
Principle of IBBCEAS HONO Measurement



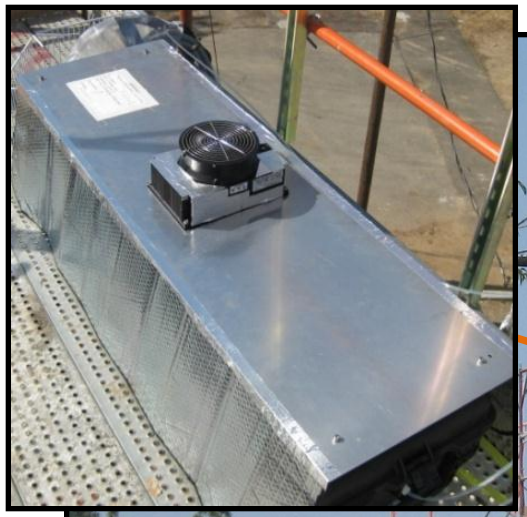


Principle of IBBCEAS HONO Measurement

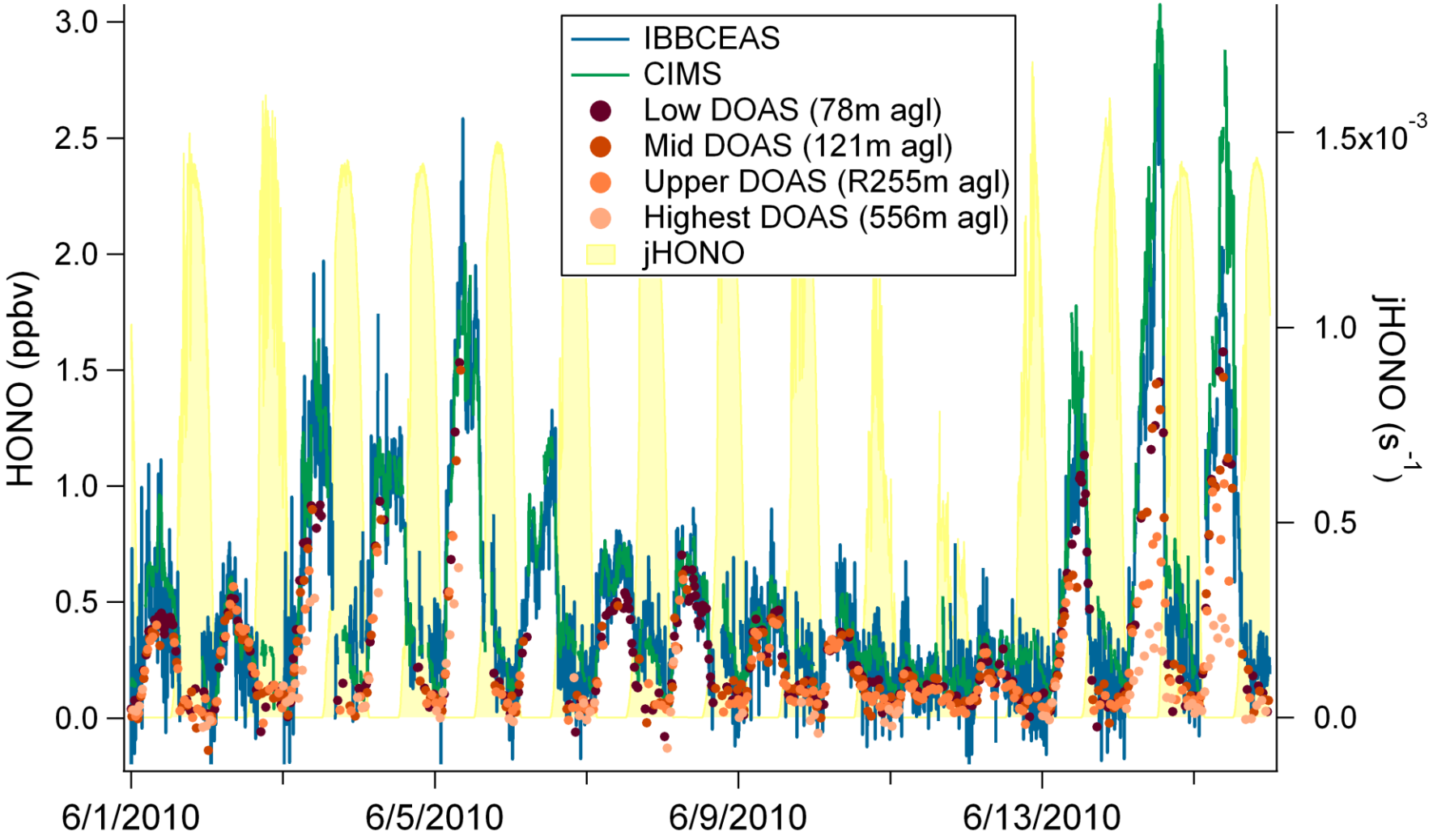
- IBBCEAS is a useful optical technique in areas where multiple species absorb.
- In much of the visible and near-UV, NO_2 absorbs broadly and prevents detection of other species using optical techniques such as cavity ring-down spectroscopy.



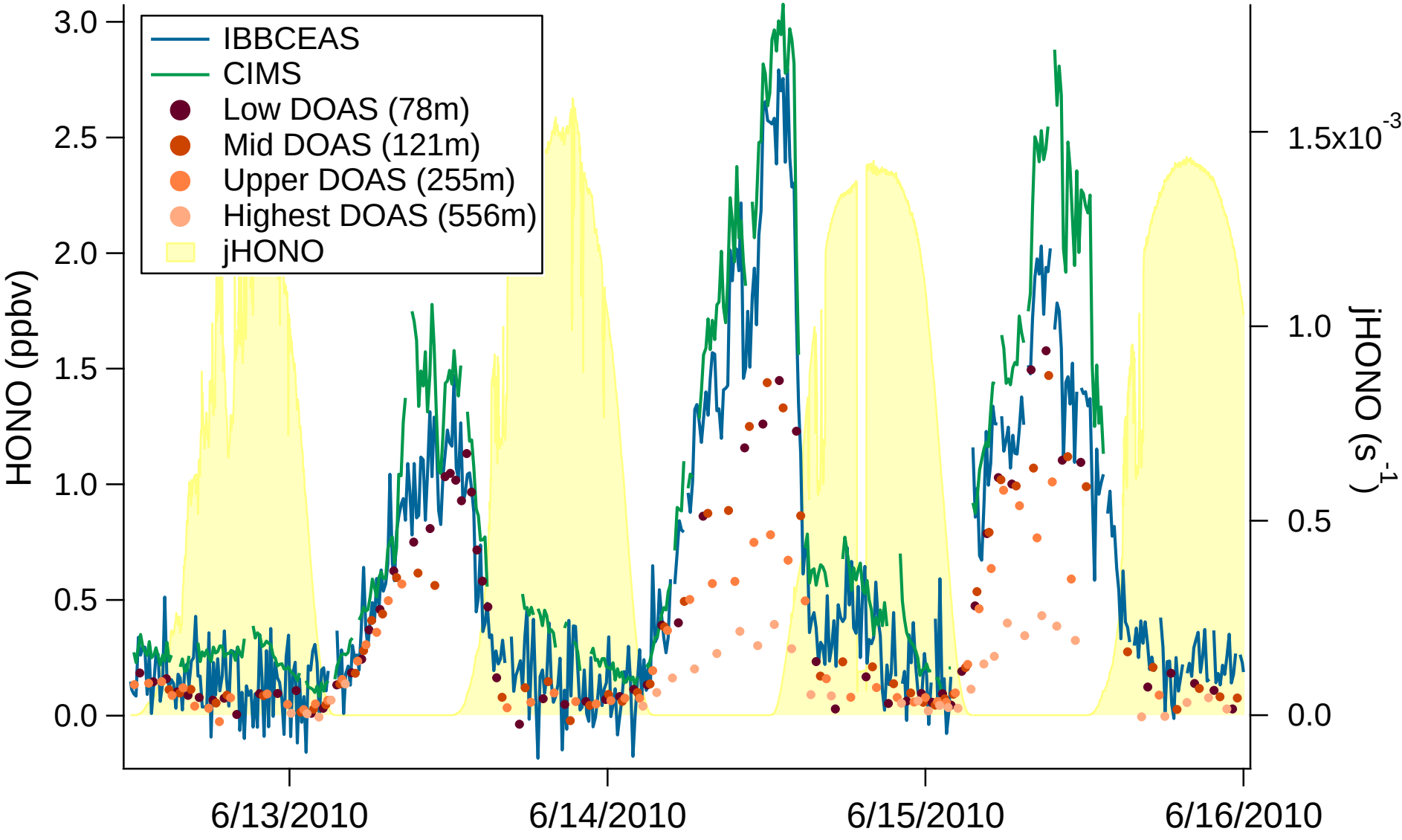
CalNex Pasadena Setup



Comparison of HONO Measurements



HONO Vertical Distribution



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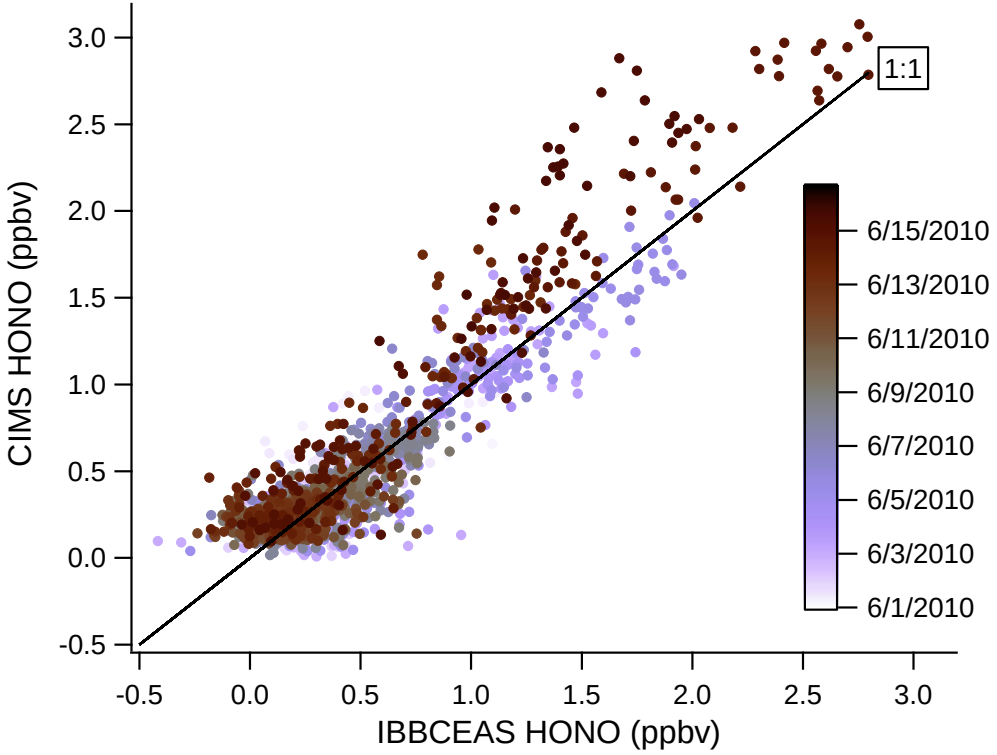
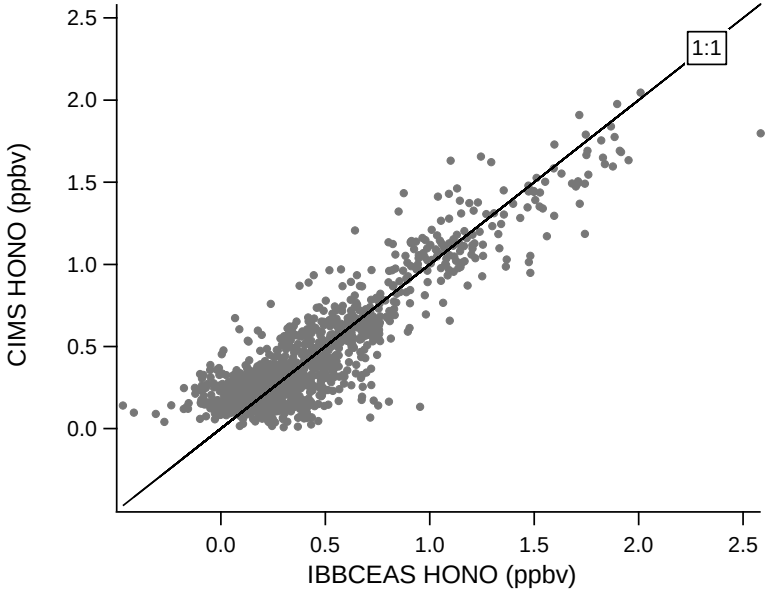
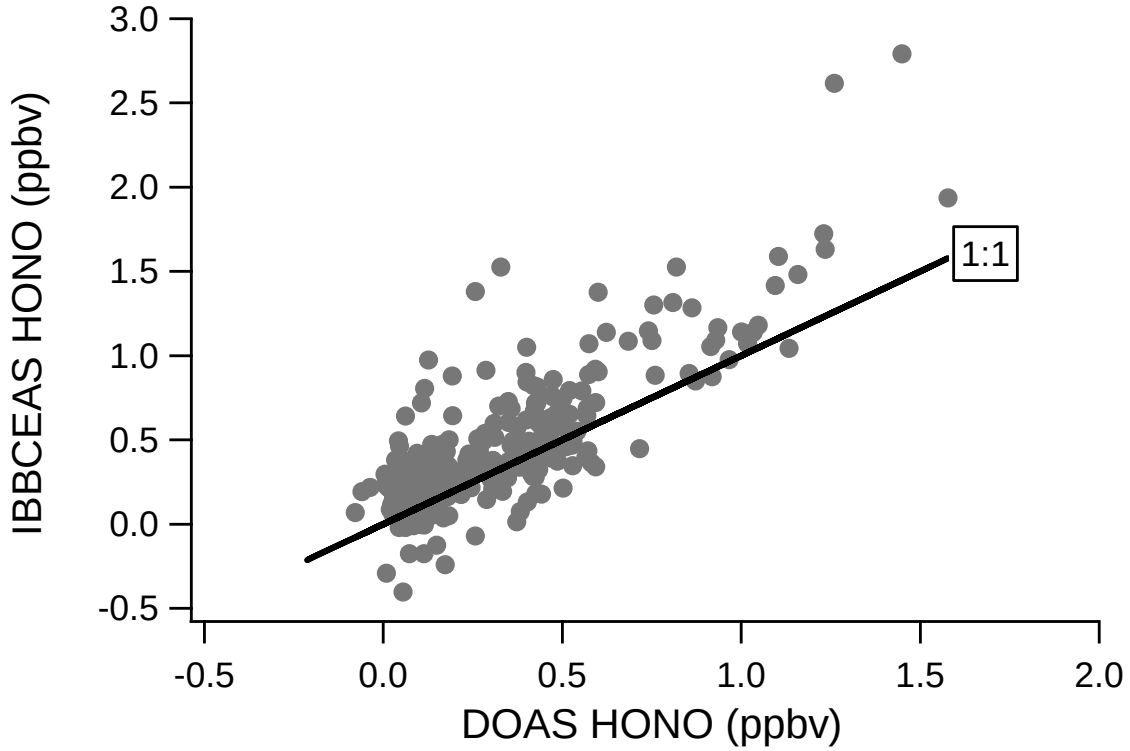


- Good agreement between two in situ instruments.
- CIMS measures higher at the end of the campaign when distinct vertical gradients were observed (CIMS ~6-7m below IBBCEAS).



- Removing the three vertical gradient days at the end of the campaign brings the in situ instruments into agreement, within 10%.

Comparison of HONO Measurements



- In situ instruments measure higher HONO than the lowest DOAS path.
- Similar results are obtained when last three days of campaign are excluded.

Possible Reasons for Discrepancy

- Vertical HONO gradient due to ground source.
- ~5km averaging distance of DOAS path.

- Based on the comparative data, the in situ HONO instruments performed well and data obtained by these instruments can be used to determine a budget of new radical production.

Contributions to Radical Formation

• Excellent availability of measurements from Pasadena ground site to create a detailed budget of new radical formation.

O_3 (U Houston)
j Values (U Houston)
HCHO (U Houston)
HONO (NOAA)

$$O(^1D) + H_2O \longrightarrow 2\ OH$$

$$HONO \xrightarrow{h\nu} OH + NO$$

$$HCHO \xrightarrow{h\nu} HO_2 + HCOO$$

Alkenes (GC, NOAA)
CHOCHO (NOAA)
CH_3CHO (GC, NOAA)
$ClNO_2$ (U Calgary)

$$Alkene + O_3 \longrightarrow OH + ROO$$

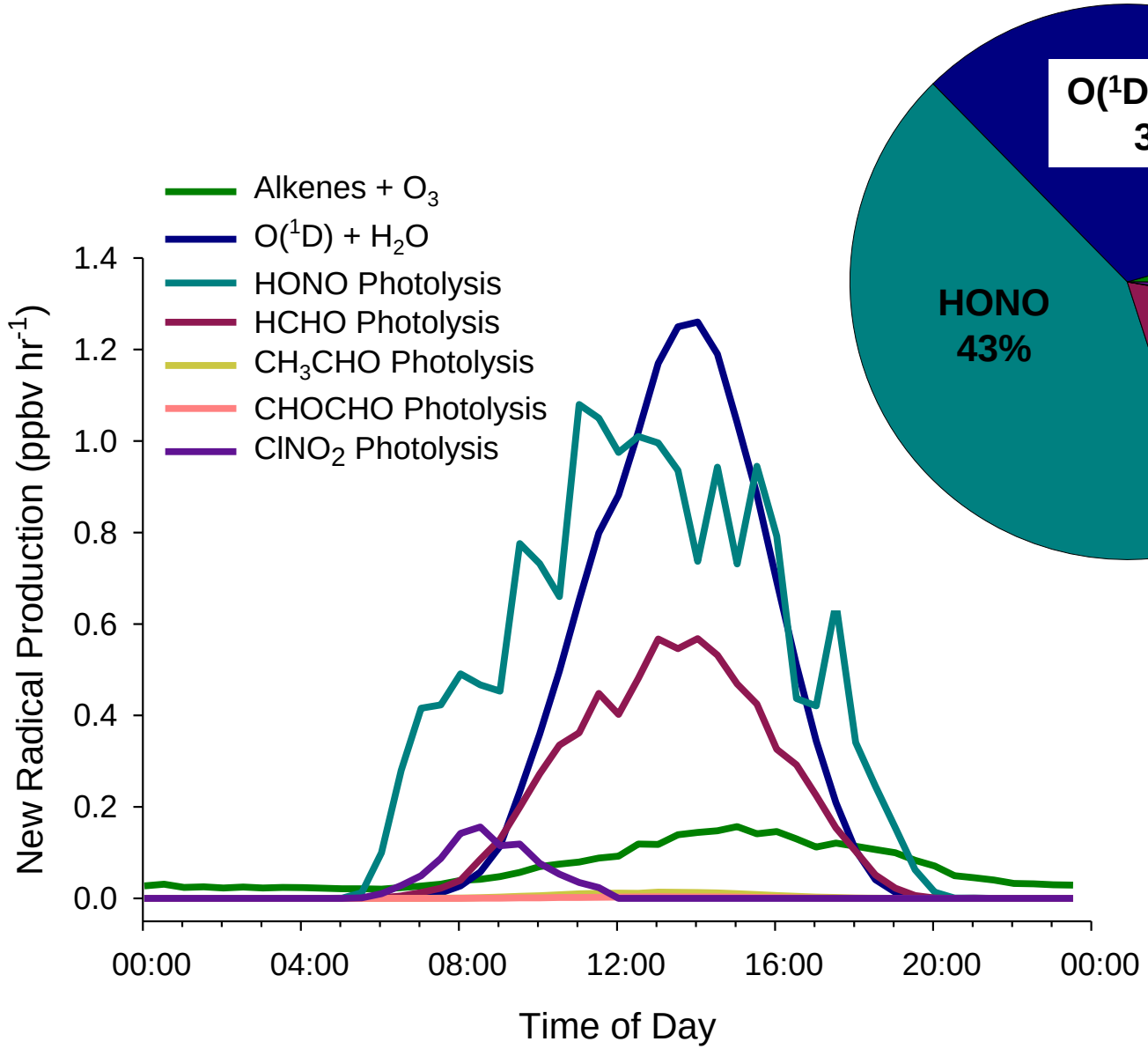
$$CHOCHO \xrightarrow{h\nu} 2\ HCOO$$

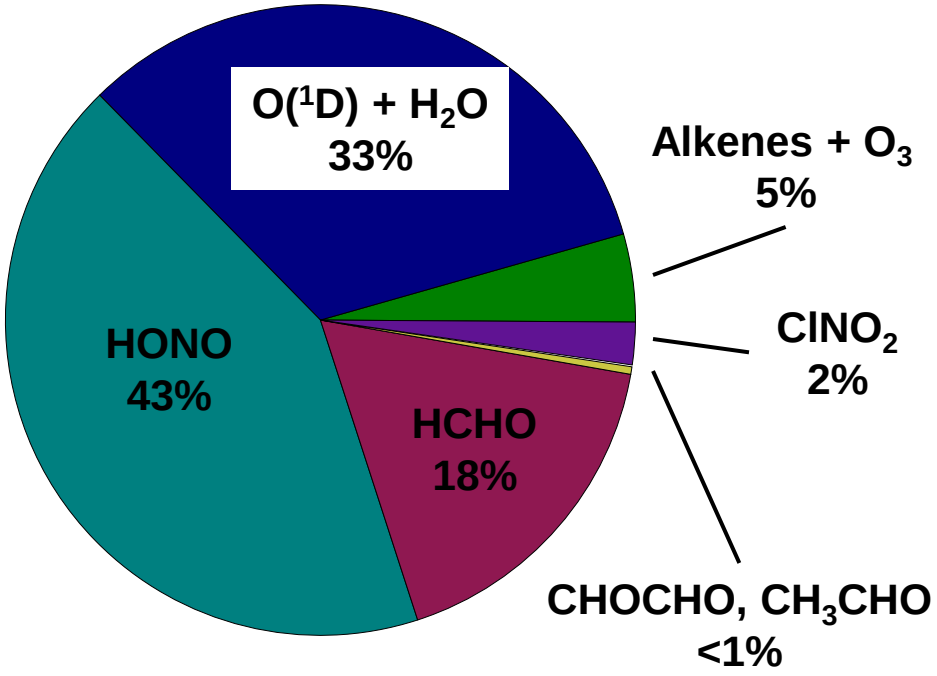
$$CH_3CHO \xrightarrow{h\nu} HO_2 + CH_3CHOO$$

$$ClNO_2 \xrightarrow{h\nu} Cl + NO_2$$

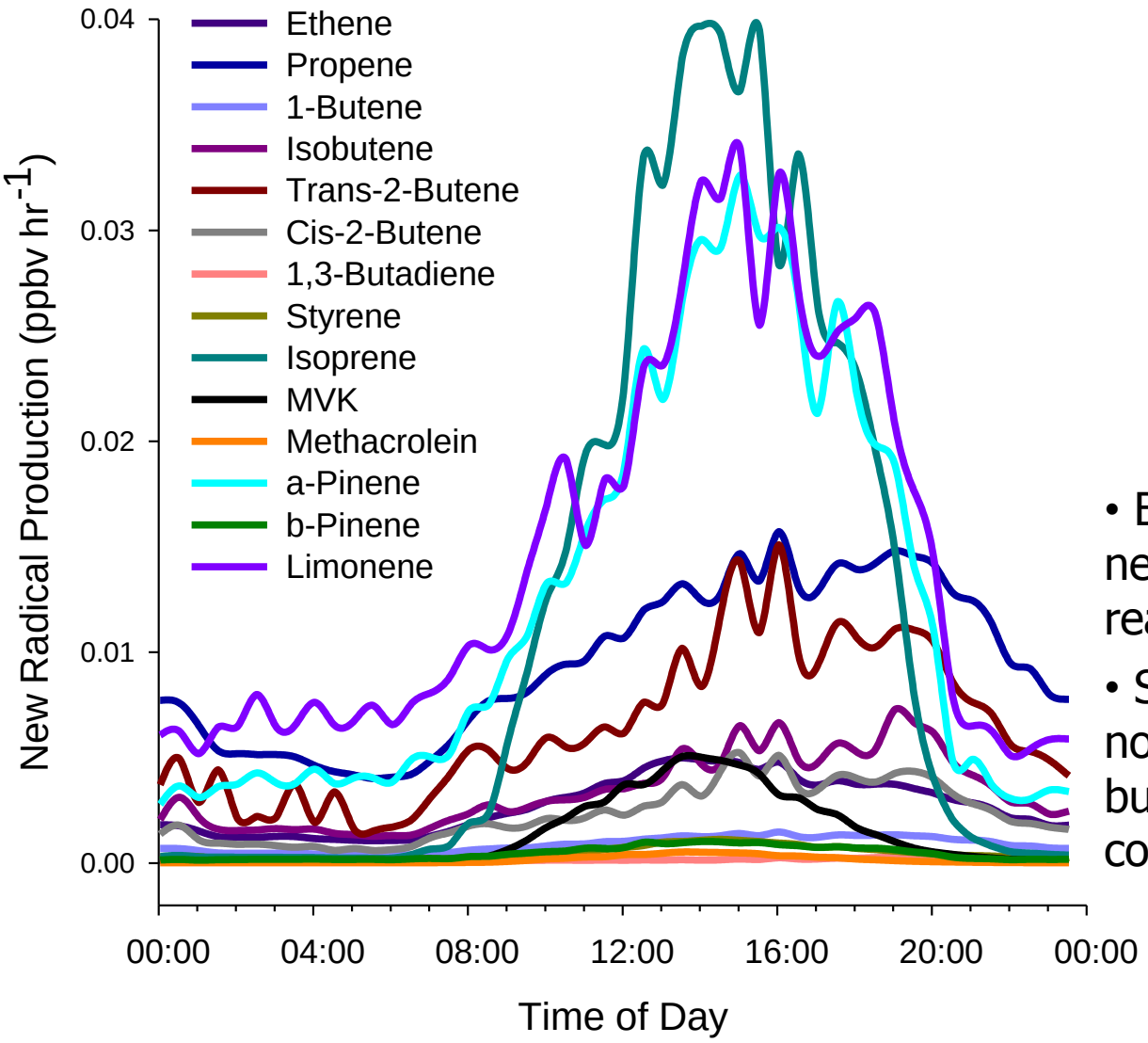
* $jClNO_2$ and jCHOCHO for Pasadena determined as a function of jNO_2 and jO_3, determined from aircraft measurements.
* Much of this data is still preliminary.

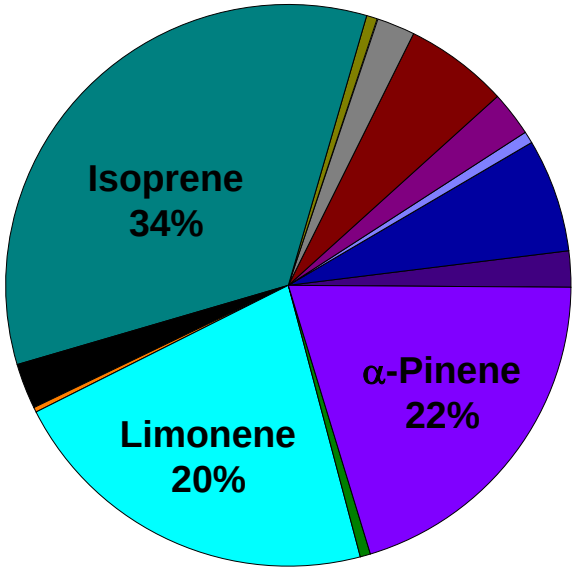
Contributions to OH Formation





Speciated Contribution of VOCs





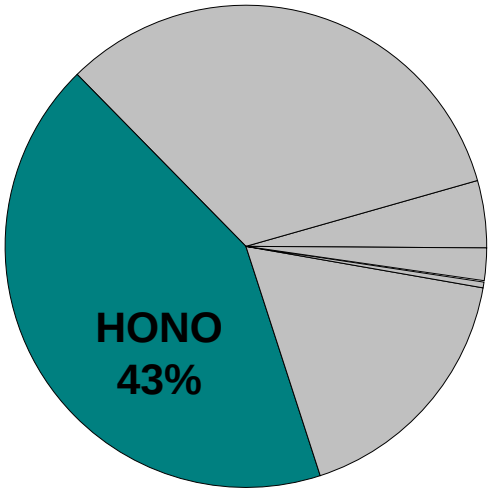
- Biogenics account for 79% of new radicals generated from the reaction of VOCs plus ozone.
- Some highly reactive alkenes not measured (e.g. pentenes), but likely make a minor contribution.

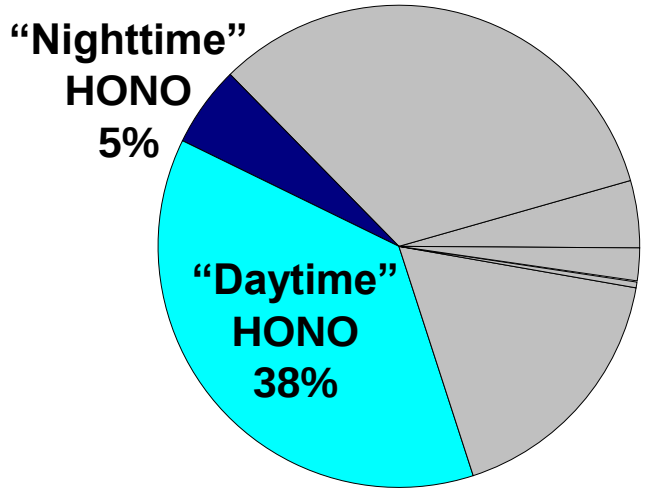
Radical Sources in Other Locations

Location	HONO Photolysis	$O(^1D) + O_3$	HCHO Photolysis	O_3 + Alkenes	Other	Reference
Pasadena, 2010	43	33	18	5	3	
Milan, 1998	16	20	34	8	20	Alicke et al., 2002
Pabstum, Germany, 1998	17	39	37	6	2	Alicke et al., 2003
Mexico City, 2003	12	19	19	12	38	Volkamer et al, 2010
Mexico City, 2006	34	6	24	19	17	Dusanter et al., 2009

- Estimated contribution of HONO at Pasadena is unusually high.
- All other HONO measurements included in radical source budgets were made using DOAS.

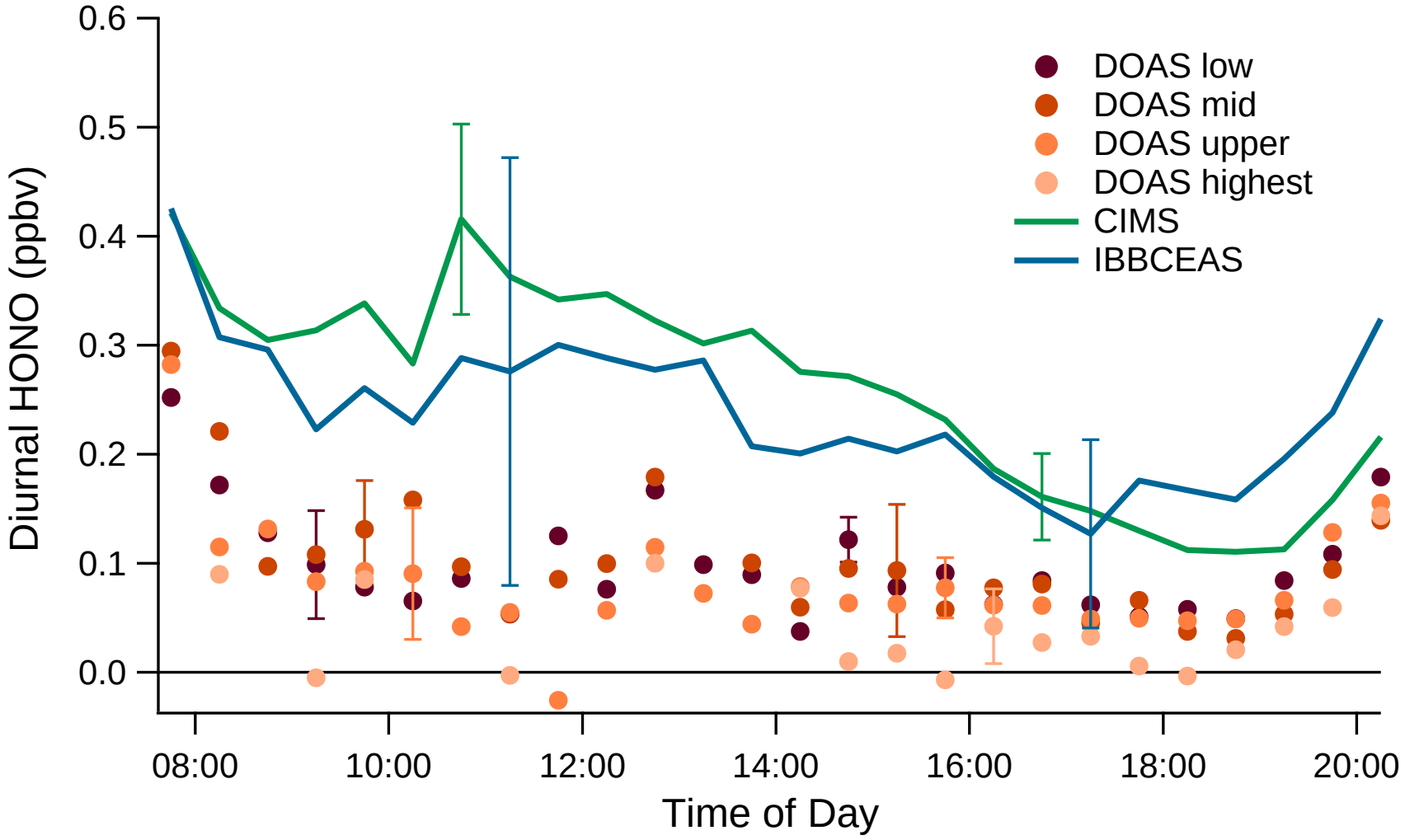
Nighttime vs Daytime HONO





- The portion of radicals that result from nighttime accumulated HONO accounts for 12% of the total radicals produced from HONO or 5% of the total new radicals.
- The remaining new radicals from HONO are attributed to the much more uncertain daytime HONO measurements.
    - This uncertain radical source is up to 38% of the total new radicals produced at the Pasadena ground site.

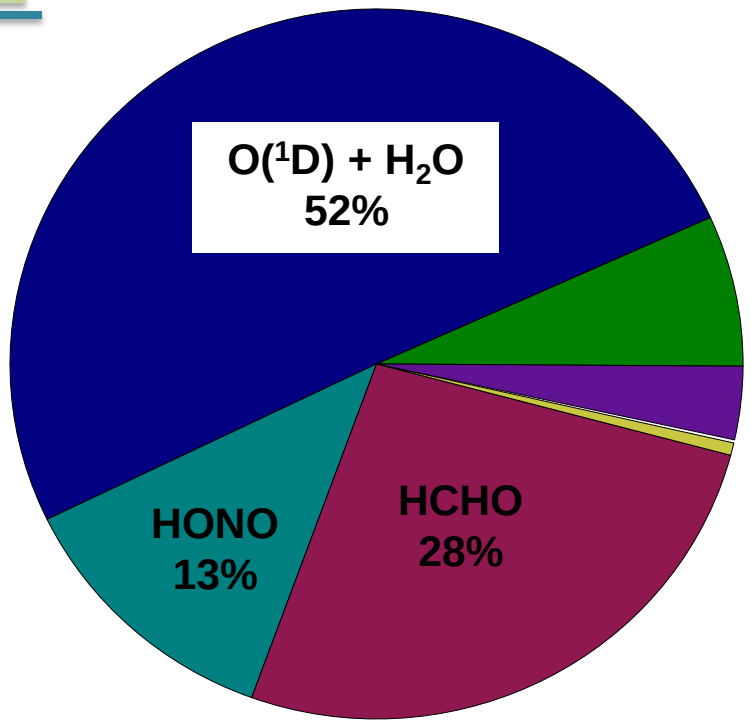
Impact of Daytime HONO



• DOAS measures an average concentration over 5km at heights >30m above the in situ instruments.

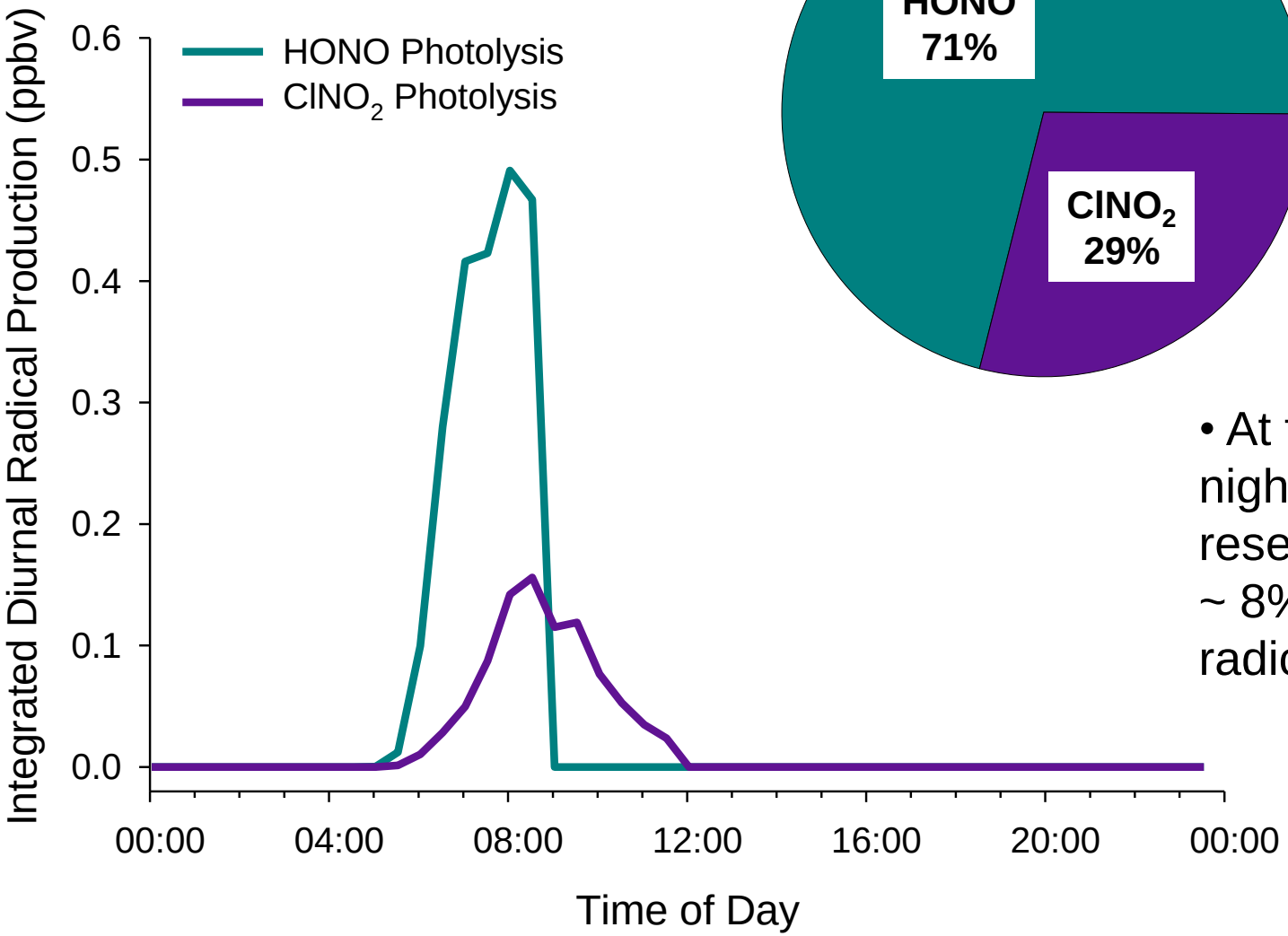
Impact of Daytime HONO

- Assuming that DOAS HONO is more representative and the daytime level is approximately 100 pptv, the budget of new radical formation changes dramatically.
- A small change in measured levels of daytime HONO has a large impact on the radical budget.
- The observed vertical gradient of HONO results in large differences in radical budgets with altitude.



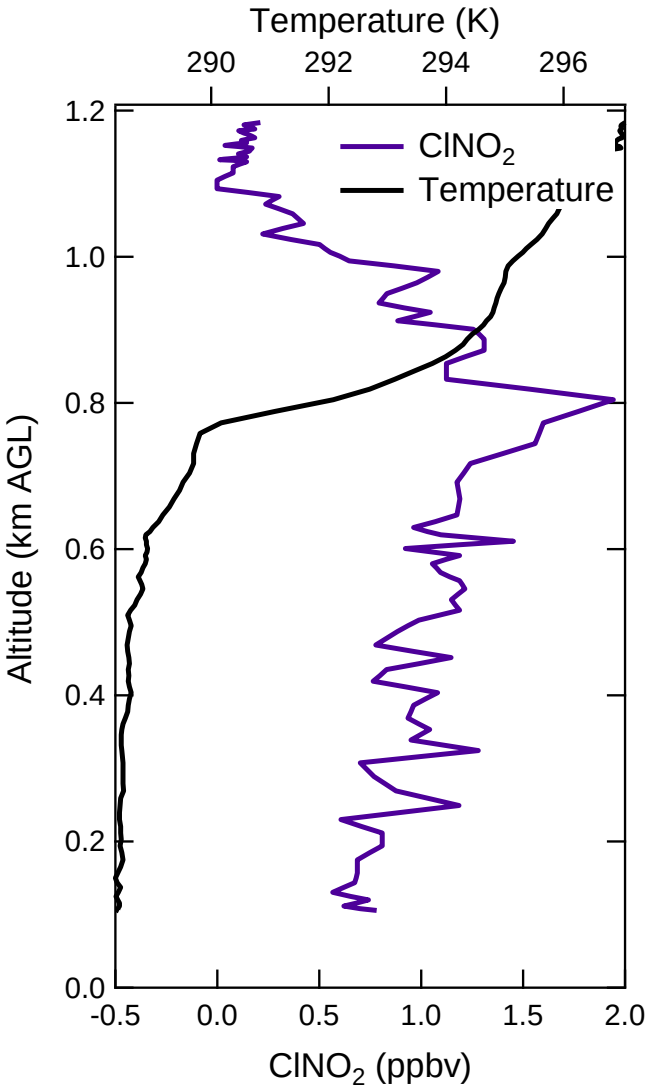
- **It is important to better understand daytime HONO and its vertical gradient to further constrain its importance to new radical formation.**

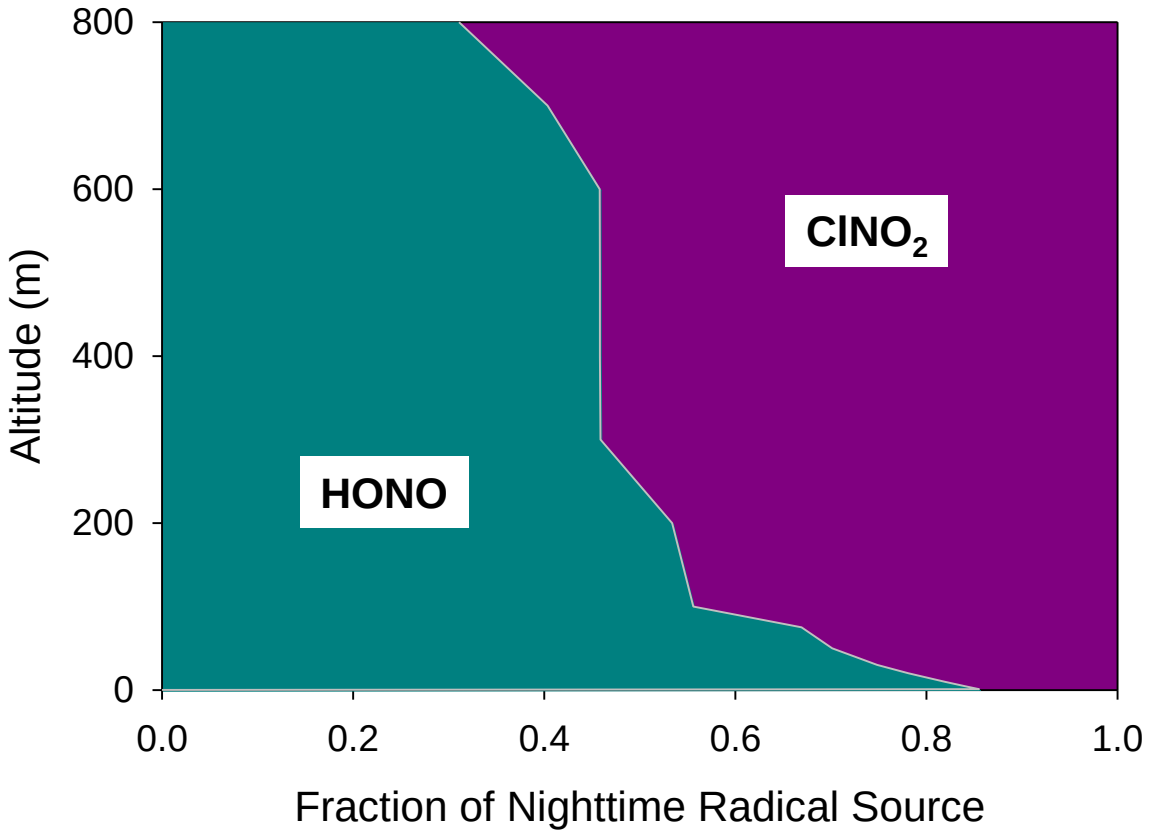
Nighttime Radical Reservoirs



- At the ground site, nighttime radical reservoirs contribute ~ 8%-13% of new radical formation.

Nighttime Radical Reservoirs





- When integrating over the boundary layer, importance of $ClNO_2$ relative to HONO increases.

*June 2 05:00 local time El Monte airport missed approach

Summary and Conclusions

- HONO was successfully measured at Pasadena using two new in situ instruments.
- The contribution of HONO to new radical formation is estimated at 43% using data from the IBBCEAS in situ instrument.
    - This estimation is higher than those found in other radical source budgets, all of which were constructed using DOAS data.
    - The bulk of HONO radical production is due to daytime HONO.
    - Using daytime HONO as measured by the DOAS, HONO accounts for 13% of new radical formation.
- Improved understanding of daytime HONO and spatial gradients is necessary to better constrain radical budgets.
- Nighttime accumulated radical sources account for about 10% of new radicals at Pasadena ground site.
- Vertical profiles are important when considering the contribution of nighttime radical reservoirs.

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