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# Nighttime photochemistry: nitrate radical destruction by anthropogenic light sources

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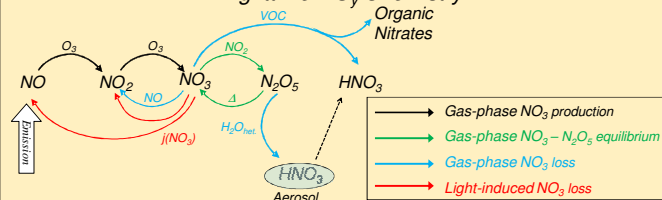
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## Motivation

Nighttime chemistry is an important aspect of tropospheric chemistry. A key molecule for nighttime chemistry is the nitrate radical,  $\text{NO}_3$ . It serves as a nighttime oxidant, comparable to the hydroxyl radical ( $\text{OH}$ ) during the day. Also, through its equilibrium with  $\text{N}_2\text{O}_5$  via reaction with  $\text{NO}_2$ , it can be a source of aerosol acidification. Further, under clean and dry conditions,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are nighttime reservoirs for  $\text{NO}_x$  and can influence ozone production during daytime. Recent ground, ship, and airborne in-situ measurements of  $\text{NO}_3$  have shown a large variety of lifetimes, indicating very different magnitudes of loss rates for  $\text{NO}_3$ . Nitrate radical is readily photolyzed by visible light, such that both  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are present at significant levels only at night. We will show airborne and ground measurements of absolute light intensities from anthropogenic and natural light sources (e.g. industrial and street lighting, full moon) as a newly discovered  $\text{NO}_3$  loss process. This loss process has implications for nighttime pollutant levels and next-day ozone production.

## Nighttime $\text{NO}_y$ Chemistry



## Photolysis rates

Chemical reaction:  $\text{A} + \text{light} \rightarrow \text{A}_1 + \text{A}_2$

Actinic Flux  $I(\lambda)$  (measured) Absorption spectrum  $\sigma_A(\lambda)$  (literature) Quantum yields  $\Phi_A(\lambda)$  (literature)

$$J_A = \frac{1}{[A]} \cdot \frac{d[A]}{dt} = \int I(\lambda) \cdot \sigma_A(\lambda) \cdot \Phi_A(\lambda) d\lambda$$

Photolysis rate  $j$

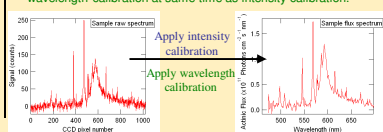
## Measurement Technique for Spectral Actinic Flux: "Actinic Flux Spectroradiometer" (AFSR)

### CCD-array grating spectrometer with 4x homogeneous response receptors:

- 460-690 nm
- 1024x256 CCD array
- Pixel resolution = 0.25 nm
- FWHM = 1 nm
- Data averaged to 1 nm
- High sensitivity from 80% duty cycle
- 4 sec integration time
- 0.2 Hz repetition rate
- Optical fibers from receptors to spectrometers
- Optical receptors with angle-independent light response
- Hemispheric separation using shadow rings

### Calibration procedures for intensity and wavelength:

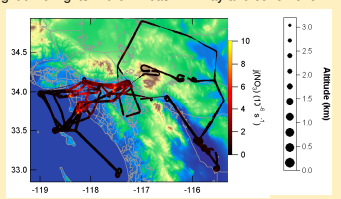
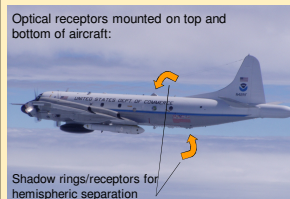
- Intensity calibration:
  - Field standard 250-W halogen lamps were calibrated before and after the campaign in the laboratory using NIST-traceable radiation standards.
  - Intensity calibration performed regularly during field campaigns.
- Wavelength calibration:
  - Hg, Cd, and Ne atomic emission lamps used in conjunction with sunlight.
  - Atomic emission lines and solar Fraunhofer lines used for wavelength calibration at same time as intensity calibration.



Platform: NOAA WP-3D

Locations:

4 night time flights in the LA basin in May and June 2010:



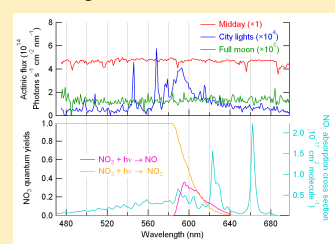
## Light Intensities from Sun, Street Lights, and Full Moon

- Street lights are more than 4 orders of magnitude dimmer than the sun
- Street lights are up to 25 times brighter than the full moon
- Spectral overlap between street lights and  $\text{NO}_3$  spectrum and quantum yields

$\text{NO}_3$  Photolysis rates and lifetimes ( $\tau$ ):

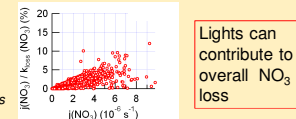
- Daytime:  $1 \times 10^{-1} \text{ s}^{-1}$  ( $\tau = 10 \text{ sec}$ )
- Anthropogenic lights:
  - Airborne (800m):  $1 \times 10^{-5} \text{ s}^{-1}$  ( $\tau = 28 \text{ hrs}$ )
  - Ground:  $5 \times 10^{-5} \text{ s}^{-1}$  ( $\tau = 6 \text{ hrs}$ )
- Full moon:  $4 \times 10^{-7} \text{ s}^{-1}$  ( $\tau = 25 \text{ days}$ )

Anthropogenic lights can photolyze  $\text{NO}_3$

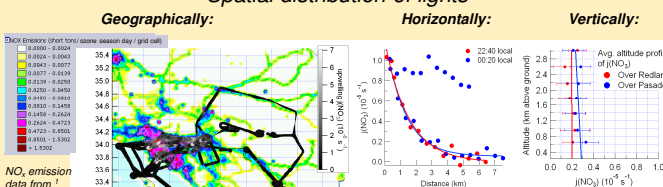


## Comparison with measured $\text{NO}_3$ loss rates

- Steady-state loss rates calculated after Brown et al. <sup>2</sup>
- Using in-situ measurements of  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{O}_3$ , and  $\text{NO}_2$
- Photolysis contributed up to 10% to instantaneous  $\text{NO}_3$  loss during CalNex



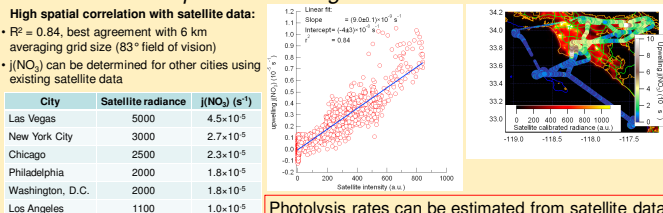
## Spatial distribution of lights



- $\text{NO}_3$  emissions and light are co-located
- Horizontal extent about 6 km at 800 m above ground, exponentially decaying
- Vertically nearly constant up to 3 km

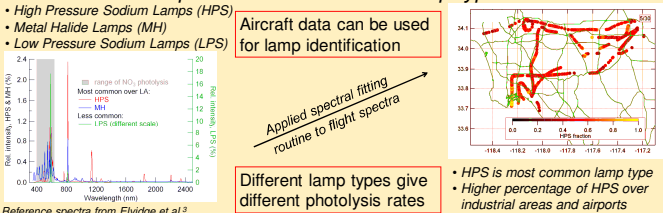
Light extends into  $\text{NO}_3$  - relevant regions

## Comparison with Nighttime Satellite Data



Photolysis rates can be estimated from satellite data

## Spectral identification of lamp types

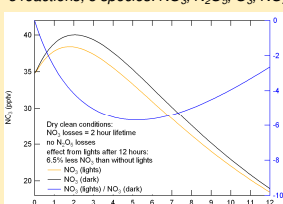


Different lamp types give different photolysis rates

## Implications for tropospheric chemistry

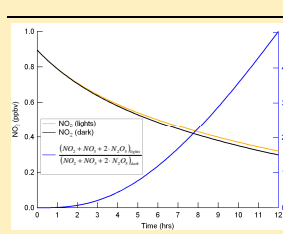
Chemical box model calculations: 8 reactions, 5 species:  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$

Reduced  $\text{NO}_3$  levels:



- Street lights can reduce  $\text{NO}_3$  by up to 7% over Los Angeles
- Higher reduction levels possible over brighter areas (under clouds, over snow)
- $\text{N}_2\text{O}_5$  reductions of similar magnitude
- Slower nighttime oxidation:
  - Increased levels of primary pollutants
  - Decreased levels of secondary pollutants (e.g.  $\text{HNO}_3$ ,  $\text{ClNO}_2$ , organic nitrates)
- Lower  $\text{HNO}_3$  production

Reduced  $\text{NO}_3$  can lead to increased primary and decreased secondary pollutants



- Equilibrium shift towards  $\text{NO}_2$  in  $\text{NO}_2 + \text{O}_3 \rightleftharpoons \text{NO}_3 + \text{O}_2$ :
  - Street lights can reduce nocturnal  $\text{NO}_3$  loss
  - Ozone production on following day can be increased
- 5% additional  $\text{NO}_x$  available for daytime photochemistry for Los Angeles model
- Higher  $\text{NO}_x$  levels possible over brighter areas (under clouds, over snow)

Anthropogenic lights can lead to increased ozone production after sunrise

## Additional nighttime photolysis processes

- Overtone photolysis of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  to produce nighttime OH
- Donaldson et al. <sup>4</sup> proposed process OH production through absorption of visible and infrared light into vibrational overtones of OH-stretch transition followed by intramolecular vibrational energy redistribution (IVR):  $\text{X-OH} + \text{hv} \rightarrow \text{X-(OH)}^* \rightarrow \text{X-OH}^* \rightarrow \text{X} + \text{OH}$
- Possibly important at low UV light levels where other OH production channels are slow
- Overtone transitions measured with cavity ringdown spectroscopy for  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ , and others
- Using integrated absorption cross sections from Brown et al. <sup>5</sup> and average actinic fluxes at absorption feature wavelengths, overtone photolysis rates for OH production are  $0.3 \times 10^{-15} \text{ s}^{-1}$  and  $1 \times 10^{-15} \text{ s}^{-1}$  for  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ , respectively
- Assuming 3 ppb of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  each, overtone photolysis of these compounds together would produce on the order of a few hundred molecules of OH per hour, a negligible amount

Anthropogenic lights can not produce significant amounts of OH

## Conclusions

- First measurement of nighttime photolysis rates for  $\text{NO}_3$  from anthropogenic and natural light sources
- Photolysis rates contributed up to 10% to instantaneous  $\text{NO}_3$  losses during CalNex
- Anthropogenic lights can reduce nighttime  $\text{NO}_3$  levels in the range of up to 7% based on data from CalNex
- Airborne validation of nighttime satellite radiance measurements
- Higher intensities possible in brighter cities, over snow, and/or under clouds
- Characterized horizontal and vertical distribution of light intensities over Los Angeles
- Identified 2 major components of nighttime light: high pressure sodium and metal halide lamps
- Different lamp types give different photolysis rates
- Nighttime oxidation can be slower due to lights
- Primary pollutants may be increased while secondary pollutants could be decreased
- Nocturnal OH production from overtone photolysis is insignificant
- Ozone production during daytime could be increased by nighttime light sources

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