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Nighttime photochemistry: nitrate radical destruction by anthropogenic light sources

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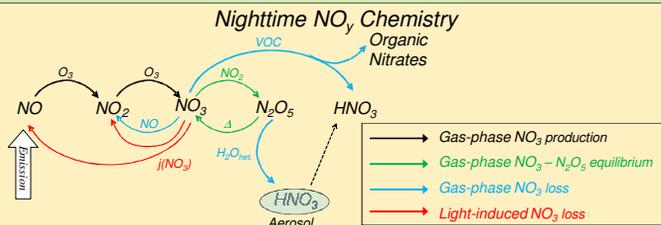
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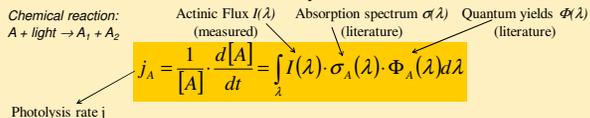
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Motivation

Nighttime chemistry is an important aspect of tropospheric chemistry. A key molecule for nighttime chemistry is the nitrate radical, NO_3 . It serves as a nighttime oxidant, comparable to the hydroxyl radical (OH) during the day. Also, through its equilibrium with N_2O_5 via reaction with NO_2 , it can be a source of aerosol acidification. Further, under clean and dry conditions, NO_3 and N_2O_5 are nighttime reservoirs for NO_x and can influence ozone production during daytime. Recent ground, ship, and airborne in-situ measurements of NO_3 have shown a large variety of lifetimes, indicating very different magnitudes of loss rates for NO_3 . Nitrate radical is readily photolyzed by visible light, such that both NO_3 and N_2O_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 NO_3 loss process. This loss process has implications for nighttime pollutant levels and next-day ozone production.



Photolysis rates



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

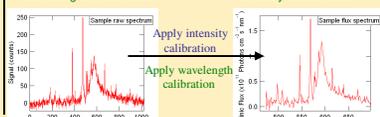
CCD-array grating spectrometer with 4x homogeneous response receptors:

- 460-690 nm
- 1024x256 CCD array
- Pixel resolution = 0.25 nm
- FWHM = 1 nm
- Data averaged to 1 nm
- 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:

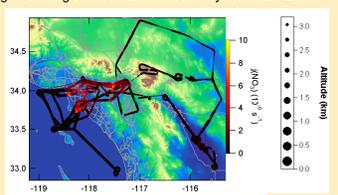
- Intensity calibration:**
- Field standard 250-W halogen lamps were calibrated before and after the campaign in the laboratory using NIST-traceable radiation standards.
 - Intensity calibration performed regularly during field campaigns.
- Wavelength calibration:**
- Hg, Cd, and Ne atomic emission lamps 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

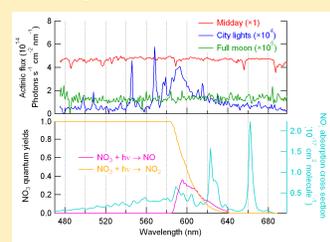
Locations:

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 NO_3 spectrum and quantum yields



- NO_3 Photolysis rates and lifetimes (τ):
- 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 NO_3

Comparison with measured NO_3 loss rates

- Steady-state loss rates calculated after Brown et al.²

$$\tau_{ss}(\text{NO}_3) = \frac{[\text{NO}_3 + \text{N}_2\text{O}_5]}{k[\text{O}_3][\text{NO}_3]} = (k_{ss}[\text{NO}_3])^{-1}$$

Using in-situ measurements of NO_3 , N_2O_5 , O_3 , and NO_2

Photolysis contributed up to 10% to instantaneous NO_3 loss during CalNex

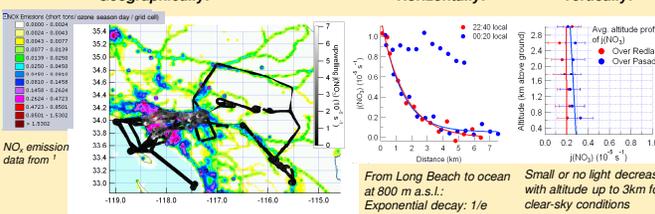
Lights can contribute to overall NO_3 loss

Spatial distribution of lights

Geographically:

Horizontally:

Vertically:



- NO_3 emissions and light are co-located
- Horizontal extent about 6km at 800 m above ground, exponentially decaying
- Vertically nearly constant up to 3 km

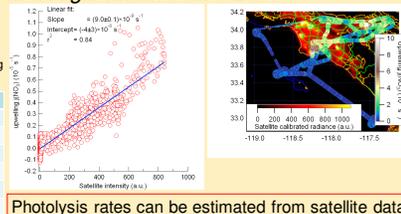
Light extends into NO_3 - relevant regions

Comparison with Nighttime Satellite Data

High spatial correlation with satellite data:

- $R^2 = 0.84$, best agreement with 6 km averaging grid size (83° field of vision)
- $j(\text{NO}_3)$ can be determined for other cities using existing satellite data

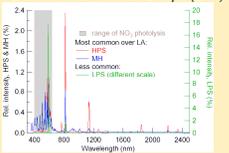
City	Satellite radiance	$j(\text{NO}_3)$ (s^{-1})
Las Vegas	5000	4.5×10^{-5}
New York City	3000	2.7×10^{-5}
Chicago	2500	2.3×10^{-5}
Philadelphia	2000	1.8×10^{-5}
Washington, D.C.	2000	1.8×10^{-5}
Los Angeles	1100	1.0×10^{-5}



Spectral identification of lamp types

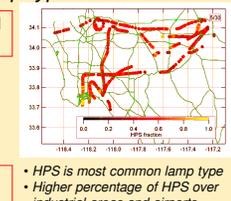
- High Pressure Sodium Lamps (HPS)
- Metal Halide Lamps (MH)
- Low Pressure Sodium Lamps (LPS)

Aircraft data can be used for lamp identification



Applied spectral fitting routine to flight spectra

Different lamp types give different photolysis rates

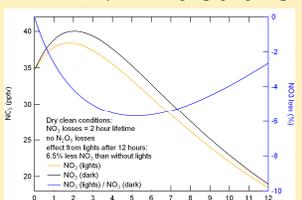


Implications for tropospheric chemistry

Chemical box model calculations:

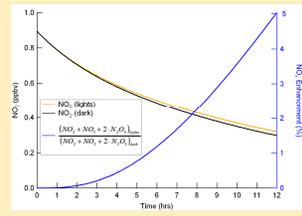
8 reactions, 5 species: NO_3 , N_2O_5 , O_3 , NO_2 , NO

Reduced NO_3 levels:



- Street lights can reduce NO_3 by up to 7% over Los Angeles
- Higher reduction levels possible over brighter areas (under clouds, over snow)
- N_2O_5 reductions of similar magnitude
- Slower nighttime oxidation:
 - Increased levels of primary pollutants
 - Decreased levels of secondary pollutants (e.g. HNO_3 , ClNO_2 , organic nitrates)
- Lower HNO_3 production

Reduced NO_3 can lead to increased primary and decreased secondary pollutants



- Equilibrium shift towards NO_2 in $\text{NO}_2 + \text{O}_3 \rightleftharpoons \text{NO}_3 + \text{O}_2$:
- Street lights can reduce nocturnal NO_3 loss
 - Ozone production on following day can be increased
 - 5% additional NO_3 available for daytime photochemistry for Los Angeles model
 - Higher NO_3 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 HNO_3 and H_2O_2 to produce nighttime OH

- Donaldson et al.⁴ 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): $X\text{-OH} + h\nu \rightarrow X(\text{OH})^* \rightarrow (\text{X-OH})^* \rightarrow \text{X} + \text{OH}$
- Possibly important at low UV light levels where other OH production channels are slow
- Overtone transitions measured with cavity ringdown spectroscopy for HNO_3 , H_2O_2 , and others
- Using integrated absorption cross sections from Brown et al.⁵ and average actinic fluxes at absorption feature wavelengths, overtone photolysis rates for OH production are $0.3 \times 10^{-15} \text{ s}^{-1}$ and $1 \times 10^{-12} \text{ s}^{-1}$ for HNO_3 and H_2O_2 , respectively
- Assuming 3 ppb of HNO_3 and H_2O_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 NO_3 from anthropogenic and natural light sources
- Photolysis rates contributed up to 10% to instantaneous NO_3 losses during CalNex
- Anthropogenic lights can reduce nighttime 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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