The study of nitrite formation from ammonium nitrate photolysis on different substrates.

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Abstract

In recent years, the process of nitrate being reconverted to NOx—known as renoxification—has received increasing attention. Nitrate can rapidly undergo photolysis, returning to the gas phase in the form of NO_x or HONO. Among these, gaseous nitrous acid (HONO) is an important nitrogen-containing trace gas in the troposphere, capable of generating hydroxyl radicals (OH) through photolysis, thereby enhancing the oxidative capacity of the atmosphere.

In this study, UVB lamps were installed in a chamber to investigate the ability of nitrate to produce HONO under different light intensities, as well as the efficiency of HONO formation on various solid surfaces (Glass, Asphalt, Passenger path). Furthermore, this study also utilized filters collected from past sampling campaigns in Taichung to examine how different light intensities affect the efficiency of HONO production from nitrate photolysis when multiple ionic components are present on the material surfaces.

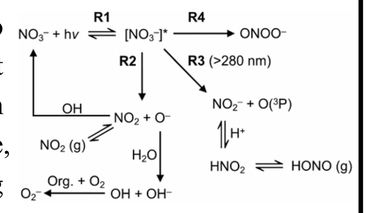


Figure 1. Simplified nitrate photolysis mechanisms.
Source: K. B. Benedict et al. (2017).

Calculations

$$j_{pNO_3^-} = \frac{P_{NO}+P_{NO_2}+P_{HNO_3}+P_{HONO}}{pNO_{3_{total}}^-}:$$

$$P_{HONO}\left[\frac{nmole}{hour}\right] = \frac{60\times F_g}{1000\times(t_1-t_2)} \times \frac{P}{R\times T} \times \int_{t_1}^{t_2}(\mathrm{HONO})dt$$

$$P_{NO_x}\left[\frac{nmole}{hour}\right] = \frac{60\times F_g}{60\times 1000\times(t_1-t_2)} \times \frac{P}{R\times T} \times \int_{t_1}^{t_2}(\mathrm{HONO})dt$$

$$pNO_3 + h\nu \rightarrow HONO + NO_2$$

$$NO_3^- \xrightarrow{h\nu} [NO_3^-]^*$$

$$[NO_3^-]^* \rightarrow NO_2^- + O(^3P)$$

Experimental set up

Figure 2 shows the diagram of the experiment setup. Ambient air is pumped into the tubing system by an air compressor and passed through a water trap to remove moisture before entering the zero-air generator (**Eco Physics AG PAG 003**), producing clean zero air for the experiment. The zero air is then fed into a gas diluter (**Molecular Analysis series 7800**) to control the gas flow and enters the chamber at a fixed flow rate of 3 LPM. The chamber is a rectangular stainless steel box with dimensions of 50 × 60 × 100 cm, equipped with two UVB lamps **(Sankyo Denki UV-B lamp)**, two fans to enhance internal circulation, a water droplet atomizer to control internal humidity, and an Arduino system to monitor internal temperature and humidity.

On the other side of the chamber, two outlet lines allow gases to exit: one line connects to the NOx analyzer (**Model 42i-TL TRACE Level NOx Analyzer**) at a flow rate of 1 LPM, and the other connects to the HONO analyzer (**TILDAS Dual Laser HNO3, HONO Analyzer**) at a flow rate of 0.6 LPM. All tubing connecting the apparatus is made of Teflon, while the fittings for connections and bypass lines are made of stainless steel.

Figure 2. Diagram of the experimental setup.

Results and Discussion

a. The experiment status:

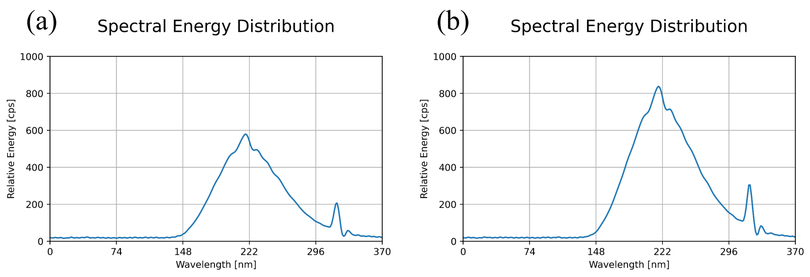


Figure 3. The UVB light spectrum.
(a) One light. (b) Two light.

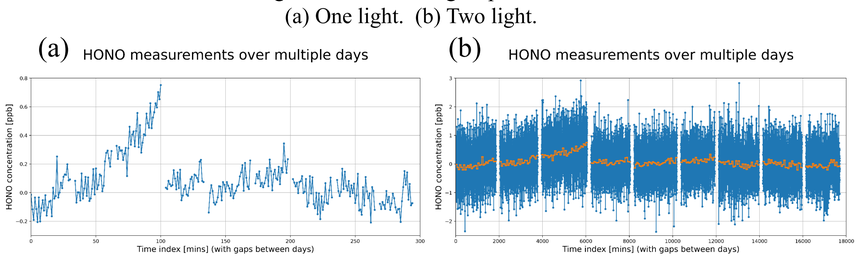
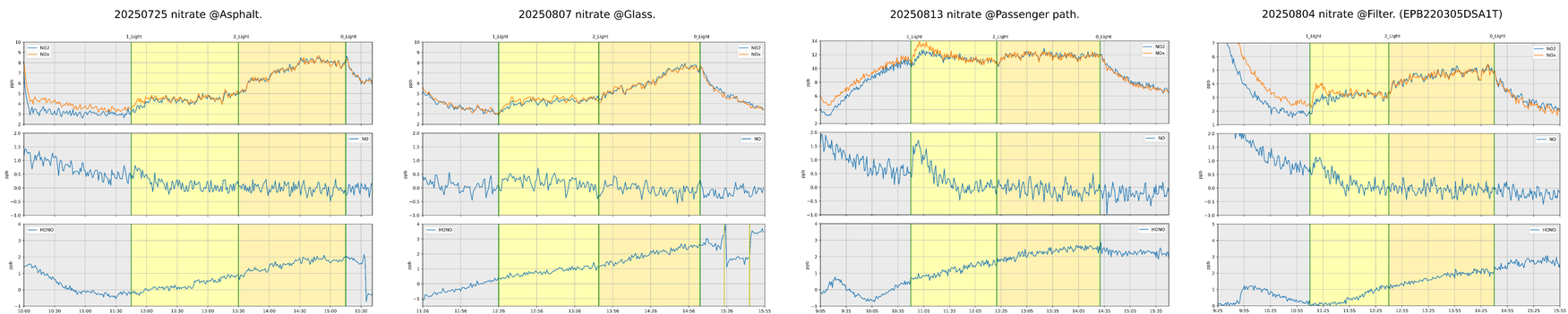


Figure 4. Measurement error of Tildas .
Deviation in (a) minutes. (b) seconds.

b. Measured concentrations:



c. The production rates:

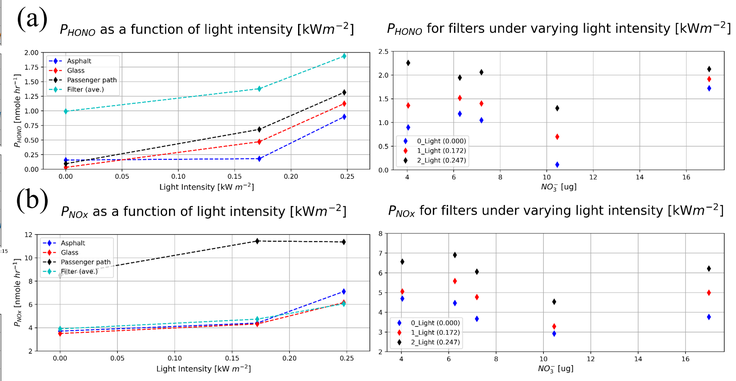


Figure 5. The production rate on different materials.
(a) HONO. (b) NO_x.

Figure 6. The production rate on different filters.
(a) HONO. (b) NO_x.

d. The photolysis rate constant:

The photolysis rate constant of particulate nitrate.

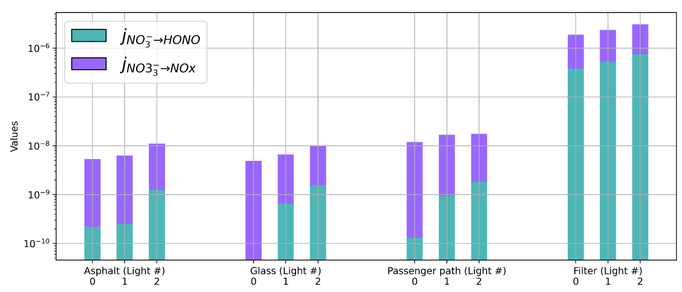


Figure 7. The photolysis rate constant of different materials.
(a) HONO. (b) NO_x.

Conclusion

1. Regardless of the substrate, increasing light intensity led to higher photolysis rate constants of nitrate for HONO production. Compared to ammonium nitrate pipetted onto asphalt, glass, and passenger path surfaces, the photolysis rate constants observed on filters indicate that the majority of nitrate on filter paper is converted to HONO.
2. The amount of nitrate on filters didn't show a significant correlation with the final photolysis rate constants in this study.
3. The photolysis rate constants of nitrate measured on filters ranged from 1.88×10^{-6} to 3.07×10^{-6} [s^{-1}]. Ye et al. (2017) reported nitrate photolysis rates in New York ranging from 6.2×10^{-6} to 5.0×10^{-6} [s^{-1}], with a median of 8.3×10^{-6} [s^{-1}], indicating comparable magnitudes with previous studies.
4. A mass of 12.402 [mg] of nitrate ion was pipetted onto asphalt, glass, and passenger path surfaces, while naturally sampled nitrate on filters ranged from 4.043 to 16.985 [ug]. Despite the lower nitrate mass, P_{HONO} and the $j_{NO_3^-\rightarrow HONO}$ conversion efficiency on filters remained higher than those on asphalt, glass, and passenger path.
5. The experimental light intensity within the 130~340 [nm] wavelength range was 0.172 and 0.247 [kW · m^{-2}], considerably higher than typical environmental conditions. For comparison, under a UV index of 8 in Taiwan, the maximum total UV irradiance is approximately 2×10^{-4} [kW · m^{-2}].

Acknowledgements

I sincerely thank **Yi-Cheng Xiao** for assistance with the experiments and **Chun-chiang Kuo**, and **Kuan-Lin Lai** for valuable discussions.

References

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