

称号及び氏名 博士（工学） Trinh Thai Ha

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論文名 A Study of Gaseous Nitrous Acid: Exhaust-Induced Emission and Variations in the Ambient Atmosphere of Japan and Vietnam Urban Sites

論文審査委員 主査 竹中 規訓
副査 長岡 勉
副査 林 晃敏

論文要旨

Due to its significant role to the atmospheric processes as one dominant source of hydroxyl (OH) radical, nitrous acid (HONO) catches more and more attention from the scientific community. Previous studies have reported that HONO can contribute up to 33 - 56 % of total OH radical production in urban, rural and forest areas. In recent years, numerous field campaigns and simulation studies have been conducted in order to enrich scientific understandings on HONO chemistry, its sources and sinks under different conditions. In general, scientists have proposed five formation pathways of HONO, including direct emission, homogeneous gas phase reactions, heterogeneous reactions, photolysis / photo-enhanced reactions, and biological processes.

Reactive nitrogen species emission from the exhausts of gasoline and diesel vehicles, including nitrogen oxides (NO_x) and HONO, contributes as a significant source of photochemical oxidant precursors in the ambient air. The HONO / NO_x ratio is commonly used to quantify the HONO emission from vehicle exhaust and traffic. A profound traffic-induced HONO / NO_x ratio of approximately 0.8 %, established by Kurtenbach et al. (2001), is recently under controversial discussion because it possibly linked to the underestimation of OH radical budget and ozone level in the morning.

Most of the published studies on HONO were performed in America, Europe and China. Up to the present, only a few HONO measurement studies have been conducted in Japan; therefore, understanding of HONO chemistry in the region is limited. Meanwhile, continuous measurement of HONO has never been conducted in Vietnam, particularly in Hanoi (Vietnam). The works presented in this thesis focused on the measurement of HONO emission in vehicle exhaust and monitoring of HONO in the ambient atmosphere in Sakai (Japan) and Hanoi. It is believed that the results will contribute significantly to the understanding of atmospheric HONO production and loss, its emission factors from diesel- and gasoline-fueled vehicles and the expansion of the global HONO mixing ratios map into two under-reported urban sites.

In Chapter 1, an introduction of HONO's role in atmospheric chemistry and its measurement methods, HONO emission from vehicle exhaust, and the current state of global and regional researches on ambient HONO, were presented. The content of the thesis was also rationalized.

In Chapter 2, the chassis dynamometer measurement of exhaust gases from two diesel and gasoline vehicles equipped with the updated emission reduction technologies was reported. The results comprised of (1) integrated emission as well as temporary profiles of HONO and NO_x emission from the tested vehicles in compliance with the Japanese new long-term emission regulation; (2) the HONO / NO_x mixing ratios in the exhausts from these vehicles and the comparison of our results with previous studies. The emission of regulated gaseous compounds was also measured and reported in this work. For the tested gasoline vehicles equipped with three-way catalytic converter (TWC) after-treatment device, HONO / NO_x ratios ranged from 0 to 0.95 % with very low average HONO concentrations. For the tested diesel vehicle equipped with diesel particulate active reduction (DPR) device, HONO / NO_x ratios varied from 0.16 to 1.00 %. Under the JC08 real-world driving cycles, the average HONO emission from the tested diesel vehicle (approximately 868.8 ppb) was dramatically greater than that from the tested gasoline vehicle (1.2 ppb). Our study suggested that the unexpected exceedance of NO₂ concentration for soot oxidation process in diesel particulate filter was a significant factor which affected the production of HONO. The results also suggested a minor contribution of TWC-installed gasoline vehicle emission to the total HONO budget while such contribution of DPR-installed diesel vehicle emission is dramatically higher.

Chapter 3 focused on seasonal variations of gaseous HONO in the urban ambient atmosphere in Sakai and Hanoi. It provided the major results on (1) modification of the air-dragged aqua-membrane denuder / fluorescence detector system for online measurement of gaseous HONO, which was free of NO₂ interferences with high sensitivity (limit of detection = 0.04 ppb); (2) observation of trace gases and

meteorological parameters in Sakai during spring / autumn (2014 - 2015) and in Hanoi during spring (2015); and (3) discussion of diurnal variations of gaseous species in the two mentioned cities. A same system was used to measure HONO in Sakai and Hanoi. The obtained results well-represented the occurrences of HONO in association with variations of other trace gases and meteorological parameters. Correlation analysis was employed to justify the influences of different factors on diurnal HONO variations in Japan and Vietnam. The average concentrations of HONO in Sakai during spring / autumn were 0.71 ± 0.35 , 0.86 ± 0.50 ppb, respectively. The average concentration of HONO in Hanoi during spring was 1.73 ± 0.76 ppb.

In Chapter 4, vertical behaviors of gaseous nitrous acid in the urban atmosphere of Osaka (Japan) were presented. The study investigated the vertical profiles of HONO at 4 different heights (0, 5, 16, and 25 m) above the ground level (AGL) in an urban site in Osaka, Japan during two measurement periods (January 21st - 22nd and February 3rd - 4th, 2016). The correlations of HONO and various factors, including nitrogen oxides levels, PM_{2.5} and meteorological parameters, were analyzed. Average diurnal HONO concentrations at 0, 5, 16, and 25 m were 1.7, 1.5, 2.2, and 1.2 ppb, respectively. Even though, nocturnal HONO concentrations presented a slightly increasing trend with the increase of heights; daytime and diurnal HONO mixing ratios showed no specific trend. The results of correlation analysis suggested that heterogeneous conversion NO₂ on wet surface had a great influence on the total HONO production. Besides, the HONO / NO_x ratios were 0.06 ± 0.01 , 0.11 ± 0.02 , and 0.04 ± 0.05 for 5, 16, and 25 m AGL, respectively. It implied that direct emission from traffic positively affected the total HONO mixing ratios of the ambient air and this influence was lower at higher altitude, where the air was diluted by active turbulence. Meanwhile heterogeneous formation of HONO on ground surface was likely a significant source after sunrise. Furthermore, high correlations of HONO, NO and solar radiation levels suggested that photolysis of HONO was dominated and contributed to the loss of day-time HONO.

In Chapter 5, general conclusions and future researches were presented.

審査結果の要旨

大気中の亜硝酸ガス(HONO)は大気の浄化に最も重要であると考えられている OH ラジカルの発生源であるが、HONO の生成メカニズムはまだ解明されていない。また、オゾン濃度にも影響を与えるにもかかわらず、その測定は欧米や中国など限られた地域だけで日本やベトナムではほとんど行われていない。本論文は、自動車排ガスや日本やベトナムでの HONO の測定に関する報告であり、次のような重要な結果を得ている。

- 1) 新長期規制のディーゼル車およびガソリン車から直接排出される HONO 濃度を測定し、HONO/NO_x 比がガソリン車で 0~0.95%、ディーゼル車で 0.16~1.0%であり、この値は従来報告されている値と同程度であることを報告した。さらにディーゼル車のスピードと HONO 濃度の関係より、HONO の生成がディーゼル粒子フィルターで粒子が除去されるまでに生成している可能性が高いことを推測し、排ガスからの HONO は、エンジンからテールパイプより排気されるまでの間に粒子上で NO₂ から二次生成したものであることを指摘した。
- 2) 日本やベトナムで HONO を測定するために所属する研究室で開発された従来の HONO 測定装置の改良を行った。HONO 吸収部のガラス管の内面を磨りガラス状にし、さらに 2 つの吸収管を直列に並べることで、HONO 以外の物質の干渉を低減した。この装置により、ハノイ市の HONO 濃度および HONO/NO_x 比が堺市に比べて非常に高いことを報告した。ベトナムでの HONO の連続測定はこれまでに報告がなく非常に貴重なデータを報告した。
- 3) HONO の発生源を明らかにする目的で高度別の HONO 濃度の測定を行い、他の物質との相関、気象要素との関係を調べた。その結果、自動車からの排出が HONO 濃度に大きな影響を与えていること、日の出後の HONO は地面での NO₂ の不均一反応による生成の可能性が高いこと、日中の HONO は光分解による消失過程が大きいことを示した。

以上の諸成果は、従来データがなかった新長期規制車排ガス、ベトナムハノイの HONO 濃度のデータを初めて報告し、まだ解明されていない HONO の発生源や消失過程解明に対して重要な知見を示したもので、大気化学の進展に貢献するところ大である。また、申請者が自立して研究活動を行うのに十分な能力と学識を示したものである。