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[Sea-Ho Oh](#) , [James J. Schauer](#) , [Hajeong Jeon](#) , [Dong-Hoon Ko](#) , [Seoyeong Choe](#) , [Min-Suk Bae](#) *

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Article

Efficiency and Interference Verification of a HONO Collection System Using an Ultrasonic Nozzle Coupled with a Recirculating Spray Chamber for Ambient Air Monitoring

Sea-Ho Oh ¹, James J. Schauer ², Hajeong Jeon ¹, Dong-Hoon Ko ¹, Seoyeong Choe ¹ and Min-Suk Bae ^{1,*}

¹ Department of Environmental Engineering, Mokpo National University, Muan 58554, Republic of Korea; d17418202@365.mokpo.ac.kr

² Department of Civil & Environmental Engineering, University of Wisconsin-Madison, Madison 53705, USA

* Correspondence: minsbae@mnu.ac.kr

Abstract: This study explores the efficiency and applicability of a HONO collection system that incorporates an ultrasonic nozzle and spray chamber for the measurement of ambient air. The system demonstrates (1) a remarkable efficiency of 97.7% across two serial stages, (2) lower detection limits of 0.1 ppbv for HONO, and (3) absence of interference from NO₂ or OH radicals. Practical ambient monitoring with the HONO collection system revealed typical diurnal variations in HONO, O₃, and HNO₃ concentrations, aligning with photolysis dynamics. Notably, HONO concentrations peaked at 0.37 ppb during nighttime and decreased to 0.27 ppb by midday. O₃ demonstrated an inverse relationship with HONO, especially during ozone depletion phases, with r^2 values of 0.94, 0.81, and 0.52 across various intervals. The HONO/NO_x ratio during periods of enhanced HONO suggested the presence of additional formation mechanisms beyond heterogeneous NO_x reactions. Moreover, ozone levels often fell below 20 ppb, indicating a consistent inverse correlation with HONO, thereby confirming periods and highlighting further mechanisms of HONO formation beyond heterogeneous NO_x reactions. The real-time atmospheric chemical reactions involving HONO, monitored concurrently with O₃ and NO_x, were effectively validated by the HONO collection system employed in this investigation.

Keywords: HONO; ultrasonic nozzle; spray chamber

1. Introduction

Nitrous acid (HONO) is acknowledged as a significant precursor of hydroxyl radicals, as suggested by [1,2]. Previous research highlights an average production rate of OH radicals stemming from HONO to be 0.63 ppb/hr, with its maximum contribution rate surpassing 90% [3]. Hendrick et al. [4] similarly pinpointed HONO as a dominant factor in OH radical production, underscoring its crucial role in their generation. Although the specific sources of atmospheric HONO remain somewhat ambiguous, the interaction between NO and OH is often cited as the principal pathway [2]. Potential sources also include emissions from asphalt surfaces [5], direct vehicular emissions from gasoline combustion [6], soil nitrite emissions [7], and biological nitrate reduction processes in soils [8].

Several methods exist for the collection and analysis of atmospheric HONO, typically divided into wet chemical and spectroscopic approaches. Table 1 details the variety of techniques previously employed. Prominent wet chemical methods encompass the Monitor for Aerosols and Gases in ambient Air (MARGA), the long-path absorption photometer (LOPAP), and denuder techniques,

which capture HONO in a solution for subsequent analysis in a liquid phase [9–13]. In contrast, spectroscopic methods frequently involve Differential Optical Absorption Spectroscopy (DOAS) and tunable laser absorption spectroscopy (TLAS) [14,15].

Previous research has explored various strategies for measuring atmospheric HONO. Song et al. [16] documented HONO levels using a high-efficiency denuder scrubber paired with an ion chromatograph (IC), noting an average concentration of 0.36 ppb. Moreover, Gil et al. [17] utilized a quantum cascade-tunable infrared laser differential absorption spectrometer, recording an average concentration of 0.93 ppbv. Kim et al. [11] implemented MARGA to concurrently measure HNO₃ and HONO at hourly intervals, finding concentrations that spanned roughly 1 to 7 µg/m³.

In this research, a spray chamber integrated with an ultrasonic nozzle system was developed to collect HONO, alongside comparisons with PM_{2.5} and other gaseous components. The ultrasonic nozzle system, applied in diverse fields such as food, pharmaceuticals, and coatings, is noted for its ability to generate droplets of consistent size [18–20]. This system offers economic benefits by facilitating the application of IC under similar conditions employed in conventional PM_{2.5} ion component analysis.

Table 1. Summary of Analytical HONO Techniques Classified by Spectroscopic Methods and Wet Chemical Methods.

Category	Technique		Reference
Spectroscopic Analytical Methods	TLAS ¹		[14]
	MAX-DOAS ²		[15]
	IBBCEAS ³		[21]
	CRDS ⁴		[22]
	LIF ⁵		[23]
	TD-CL ⁶		[24]
	CIMS ⁷		[25]
Wet Chemical Analytical Methods	sampler	detector	
	mist-chamber	ion chromatograph	[26]
	stripping coil	long path absorption photometer	[10,12,27]
	stripping coil	ion chromatograph	[26]
	MARGA ⁸	ion chromatograph	[28]
	annular denuder system	ion chromatograph	[29]

¹ tunable laser absorption spectroscopy. ² multi axis differential optical absorption spectroscopy. ³ incoherent broadband cavity-enhanced absorption spectroscopy. ⁴ cavity ring-down spectroscopy. ⁵ laser-induced fluorescence. ⁶ thermal dissociation and chemiluminescent. ⁷ chemical ionization mass spectrometry. ⁸ monitor for aerosols and gases in ambient air.

2. Methods

2.1. Sampling Site

HONO, PM_{2.5}, and additional gases were sampled from the second floor of the College of Engineering Building No. 3 at Mokpo National University, Korea. A duct extending from the second-floor laboratory to the rooftop facilitated the transport of air, driven by a blower, to the measurement devices; these devices accessed the air via an inlet located within the duct (Figure 1). The sampling period occurred from 18:00 on December 11, 2023, to 15:00 on December 25, 2023. In this investigation, PM_{2.5} was analyzed at 1-hour intervals, while HONO and HNO₃ were analyzed every 40 minutes, and other gases every minute. Meteorological data was acquired from a meteorological station located approximately 10 km away from the sampling site through the Open MET Data Portal (www.data.kma.go.kr).

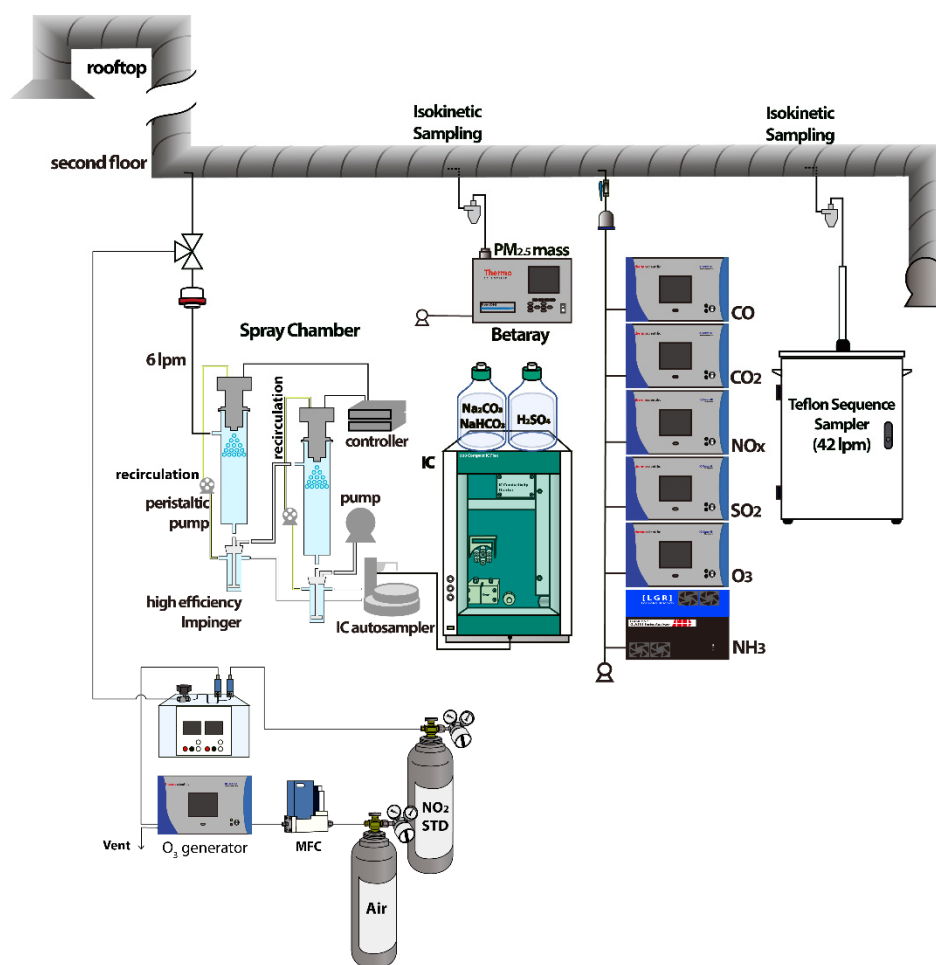


Figure 1. Schematic Diagram of a HONO Collection System Using an Ultrasonic Nozzle Coupled with a Spray Chamber and Ion Chromatography.

2.2. Analytical Method for $PM_{2.5}$ and Gaseous Compounds

The mass concentration of $PM_{2.5}$ was determined using Teflon filter sampling and the beta-ray absorption method (5014i Beta Continuous Ambient Particulate Monitor, Thermo, USA). We conducted three-hour integrated sampling employing Teflon filters with a Mid-Volume Air Sampler (MAS-16, APM, Korea) coupled with a cyclone (URG-2000-30EC, URG Corp., USA), which operated at a flow rate of 42 L/min. The beta-ray absorption method involved collection at a flow rate of 16.7 L/min, with hourly mass concentrations adjusted based on the weight change of the Teflon filter pre- and post-sampling. To collect $PM_{2.5}$ from the main duct on the roof, we adjusted the cross-sectional area of the inlet to achieve isokinetic sampling conditions. Subsequent analysis of three-hour integrated $PM_{2.5}$ samples from Teflon filters included extraction and analysis for anions and cations. Each Teflon filter was placed in a 20 mL vial, moistened with 3 mL of MeOH, followed by the addition of 16 mL of water. Following 2 hours of sonication, the sample was filtered through a Polyvinylidene Fluoride (PVDF) syringe filter to prepare for IC analysis. Analyzed ionic components of $PM_{2.5}$ included NH_4^+ , NO_3^- , and SO_4^{2-} . For the cation analysis, a Metrohm Metrosep C4 250/4.0 column was utilized alongside a 5 mM HNO_3 eluent.

We measured gaseous concentrations using the same duct sampling inlet method as for $PM_{2.5}$. The concentrations of NO-NO₂ (42iQ NO-NO₂-NO_x Analyzer, Thermo Fisher Scientific, USA), CO (48iQ CO Analyzer, Thermo Fisher Scientific, USA), CO₂ (410iQ CO₂ Analyzer, Thermo Fisher Scientific, USA), O₃ (49iQ O₃ Analyzer, Thermo Fisher Scientific, USA), SO₂ (43iQ SO₂ Analyzer, Thermo Fisher Scientific, USA), and NH₃ (LA331-EAA, ABB-Los Gatos Research, USA) were determined. All instruments were calibrated prior to measurements. Detailed methodologies and

procedures on quality assurance/quality control (QA/QC) are documented in prior publications [30–35].

2.3. Configuration and Analytical Methods for HONO Collection Using Ultrasonic Nozzle Coupled with Spray Chamber and Ion Chromatography

The configuration of the HONO collection system using an ultrasonic nozzle is depicted in Figure 1. Air drawn through the inlet and duct system was first purified by a Teflon filter, which was replaced daily. Subsequently, the air was channeled into the first spray chamber and then directed to an impinger. This impinger, containing a specific volume of an absorbing solution, was designed to minimize mist carryover to subsequent stages, functioning similarly to the gas-liquid separator found in a stripping coil [13].

The experimental chamber featured a diameter of 40 mm and a height of 200 mm, with the absorbing solution being sprayed from the top, while air was introduced through a side branch. The duration of sampling using the spray chamber was set at 40 minutes. The impinger, equipped with branches on both sides, facilitated the transport and recirculation of absorbing solutions to the chamber for repeated spraying. Absorption solution circulation was achieved through a peristaltic pump connected to the impinger, maintaining a flow rate of approximately 13.06 mL/min. This recirculation aimed to reduce the method detection limits (MDLs) below those of previous real-time systems [9–13]. The spray nozzle, constructed from stainless steel with a height of 140 mm and a diameter of 66 mm, atomized the injected fluid using a vibration frequency of 120 kHz. Following a 40-minute sampling period, the sample was analyzed using an ion chromatograph (IC) during a concurrent 40-minute sampling session. HONO and HNO₃ collected were analyzed as NO₂⁻ and NO₃⁻ ions, respectively, with the MDLs established at 0.1 ppbv for both HONO and HNO₃, expressed as atmospheric volume concentrations. These MDLs represent a reduction of up to five times compared to those of prior real-time systems, as documented in Table 1.

In pursuit of higher efficiency, the configuration of the spray chamber and impinger was organized in two serial stages. Various absorbing solutions and probes have been employed for HONO collection in earlier studies, including boron dipyrromethene [36], pure water [13,37], 2,4-dinitrophenylhydrazine [38], and Azo dye [39]. In this study, a 25 µM Na₂CO₃ solution was utilized to minimize the interference from SO₂ [13,26]. This solution was drawn into the ultrasonic nozzle via a peristaltic pump, ensuring consistent droplet formation irrespective of airflow rate variations during sampling. A total of 50 mL of absorbing solution was used, with a flow rate maintained at 6 L/min for a duration of 40 minutes. Previous studies established methods to assess the efficacy of wet chemical techniques [13,26,40]. This study applied those established methods, analyzing the absorbing solution collected from each of the two serially connected spray chambers in order to calculate the effectiveness.

The absorbing solution collected in the spray chamber was transferred into 60 mL vials and analyzed using ion chromatography (IC, 930 Compact IC Flex, Metrohm, Switzerland). For IC, a Metrohm Metrosep A Supp 5 150/4.0 column was utilized alongside 3.20 mM Na₂CO₃ and 1.00 mM NaHCO₃ as the eluent, with H₂SO₄ (50 mM) acting as the suppressor. The processes of replenishing and retrieving the absorbing solution from the spray chamber, as well as conducting IC analysis, were automated by an autosampler (858 Professional Sample Processor, Metrohm, Switzerland).

3. Results

3.1. Efficiency and Interference Verification of a HONO Collection System

As previously described, the efficiency of the system was determined, resulting in 97.7 % for the two serial stages with MDLs of 0.15 ppbv for HONO and 0.11 ppbv for HNO₃. The current spray chamber system exhibits enhanced performance in terms of both efficiency and MDLs. Concentrations have been corrected for efficiency in the ensuing results. To verify interference in the spray chamber, NO₂ and O₃ generators (49iQPS, Thermo Fisher Scientific, USA) were employed [41,42]. The setup of interference verification is shown at the bottom of Figure 1. In addition to NO₂

interference, the potential formation of OH radicals by microdroplets, which could impact HONO measurement, was examined using an OH radical probe (terephthalic acid) [43,44]. The O₃ generator produced a consistent O₃ concentration using compressed air, mixed with the NO₂ standard in a specially designed mixer. The mixed air was then collected and analyzed in the spray chamber to verify any interference. The air mixture used had final concentrations of 50 ppb for O₃ and 33 ppb for NO₂, and testing confirmed that there was no interference from either NO₂ or OH radicals.

3.2. Ambient Air Measurement with a HONO Collection System

From December 11 to December 25, 2023, both PM_{2.5} and gaseous species such as HONO, NO_x, and others were measured. The average ± standard deviation of the measured components throughout this period is summarized in Table 2. HONO was detected at an average of 0.31 ppb, peaking at 0.60 ppb (Figure 2a), which is comparable to previous measurements of HONO concentration in Seoul (0.36 ppb) recorded by Song et al. [16]. The mean concentration of O₃ was 32.44 ppb, while NO and NO₂ concentrations were 0.77 ppb and 3.28 ppb, respectively (Figure 2a,c). On the dates of December 13, 19, and 24, O₃ levels dipped below 20 ppb before rebounding and consistently remaining above 25 ppb for the rest of the measured period. Regarding PM_{2.5}, the average concentration during this interval was 9.38 µg/m³, with the maximum concentration reaching 25.56 µg/m³ at 3 AM on December 20 (Figure 1f). Given the winter mean PM_{2.5} concentration from 2015 to 2022 in South Korea has been above 20 µg/m³, the study period exhibited notably lower particulate levels, although there were occasional increases potentially attributable to external influxes, as noted by Jeong et al. [45]. The mean concentrations of CO and CO₂ registered at 212 ppb and 449 ppm respectively, with the peak CO/CO₂ ratio of 0.87 occurring at 3 AM on December 20 (Figure 2b), significantly, the CO/CO₂ ratio stood at 0.87 at the recorded time, which was higher than the mean value of 0.47 for the entire study period. This heightened CO/CO₂ ratio may signify decreased combustion efficiency or substantial long-range transport from China to the Korean Peninsula, according to previous research [46–48]. Figure 2d presents the average concentrations of ionic components (NH₄⁺, NO₃⁻, SO₄²⁻) throughout the study period as 0.99, 1.30, and 2.00 µg/m³ respectively. Notably, the concentrations peaked on December 20 and December 24 at 3.57 µg/m³ for NH₄⁺, 5.75 µg/m³ for NO₃⁻, and 7.09 µg/m³ for SO₄²⁻. The concurrent increase in particulate matter and concentrations of CO and CO₂ on these dates indicates a regional influx of polluted air.

SO₂ was measured at an average of 0.79 ppb throughout the study period and NH₃ was measured at 4.33 ppb (Figure 2g). The concentration trend of NH₃ levels paralleled temperature changes, which likely influenced ammonia release into the atmosphere [49–51]. HNO₃ concentrations during the study period averaged 0.32 ppb, reaching a peak of 0.83 ppb during PM_{2.5} episodes. Previous studies recorded winter HNO₃ levels in Seoul that varied from 0.16 ppb (non-hazy days) to 0.34 ppb (hazy days). Concurrently, Daejeon recorded winter concentrations of 0.72 ppb and summer concentrations of 0.1 ppb, with the annual averages in Chuncheon and Seoul ranging from 0.60 to 1.06 ppb. These results imply that the observed concentrations in this study are influenced by factors such as temperature, seasonal variations, and haze phenomena [52–54].

Table 2. Results of Mean Concentrations of PM_{2.5} and Gaseous Compounds.

Compounds	Unit	mean ± std
PM _{2.5}	µg/m ³	9.38±5.34
NO ₃ ⁻	µg/m ³	1.3±1.5
SO ₄ ²⁻	µg/m ³	2±1.16
NH ₄ ⁺	µg/m ³	0.99±0.76
HONO	ppb	0.31±0.1
HNO ₃	ppb	0.32±0.19
NO	ppb	0.77±1.29
NO ₂	ppb	3.28±2.22
O ₃	ppb	32.44±7.97
SO ₂	ppb	0.79±0.29

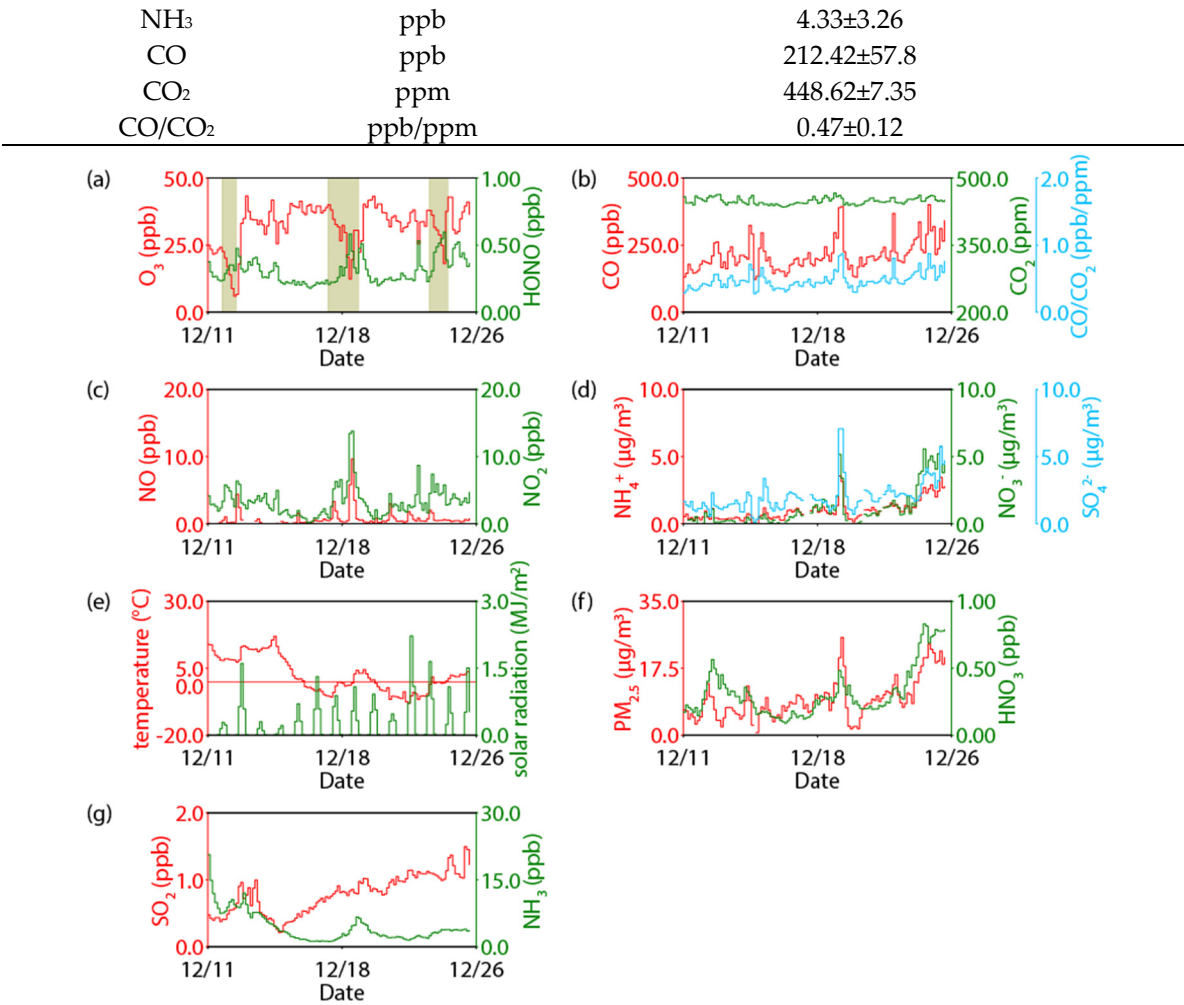


Figure 2. Time Series Variation of (a) O₃ and HONO, (b) CO, CO₂, and CO/CO₂, (c) NO and NO₂, (d) NH₄⁺, NO₃⁻, and SO₄²⁻, (e) Temperature and Solar Radiation, (f) PM_{2.5} mass and HNO₃, and (g) SO₂ and NH₃.

3.3. Diurnal Variation and Validation of a HONO Collection System for Ambient Air Measurement

To determine the feasibility of using the HONO collection system in ambient air measurements, the typical diurnal behavior of HONO (i.e., nighttime increase and daytime decrease) was validated. Figure 3a–c illustrates the diurnal fluctuations in gas-phase concentrations of HONO, HNO₃, and O₃. The highest average HONO concentration was recorded at 08:00, measuring 0.372 ppb, closely followed by 21:00 with a concentration of 0.369 ppb. The lowest levels occurred from 11:00 to 16:00, at 0.27 ppb. In contrast, the peak concentration of O₃ was recorded at 15:00, reaching 36.27 ppb. The corresponding diurnal peak of solar insolation (Figure 3d) was observed between 13:00 and 14:00. These trends corroborate earlier findings that HONO increases after sunset and decreases due to photolytic degradation [55,56]. HNO₃ demonstrated its highest concentration of 0.38 ppb at 15:00, with the lowest at 20:00, measuring 0.27 ppb. The daytime increase in HNO₃ is believed to result from the reaction of OH radicals with NO₂, whereas the second-highest concentration (0.36 ppb at 00:00) is attributed to heterogeneous reactions involving water vapor and N₂O₅ during the night [56–58].

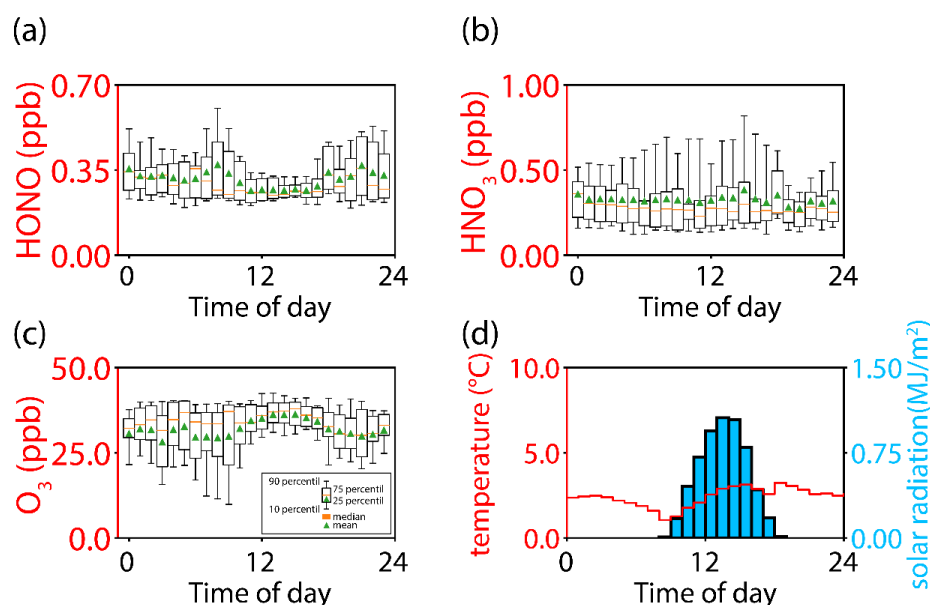


Figure 3. Diurnal Patterns of (a) HONO, (b) HNO₃, (c) O₃, and (d) Temperature and Solar Radiation.

3.4. Inverse Relationship Between Ozone and HONO

During the study period, it was observed that ozone concentrations fell below 20 ppb and an inverse relationship between HONO and O₃ became evident. This phenomenon occurred three times, each lasting between 18 to 24 hours, as denoted by the shading in Figure 2a and presented in Figure 4a. The most notable period spanned from 03:00 on December 18 to 21:00 on December 19, with a correlation coefficient (r^2) of 0.94, firmly establishing the inverse relationship between ozone and HONO. The other periods occurred from 12:00 on December 23 to 15:00 on December 24 (r^2 : 0.81) and from 12:00 on December 12 to 06:00 on December 13 (r^2 : 0.52). The reduction in ozone levels can be attributed to NO₂ s titration effect, whereas the rise in HONO levels is linked to its formation from nitrate particles and NO₂ [59–63]. Throughout the study period, HONO demonstrated a correlation with NO₂ (r^2 : 0.42), while NO showed a lower correlation, even with excluded periods featuring NO concentrations exceeding 0.8 ppb (Figure 4b). The correlation between NO₂ and HONO increased to 0.65 during nighttime (21:00 - 06:00), attributable to the heterogeneous conversion of NO₂ on wet surfaces, which enhances nocturnal HONO production. Noticeable diurnal variations in HONO were also observed, with peaks occurring in the early morning and dips in the late afternoon. At night, the primary source of HONO was from emissions and RH-dependent NO₂ conversions, whereas during the day, HONO primarily stemmed from NO-OH reactions, influencing OH production and atmospheric oxidation processes [64]. During the notable increase of HONO on December 23, the HONO/NO_x ratio averaged 0.085, higher than in the other periods (0.068 and 0.060), suggesting that mechanisms beyond heterogeneous NO_x reactions play a more significant role in HONO formation during this time [65,66]., the atmospheric chemical reactions of HONO, which are trackable through real-time measurement instruments (O₃, NO_x), have been corroborated by the HONO collection device employed in this study.

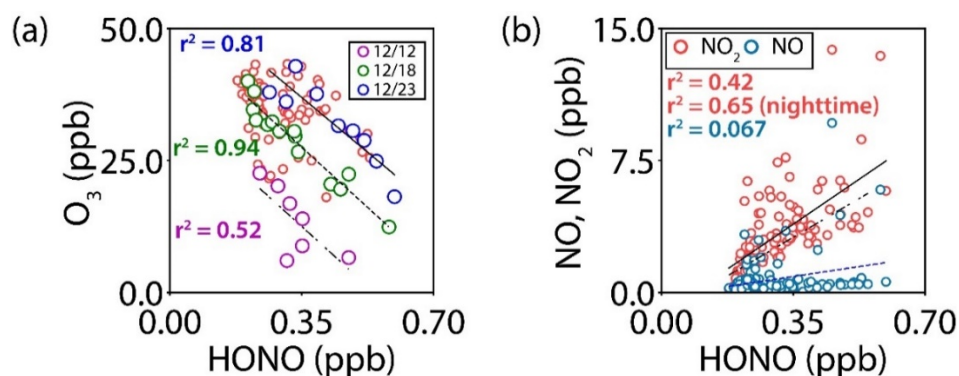


Figure 4. Scatter Plots Between (a) O₃ and HONO, and (b) NO, NO₂, and HONO.

4. Discussion

This study successfully demonstrated the efficiency and applicability of the HONO collection system using an ultrasonic nozzle and spray chamber for ambient air measurements. The system attained an efficiency of 97.7 % and MDLs of 0.1 ppbv for HONO across two serial stages. Interference checks revealed negligible impacts from NO₂ or OH radicals. From December 11 to December 25, 2023, the collected data showed that HONO concentrations exhibited typical diurnal variations, with peaks during the night and troughs around midday. This pattern corresponds with established photolysis dynamics and previous studies. Diurnal variations for O₃ and HNO₃ also occurred as expected, with O₃ reaching its maximum during daylight and HNO₃ escalating due to photochemical responses. Throughout the study, we observed specific instances of inverse correlations between HONO and O₃ concentrations, particularly during episodes of ozone depletion. These correlations, with r^2 values of 0.94, 0.81, and 0.52 across different timeframes, highlighted the interplay between ozone titration and HONO formation. Moreover, variations in the HONO/NO_x ratio indicated the influence of heterogeneous reactions beyond simple NO_x chemistry. Overall, the findings confirm that the HONO collection system is capable of reliably capturing atmospheric chemical reactions involving HONO, corroborating data from real-time measurement devices (O₃, NO_x). This validation promotes the systems utility in ambient air quality monitoring and research, offering valuable insights into the atmospheric mechanisms regulating HONO dynamics.

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