

Photochemical production of nitrous acid on glass sample manifold surface

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[1] Significant production of HONO was observed on glass sample manifold wall surface when exposed to sunlight during the PROPHET 2000 summer measurement intensive. It is hypothesized that the artifact HONO was produced by photolysis of adsorbed nitric acid/nitrate on the manifold wall surfaces followed by the subsequent reaction of produced NO₂ and adsorbed H₂O on surface. This observation suggests against the use of an unshielded glass manifold as a sampling inlet for the measurement of atmospheric HONO. It may also have some implications in interpreting field NO_x data measured using similar glass inlet manifolds, especially from the clean remote environments where NO_x is low and HNO₃ is a major fraction of NO_y. *INDEX TERMS*: 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques

1. Introduction

[2] Large diameter glass sample manifolds have been used in a number of ground-based atmospheric measurements of chemical species during major field campaigns, e.g., MLOPEX [Carroll *et al.*, 1992], SOS-ROSE [Goldan *et al.*, 1995] and PROPHET [Carroll *et al.*, 2001]. At sufficiently high air flow rate and sufficiently low residence time of sample air in the manifold, measurements can be made from the sample manifold without detectable interference for most chemical species. Exceptions to this are highly “sticky” compounds such as HNO₃ and NH₃. Material that sticks to the wall of inlet manifolds also has the potential to affect measurements of other species. Here we report an observation of artifact HONO production in a glass inlet manifold when exposed to sunlight and discuss its implication in interpreting field NO_x data.

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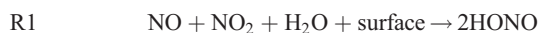
2. Experimental

[3] HONO measurement was carried out as a part of the PROPHET (Program for Research on Oxidants: PHotochemistry, Emissions, and Transport) 2000 summer intensive at the University of Michigan Biological Station in Pellston, MI. The site possesses a 31 m scaffolding tower extending through the canopy of a mixed hardwood forest. Detailed descriptions of the sampling site are given in Carroll *et al.* [2001]. A 2-channel HONO measurement system [Zhou *et al.*, 1999; Huang *et al.*, 2002] was deployed. The method was based on aqueous-phase scrubbing of HONO using a coil sampler, followed by derivatization of scrubbed nitrite into a highly light-absorbing azo dye and HPLC analysis of the derivative with a UV-Vis detector. The detection limit was 5 pptv, with a relative uncertainty of ≤15% and a precision ≤10% at the 100-pptv level.

[4] The 2-channel system was set up to measure HONO concentrations at two different heights in order to establish the vertical HONO concentration gradient over this forest site. One channel of the system was used to measure at or below canopy level via a 21-m or a 6-m 1/4” OD PFA Teflon tubing that was wrapped in aluminum foil. Total flow rate through the Teflon inlet was 15–20 L min⁻¹. The other channel sampled air from the PROPHET glass manifold via a 1 m length of 1/4” OD PFA tubing at a flow rate of 2 L min⁻¹. The top of the PROPHET glass manifold is 34 m above ground and about 15 m above canopy level. It is constructed of 3 m long sections of 5 cm ID Pyrex tube (Corning). Air was pulled through the manifold using a blower at a flow rate of about ~3300 L min⁻¹, resulting in a sample air residence time of less than 2 seconds [Carroll *et al.*, 2001]. NO and NO₂ were measured using a chemiluminescence NO detector equipped with a photolytic converter sampling from the glass manifold [Thornberry *et al.*, 2001].

3. Results and Discussion

[5] At night there was typically a positive HONO concentration gradient toward the canopy at relative humidity <100% with higher concentrations near the forest (Figure 1). This is consistent with a surface source of HONO via reactions R1–R2, with R2 being the dominant one [Calvert *et al.*, 1994; Lammel and Cape, 1996]:



When ambient relative humidity reached 100% over an extended period of time, negative gradients toward the

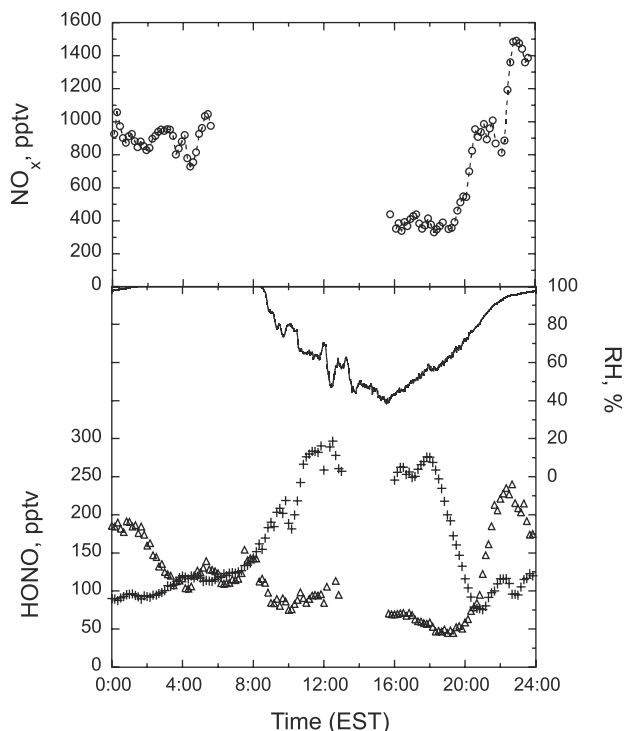


Figure 1. HONO concentrations in air samples drawn from the exposed Pyrex glass manifold at 34 m (crosses) and from a dark Teflon inlet at 5 m (open triangles), along with relative humidity (solid lines) and NO_x (circles) on July 29, 2000.

canopy were observed, suggesting that the canopy surfaces became a net sink for HONO under this condition. We attribute this behavior to the depositional loss of gas-phase HONO into dew on canopy surfaces [He *et al.*, 2002].

[6] During the day, however, an unexpected behavior was observed, with consistently higher HONO concentrations at the 34 m height, sampled via the Pyrex inlet manifold, than measured within the forest canopy (Figure 1). This is inconsistent with the idea that the 34-m inlet was farther from the expected HONO source on the canopy surfaces than the in-canopy inlet and with the shorter photolytic lifetime above the shaded canopy. The daytime HONO concentrations in the air sampled from the glass manifold were as high as 400 pptv at solar noon. To maintain this concentration against fast photolysis of HONO (~ 15 min lifetime) in the ambient atmosphere, a very large source would be required, ~ 1.6 ppbv hr^{-1} . Production rates this high would only be expected in high- NO_x , urban environments [Harris *et al.*, 1982; Calvert *et al.*, 1994; Reisinger, 2000]. Based on current understanding, they should not occur in rural regions such as the PROPHET site where NO_x is typically less than 1 ppbv [Thornberry *et al.*, 2001]. Further examination of daytime HONO and UV intensity data reveals an interesting variation pattern. The HONO concentration gradient anomaly, defined as the concentration difference between the exposed glass manifold at 34 m and the dark Teflon inlet in canopy, closely followed UV intensity. The daytime variation pattern was exemplified by the observations on July 27 (Figure 2), which was a cloudy

day with the sun moving in and out of clouds and with a high- NO_x (up to 6.5 ppbv) and high- NO_y (up to 8.2 ppbv) episode passing through the site on the previous day. This correlation led us to consider the possibility of a photochemical HONO artifact source on the glass manifold wall surface. A series of experiments were therefore conducted to examine this possibility.

[7] For the first experiment on August 11, both HONO channels were set to measure ambient HONO concentrations at the same height from the top of the sampling tower, by moving the Teflon inlet up to the level of the glass manifold. A large difference in the measured HONO concentrations was observed: 50 pptv from the dark Teflon inlet vs 80–100 pptv from the exposed glass manifold in the mid afternoon hours (Figure 3). The glass manifold was then wrapped with aluminum foil, which took about 15 minutes starting at 14:30 EST. The HONO signals dropped immediately to the level of the Teflon inlet channel, about 25–40 pptv. The NO_x concentrations measured from the manifold changed only slightly during this period, from 34 ± 3 and 131 ± 14 pptv for NO and NO_2 , respectively, during 13:45–14:30, to 30 ± 4 and 127 ± 31 pptv during 14:40–15:30.

[8] The glass manifold was kept wrapped with aluminum foil and the Teflon inlet was lowered back to the canopy height for three days while all the measurements were running as usual. During the three days, we observed daytime HONO distribution that was consistent with our expectation, i.e., low concentrations above the canopy due

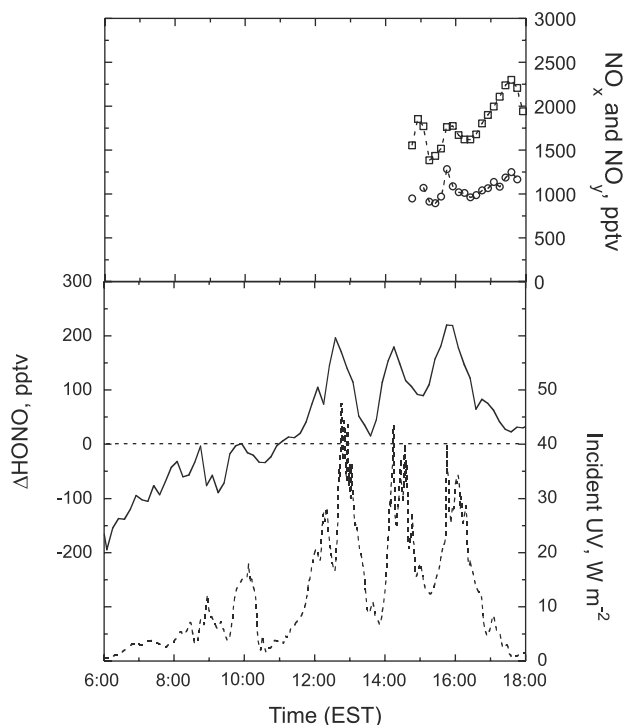


Figure 2. HONO concentration gradient anomaly, i.e., the concentration difference between the exposed glass manifold at 34 m and the dark Teflon inlet in the canopy (solid line), along with incident UV intensity (dashed line), NO_x (open circles) and NO_y (open squares) on July 27, 2000.

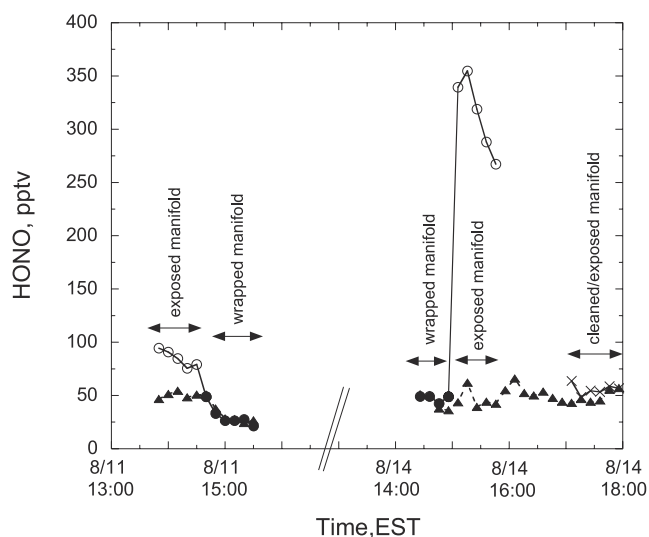


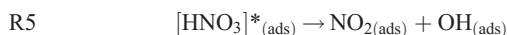
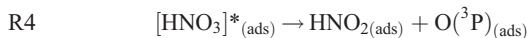
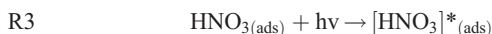
Figure 3. HONO concentrations in air samples drawn from 34 m above ground via a dark Teflon PFA inlet (solid triangles) and via the Pyrex glass manifold (open circles – exposed to sunlight, solid circles – wrapped in aluminum foil, crosses – washed/exposed to sunlight) during the 2 experiments on August 11 and August 14, 2000. The time periods and actions taken were indicated by the arrows.

to its fast photolytic loss and a positive concentration gradient toward the canopy surface [He *et al.*, 2002].

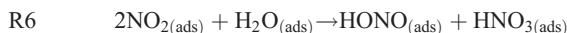
[9] For the second experiment on August 14, both HONO channels were set to measure ambient HONO concentrations from the top of the sampling tower at 14:30 EST, one from the dark glass manifold and the other from the dark Teflon inlet. The HONO signals from the two channels agreed with each other within our measurement precision of 10% (Figure 3). The aluminum foil was then removed from the glass manifold but kept on the Teflon inlet. When the glass manifold was exposed to sunlight, at about 15:00 EST, the HONO signals in the channel increased immediately from 50 pptv to 350 pptv (Figure 3) while those measured via the dark Teflon inlet remained relatively constant. At 16:00, we began cleaning the inside surface of the manifold by rinsing it with water and drawing a wet cloth through the entire length. The manifold was then allowed to dry before sampling resumed. This procedure took about an hour. Subsequent to the cleaning, the HONO signal from the sunlight-exposed glass manifold was the same level as that measured through the dark Teflon inlet (Figure 3).

[10] These results clearly indicate that the artifact HONO was produced from something on the inner surface of the glass inlet manifold via a photochemical process. While several reactions may result in HONO formation, HNO_3 photolysis seems to be the strongest candidate responsible for our observation. HNO_3 is a highly “sticky” species [Huebert and Robert, 1985; Neuman *et al.*, 1999]. Effective adsorption of HNO_3 onto glass wall surfaces has been observed [Neuman *et al.*, 1999]. Since air is constantly pulled through the manifold, HNO_3 would accumulate on the inlet wall surface over time, to form a layer of hydrated HNO_3 . When exposed to sunlight, the highly concentrated

HNO_3 absorbs the UV portion of the sunlight transmitted through Pyrex glass (UV cutoff wavelength ~ 290 nm) and undergoes photolysis:



In the actinic region of solar radiation, NO_2 is the dominant primary product of HNO_3 photolysis, with a quantum yield of near unity in the gas-phase [Atkinson *et al.*, 1992] and a $\text{NO}_2:\text{HNO}_2$ yield ratio of about 9:1 in aqueous solutions [Mack and Bolton, 1999]. The relative importance of R4 and R5 is still unknown for adsorbed HNO_3 photolysis. At the relative humidity of $\geq 40\%$ observed during the measurement intensive, there should be at least several monolayers of water on the glass manifold wall surfaces [Svensson *et al.*, 1987; Saliba *et al.*, 2001]. Thus the produced $\text{NO}_{2(\text{ads})}$ may react rapidly with adsorbed H_2O to produce HONO, which is then released from the surface into the air [Pitts *et al.*, 1984]:



This mechanism is consistent with the recent observations of photochemical production of HONO [Zhou *et al.*, 2001] and NO_x [Honrath *et al.*, 1999, 2000] in snowpack from nitrate/ HNO_3 photolysis. These observations are also supportive of a recent hypothesis that the photolysis of adsorbed HNO_3 /nitrate on ground surfaces is a major daytime source of HONO and thus is responsible for the observed elevated HONO concentrations in the rural atmospheric boundary layer [Zhou *et al.*, 2002].

[11] To produce an observed artifact HONO signal of 100 pptv at a total manifold flow rate of about 3300 L min^{-1} , a production rate of $1.5 \times 10^{-8} \text{ moles min}^{-1}$ on the manifold wall surface would be required. If a photolysis rate of $\sim 6 \times 10^{-7} \text{ s}^{-1}$ is assumed (based on the gas-phase rate), $4 \times 10^{-7} \text{ moles of HNO}_3$ needs to be present on the manifold wall surface. Assuming that ambient HNO_3 adsorbed quantitatively onto a clean manifold [Neuman *et al.*, 1999], it would take only 2.8 days to accumulate to this amount with an average ambient HNO_3 concentration of 700 pptv [Thornberry *et al.*, 2001]. After the adsorbed HNO_3 builds up to a sufficient level, a “steady state” will be reached where the rate of adsorption of HNO_3 onto the sunlight-exposed manifold wall surface is the same as its photolysis rate plus other losses, such as evaporation. The amount of HNO_3 adsorbed on the glass manifold wall surface at steady state would be highly dependent on the ambient HNO_3 concentration, temperature, and relative humidity. If only the top 15-m fully sunlit portion of the manifold wall surface was responsible for producing the artifact, a HNO_3 layer of about $1.7 \times 10^{-4} \text{ moles m}^{-2}$, corresponding to a ≥ 10 -monolayer thickness, would be required. Given the volatility of HNO_3 , it seems unlikely that such a thick layer of pure HNO_3 would remain attached to the surface. Some other factors, therefore, also must be at work to produce the observed artifact. The presence of H_2O on

glass surface as a film of monolayers at the ambient relative humidity of $\geq 40\%$ may greatly enhance the adsorption of HNO_3 via hydration. The amount of HNO_3 /nitrate on the manifold wall surface may be increased by the presence of aerosol nitrate on surface. In addition, the photolytic rate constant of HNO_3 /nitrate on the surface may be significantly different compared to either the gas or aqueous phase rates that have been measured. Detailed laboratory work on surface HNO_3 photolysis is, therefore, necessary to verify and quantify the proposed process.

[12] The observation of this HONO artifact suggests against the use of an uncovered glass manifold as a sampling inlet for the measurement of atmospheric HONO. It may also have some implications in interpreting field NO_x data obtained using a similar glass inlet manifold. HONO in the sample gas may contribute to the NO_2 signal, with a photolysis efficiency of about 20% [Ridley *et al.*, 2000]. Although the interference of this artifact HONO on NO_x measurement was found not to be significant during the PROPHET 2000 summer intensive, it could become significant in the remote clean environment where NO_x is low and HNO_3 is a major fraction of NO_y . In addition, the observed phenomenon on glass manifold surface may also occur on other surfaces and contribute to transformation of HNO_3 to NO_x in the atmospheric boundary layer, especially in the remote regions.

[13] We recommend that glass inlet manifolds be shielded from sunlight in the future to minimize interferences from light-induced surface processes.

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