Evidence of Aerosols as a Media for Rapid Daytime HONO Production over China

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Supporting Information

ABSTRACT: Current knowledge of daytime HONO sources remains incomplete. A large missing daytime HONO source has been found in many places around the world, including polluted regions in China. Conventional understanding and recent studies attributed this missing source mainly to ground surface processes or gas-phase chemistry, while assuming aerosols to be an insignificant media for HONO production. We analyze in situ observations of HONO and its precursors at an urban site in Beijing, China, and report an apparent dependence of the missing HONO source strength on aerosol surface area and solar ultraviolet radiation. Based on extensive correlation analysis and process-modeling, we propose that the rapid daytime HONO production in Beijing can be explained by enhanced hydrolytic disproportionation of NO2 on aqueous aerosol surfaces due to catalysis by dicarboxylic acid anions. The combination of high abundance of NO2, aromatic hydrocarbons, and aerosols over broad regions in China likely leads to elevated HONO levels, rapid OH production, and enhanced oxidizing capacity on a regional basis. Our findings call for attention to aerosols as a media for daytime heterogeneous HONO production in polluted regions like Beijing. This study also highlights the complex and uncertain heterogeneous chemistry in China, which merits future efforts of reconciling regional modeling and laboratory experiments, in order to understand and mitigate the regional particulate and O3 pollutions over China.

INTRODUCTION

Hydroxyl radical (OH) is a ubiquitous atmospheric oxidant that determines lifetimes of numerous air pollutants and greenhouse gases. It is well established that oxidation of water vapor (H2O) by electronically excited oxygen atoms, O(1D), from photolysis of ozone (O3) is the dominant OH source on a global scale. In situ observations showed that photolysis of nitrous acid (HONO) can be an important OH source in the planetary boundary layer (PBL).1 Current knowledge of daytime HONO sources is still incomplete. A large missing HONO source, pHONO, which is defined as the formation of HONO that cannot be explained by the gas-phase oxidation of nitrogen monoxide (NO) by OH, has been inferred from numerous in situ observations (Table S1 in the Supporting Information (SI)). To explain these observations, various mechanisms have been proposed. Most of these mechanisms involve ground or forest canopy surfaces, such as photosensitized conversion of nitrogen dioxide (NO2) by solid organics,2,3 soot,4 or titanium dioxide (TiO2);5 photolysis of nitric acid (HNO3);6,7 soil nitrite (HNO2) release,8 etc. Gas-phase sources have also been suggested, such as the reaction between electronically excited NO2 (NO2*) and H2O9 and, most recently, the reaction between NO2 and HO2·H2O.10

Ambient aerosols have been commonly regarded as an unimportant heterogeneous reaction media compared to ground or canopy surfaces, considering their small surface area and low uptake coefficients (γ = 10−7 ~10−6).11 However, in situ measured vertical gradients of HONO and its precursors to date have not ruled out the possibility of a significant airborne
HONO source.\(^1,12,13\) Moreover, recent laboratory studies showed that organic anions could catalyze and dramatically accelerate NO\(_2\) uptake by aqueous aerosols.\(^14–17\) Aerosol uptake of NO\(_2\) with \(y\) on the order of \(10^{-4} \sim 10^{-3}\) has been observed and linked to the catalysis effect of photochemically formed dicarboxylic acid anions.\(^17\) These findings suggest that tropospheric aerosols might play a much more important role in daytime HONO production than previously thought over regions with high loads of aerosols that have favorable chemical compositions.

The large abundance and complex composition of aerosols over China provide a unique yet poorly understood media for heterogeneous reactions.\(^1,8,19\) Previous studies using in situ20–24 and satellite\(^25\) data reported extraordinary levels of organic acids and dicarbonyl compounds on a regional basis over eastern China. In this work, we investigate the missing daytime HONO source observed in Beijing, China. Liu et al.\(^26\) examined the role of HONO in photochemistry during CAREBeijing-2007 by introducing a pseudo reaction of NO\(_2\) \(\rightarrow\) HONO that reproduces the observed daytime HONO. In this paper, we first explore evidence for plausible HONO formation mechanisms by examining the correlations of the missing HONO source, pHONO, with various observed physical and chemical parameters. We then simulate HONO with observation-based parametrizations of three most plausible mechanisms, and assess the key source parameters that are required to reproduce the observed HONO concentrations against results from existing laboratory kinetics studies. Lastly, we assess the regional implications of the findings from Beijing through 3-D chemical transport modeling.

**MATERIALS AND METHODS**

**Observations.** In situ observations of HONO and a suite of associated chemical species and meteorological parameters, including NO, total reactive nitrogen (NOy), peroxy acetyl nitrate (PAN), carbon monoxide (CO), \(\text{O}_3\), nonmethane volatile organic compounds (NMVOCs), oxygenated VOCs (OVOCs), ultraviolet (UVa, 315–400 nm) radiation, aerosol size distributions, were carried out at an urban site in Beijing during the CAREBeijing-2007 Experiment in August 2007. HONO was measured with a liquid coil scrubbing/UV detector.\(^29\) Size distributions of aerosols (3 nm to 10 \(\mu\)m) were measured with a differential mobility particle sizer (DPS) and were used to calculate aerosol surface areas. More details of the experimental methods are available in the SI.

**Models and HONO Source Parametrizations.** The 1-D Regional chEmical Tansport Model (REAM-1D)\(^26,30–33\) simulates \(\text{O}_3\)–NO\(_x\)–hydrocarbon photochemistry, vertical turbulent mixing, and dry/wet depositions. Meteorological parameters in the model are taken from simulations by the Weather Research and Forecasting (WRF)\(^35\) model constrained by reanalysis data from National Centers for Environmental Prediction (NCEP). Observed near-surface concentrations of CO, \(\text{O}_3\), NO, NMVOCs (C\(_2\)–C\(_9\)), OVOCs and aerosol surface areas are used to constrain the model at a 1 min time step. We use the GEOS-Chem photochemical scheme,\(^35\) and have added aromatics VOC chemistry based on the Statewide Air Pollution Research Center (SAPRC)-07 chemical mechanism.\(^25,26,31,36\)

The kinetics data have been updated based on JPL-2011 compilation.\(^37\) Dry deposition is parametrized based on the resistance-in-series model.\(^38\) Vertical turbulent mixing is computed using eddy diffusion coefficient simulated by WRF. REAM-1D has been applied to understand chemical and transport sources of peroxyacetyl nitrate (PAN),\(^33\) \(\text{O}_3\), radical chemistry and budgets, and \(\text{O}_3\) formation during CAREBeijing-2007.\(^26\)

Based on evidence from the observations, we simulate three plausible sources of HONO other than OH oxidation of NO: (1) aerosol heterogeneous uptake of NO\(_2\), (2) ground heterogeneous uptake of NO\(_2\) and (3) the reaction \(\text{HO}_2\text{H}_2\text{O} + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2 + \text{H}_2\text{O}\) as proposed by Li, et al.\(^10\)

The first-order rate constant \(k_f\) for aerosol uptake of NO\(_2\) is parametrized as

\[
k_f = \sum_{i=1}^{n} \left( \frac{r_i^2}{D_i} + \frac{4}{\omega_i} \right)^{-1} A_i
\]

where \(D_i\) is the gas phase molecular diffusion coefficient (m\(^2\) s\(^{-1}\)) for \(\text{NO}_2\), \(A_i\), and \(r_i\) are surface area (\(\mu\)m\(^2\) cm\(^{-3}\)) and particle radius (\(\mu\)m) for the \(i\)th (\(i = 1, 2, 3, \ldots, n\)) size bin; \(\omega_i\) is the mean molecular speed of NO\(_2\) in the air (m s\(^{-1}\)); \(y\) is the reactive uptake coefficient. We use a constant \(y\) of \(1 \times 10^{-6}\) for nighttime,\(^39\) and assume a linear dependence of \(y\) on short wave radiation (SWR, W m\(^{-2}\), computed by WRF) with \(y = 10^{-7}\times \text{SWR}\) in a sensitivity simulation (scenario S1), to represent photolytically enhanced NO\(_2\) uptake by aerosols that is fast enough to reproduce the observed HONO level.

HONO formation via ground uptake of NO\(_2\) is parametrized as a first order loss of NO\(_2\) via dry deposition and subsequent instantaneous release of HONO into the first model layer. The first-order HONO release rate coefficient \(k_g\) is calculated as follows,

\[
k_g = f \frac{1}{r_a + r_w + r_c} \times \frac{1}{h}
\]

where \(r_a\), \(r_w\), and \(r_c\) are aerodynamic, quasi-laminar layer, and canopy resistances, respectively; \(h\) is the height of first model layer near the surface (34 m); \(f\) is the yield of HONO from NO\(_2\) reaching the surface and is in the range of 0–1. The averaged diurnal variation of REAM-1D computed NO\(_2\) dry deposition velocity is shown in Figure S1 in the SI. We use a nighttime yield of \(f = 0.08\) to reproduce nighttime HONO observations, and use a SWR dependent daytime yield \(f = 0.003 \times \text{SWR}\) to represent a photolytically enhanced ground source that is sufficient to reproduce the observed daytime HONO level.

Five sensitivity simulations have been carried out to represent different source scenarios (S0–S4, Table 1). S0 takes into account only the reaction of NO + OH + M \(\rightarrow\) HONO + M; S1 adds to the S0 base simulation heterogeneous sources on aerosol surface (a constant \(\gamma = 10^{-6}\)) and ground surface (a constant \(f = 8\%\)); S2 differs from S1 by using a photolytically enhanced ground source during daytime with \(f = \text{SWR} \times 0.003\); S3 differs from S1 by using a photolytically enhanced aerosol source during

| Table 1. Configurations of Simulations for Different Source Scenarios |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| scenario                | configuration           |
| S0                      | NO + OH + M \(\rightarrow\) HONO + M |
| S1                      | S0 + base ground (\(f = 0.08\)) and aerosol (\(\gamma = 10^{-6}\)) uptake of NO\(_2\) |
| S2                      | S1 + photolytically enhanced ground surface NO\(_2\) uptake |
| S3                      | S1 + photolytically enhanced aerosol surface NO\(_2\) uptake |
| S4                      | S1 + \(\text{HO}_2\text{H}_2\text{O} + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2 + \text{H}_2\text{O}\) (Li, et al., 2014) |
daytime with $\gamma = 10^{-7} \times \text{SWR}$; S4 adds into S1 the reaction of HO$_2$H$_2$O + NO$_2$ → HONO + O$_2$ + H$_2$O using the reaction rate constants proposed by Li, et al. S2–S4 serve as three alternative scenarios, in which three different sources are parametrized to reproduce observed HONO level in Beijing. Key source parameters are inferred based on the observations and compared to values reported from laboratory studies.

The REAM-3D model includes the same modules of chemistry, vertical transport, and dry/wet depositions as in the 1-D model and simulates 3-D advection transport using meteorology from WRF with a spatial resolution of 70 km horizontally and 23 layers vertically up to 50 hPa. Aerosol surface areas simulated by the WRF-Chem model are used in REAM-3D to simulate the aerosol HONO heterogeneous source. More detailed descriptions of the models are available in the SI.

## RESULTS AND DISCUSSIONS

### Characteristics of the Missing Daytime HONO source.

The mean diurnal profiles for 08/10/2007–08/31/2007 in Figure 1a show high concentrations of HONO (0.8–1.6 ppbv) during daytime (10:00–15:00) along with moderate amounts of HONO precursors (i.e., ~5 ppbv of NO and ~11 ppbv of NO$_2$, SI Figure S2). The large HONO/NO$_2$ ratios (~0.04 – ~0.1) indicate highly efficient daytime HONO formation. The reaction of NO + OH can only explain ~10% of the observed HONO. The 20 day average of noontime pHONO reaches up to 5 ppbv, comparable to those observed in southern China. HONO photolysis produces OH 3–5 times faster than the reaction of O$^1$D and H$_2$O, sustaining very fast oxidation chemistry in Beijing and other polluted regions in China.7,26,51,50

The peak of HONO/NO$_2$ ratio that coincides with the maximum ultraviolet (UVa, 315–400 nm) radiation (Figure 1a) appears consistent with enhanced NO$_2$-to-HONO conversion by solar shortwave radiation. The magnitudes of HONO/NO$_2$ ratio and pHONO are much larger than what should be expected from direct HONO emission,4,52 or the NO$_2$ + H$_2$O reaction.9 Soil nitrite is also likely unimportant around our site in the urban landscape covered by buildings and pavements. Therefore, we focus our analysis on heterogeneous uptake reactions by ground and aerosols, and the gas-phase source proposed recently by Li, et al.10

We first examine the correlations of NO$_2$-to-HONO conversion efficiency (HONO/NO$_2$ ratio) and the missing HONO source strength pHONO with various parameters associated with those plausible sources (Table S2 in the SI). We found a correlation between daytime (10:00–15:00) HONO/NO$_2$ ratio and aerosol area (S$_A$). HONO/NO$_2$ ratio increases from ~0.04 to ~0.1 whereas S$_A$ increases from 200 to 1100 $\mu$m$^2$ cm$^{-2}$ (Figure 1b). Note that such a correlation is not driven by the averaged diurnal variations of HONO/NO$_2$ and S$_A$, which have opposite trends (Figure 1a), but reflects the correlated day-to-day variations of the two. The HONO/NO$_2$ ratio of 0.04 corresponding to the lowest S$_A$ (100–300 $\mu$m$^2$ cm$^{-2}$) is comparable to previously reported values for urban and suburban environments outside China (Table S1 in the SI), but is much larger than the expected ratio as a result of the OH + NO reaction alone (~0.005), implying the contributions of other NO$_2$-to-HONO conversion processes, for example, ground sources and/or other gas phase sources.

Consistent with the enhanced NO$_2$-to-HONO conversion associated with increased aerosol surface area in Beijing suggested by Figure 1b, a correlation (R = 0.62, Figure 1c) is also found between the missing HONO source strength (pHONO) and the product of NO$_2$ × UVa × S$_A$. Such a correlation would be expected if photoenhanced aerosol uptake of NO$_2$ is a dominant HONO source, given the proportional relationship between $k_t$ and $\gamma$ (as shown in eq 1) and the dependence of $\gamma$ on solar radiation strength (UVa). The correlation between pHONO and the product of NO$_2$ × UVa × S$_A$ is stronger than that between pHONO and NO$_2$ × UVa (R = 0.41) when S$_A$ is excluded in the dependent equation. It is also stronger than that between pHONO and NO$_2$ × UVa × V$_d$(NO$_2$) (R = 0.33 and V$_d$ denotes deposition velocity) or that between pHONO and H$_2$O × NO$_2$ (R = 0.43), the indicators of a ground heterogeneous source or the newly proposed gas-phase source by Li, et al. respectively. Furthermore, S$_A$ does not correlate (R = −0.14) with the inverse of PBL height (simulated by WRF), nor does it correlate with the other two source indicators above (Table S2 in the SI). Therefore, the correlation analysis results in Figure 1b and c provide direct evidence that aerosols are an important media of daytime HONO formation in Beijing. In the next section, we analyze the results from process modeling to assess the feasibility of different sources to explain HONO observations, and to assess the consistency of an aerosol-driven HONO source with existing laboratory kinetics studies.

### Model Simulations of Plausible HONO Source Scenarios.

Including baseline heterogeneous sources on ground or aerosol surfaces using source parameters determined from nighttime observations (S1, $f = 0.08$ and $\gamma = 10^{-6}$) does not lead to a notable increase of HONO (compared to S0) during daytime when HONO lifetime is much shorter, suggesting the need for stronger and photolytically dependent daytime HONO formation mechanisms. Adding to S1 any of the three plausible
sources (S2–S4) can lead to comparable levels of HONO in the afternoon, in much closer agreement with the observed HONO level than S1 (Figure 2). Nevertheless, a closer inspection of the model results still favors significant aerosol-driven HONO production. First, among S2, S3, and S4, the scenario with photolytically enhanced aerosol NO₂ uptake (S3) has the highest correlation between observed and simulated HONO (in terms of both hourly and daily correlations), and the lowest mean model bias (Figure 2). Using the NO₂ + HO₂ ·H₂O reaction rate constants reported by Li et al., a large low bias in the morning is seen in S4, reflecting an increase of HO₂ but a decrease of NO₂ (Figure 2, Figure S2 in the SI). Meanwhile, when photolytically enhanced ground NO₂ uptake is scaled to match the observed HONO (S2), the ground source yield 𝑓 reaches 100% during 11:00–14:00, which would require ground surface properties that can reach the maximum conversion efficiency and are unlikely ubiquitous. On the other hand, the required 𝑦 value for the aerosol heterogeneous source seems reasonable, as discussed in the following.

For aerosol uptake of NO₂ (S3) to reproduce the observed HONO level, the required 𝑦 reaches up to \(10^{-6}\) in the afternoon when HONO lifetime is the shortest. This is several orders of magnitude higher than those (\(\gamma = 10^{-7} \sim 10^{-6}\)) found previously for surfaces containing humid acid, solid organics, soot, and TiO₂, suggesting that a different mechanism is needed if aerosols are indeed a major media of HONO formation in Beijing. Recent laboratory studies found substantially enhanced hydrolytic disproportionation of NO₂ on aqueous aerosol surfaces due to catalysis by dicarboxylic acid anions, with 𝑦 in the range of \(10^{-4} \sim 10^{-3}\). In fact, abundant dicarboxylic acids, ketocarboxylic acids, \(\alpha\)-dicarboxyls, fatty acids, and benzoic acid have been observed in PM₄₅ at the same site in Beijing, along with high levels of gas-phase dicarbonyl compounds, such as glyoxal (CHOCHO) and methylglyoxal (CH₃C(O)CHO), and their aromatic precursors. Therefore, our observed evidence of rapid aerosol heterogeneous HONO formation is consistent with both laboratory kinetics studies and in situ observations.

It is noteworthy that the simulated HONO vertical profiles (Figure S3 in the SI) have similarly large negative vertical gradients in the three sensitivity simulations that can reproduce observed afternoon HONO concentrations (S2–S4). Even with an airborne HONO source, the negative gradient of NO₂ in the PBL over emission regions can render negative gradients in HONO production rate and HONO concentrations in S3 and S4. These results imply that measurements of HONO vertical profiles alone may not be sufficient to separate the source contributions over NO₂ emission regions.

### REGIONAL IMPACT AND IMPLICATIONS

Existing observational evidence suggests that the aerosol heterogeneous HONO source found in Beijing is also likely to exist in other regions of China. Figure 3 shows the concurrent enrichment of NO₂ and aerosols over the North China Plain (NCP) and the Pearl River Delta (PRD) based on satellite (Aura OMI) observed NO₂ vertical columns (Figure 3a) and aerosol surface areas constrained by satellite-observed aerosol optical depth (AOD) (MODIS AOD 550 nm) (Figure 3b). Comparable levels of organic acids have been measured at NCP, Mt. Tai, and PRD. Satellite observations showed large abundance of glyoxal (a precursor of dicarboxylic acid) on a regional basis in Northern China. We assess the potential regional impact of an aerosol heterogeneous HONO source through regional simulations with the REAM-3D model. We conducted a simulation with regional aerosol uptake efficiencies the same as the observation-based parametrizations in Beijing (S2). We found that the aerosol heterogeneous source is much larger than assuming 10% of automobile NO₂ emissions is in the form of HONO in a model sensitivity study. The model simulates >200 pptv of HONO from this aerosol heterogeneous source (Figure 3c), which leads to 20–70% increase of near-noontime OH concentrations over NCP and PRD compared to the simulation without this aerosol HONO source (Figure 3d). These results...
suggest that the combination of large abundance of aromatic VOCs, NOx, and aerosols over China likely leads to high levels of daytime HONO on a regional basis, which substantially increases the regional oxidizing capacity through OH production by HONO photolysis. While our study is focused on summertime observations, we expect HONO produced from this aerosol heterogeneous source to play a significant role in wintertime photochemistry when the OH source from O(1D) is much weaker.

Based on the results from correlation analysis using observed data, and quantitative assessment of the necessary aerosol uptake coefficient γ against laboratory findings, we propose that enhanced hydrolytic disproportionation of NO2 on aqueous surfaces due to catalysis by dicarboxylic acid anions is likely the dominant mechanism that explains the rapid daytime HONO formation in Beijing. Although our analysis does not exclude other sources of HONO, our results suggest that aerosols should play a significant role, in contrast to the common assumption that aerosols are unimportant in daytime HONO formation. Our study calls for increased attention to aerosols in polluted regions like Beijing, which can serve as a media for heterogeneous study calls for increased attention to aerosols in polluted regions like Beijing, which can serve as a media for heterogeneous photochemistry when the OH source from O(1D) is much weaker.

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