

An Atmospheric Constraint on the NO₂ Dependence of Daytime Near-Surface Nitrous Acid (HONO)

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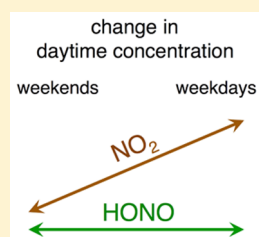
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Supporting Information

ABSTRACT: Recent observations suggest a large and unknown daytime source of nitrous acid (HONO) to the atmosphere. Multiple mechanisms have been proposed, many of which involve chemistry that reduces nitrogen dioxide (NO₂) on some time scale. To examine the NO₂ dependence of the daytime HONO source, we compare weekday and weekend measurements of NO₂ and HONO in two U.S. cities. We find that daytime HONO does not increase proportionally to increases in same-day NO₂, i.e., the local NO₂ concentration at that time and several hours earlier. We discuss various published HONO formation pathways in the context of this constraint.



INTRODUCTION

Nitrous acid (HONO) is observed during the daytime at mixing ratios of tens to hundreds of parts per trillion (pptv) in urban, urban-influenced, and remote atmospheres.^{1–7} The source(s) of daytime HONO are in part unidentified; however, they must be substantial to sustain measured abundances, because the midday summertime photolytic lifetime of HONO is only ~10 min. One product of HONO photolysis is the hydroxyl radical (OH), which drives the chemistry of ozone production and OH-initiated secondary aerosol formation. In this way, HONO is an important species in atmospheric oxidation.^{3,8}

At night, the chemical production of HONO is thought to occur by a mechanism (M1) in which two nitrogen dioxides (NO₂) are converted at a wet interface to a gas-phase HONO molecule and one surface-adsorbed nitric acid (HNO₃). M1 is first-order in NO₂, has been suggested by laboratory studies,⁹ and seems to have some general applicability to the atmosphere, but the precise stoichiometry has not been confirmed.

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Table 1. Summary of Daytime (8 am–4 pm LT) NO₂ and HONO Measurements and Weekday–Weekend Sampling Statistics in Bakersfield and Pasadena during CalNex^a

| species | analytical technique | accuracy (%) | height (m agl) | resolution (min) | N _{days} weekdays | N _{days} weekends | N _{obs} weekdays | N _{obs} weekends |
|-----------------|---|--------------|----------------------|------------------|----------------------------|----------------------------|---------------------------|---------------------------|
| Bakersfield | | | | | | | | |
| NO ₂ | laser-induced fluorescence ⁶³ | 5 | 18 | 1 | 24 | 12 | 11544 | 5772 |
| HONO | stripping-coil visible absorption photometry (SC-AP) ⁴⁵ | 15 | 13.5 | 2 | 24 | 12 | 3618 | 1910 |
| HONO | ambient ion monitor ion chromatography (AIM-IC) ^{37,43} | 20 | 4.5 | 60 | 17 | 10 | 110 | 71 |
| Pasadena | | | | | | | | |
| NO ₂ | cavity ring-down spectroscopy | 3 | 10 | 1 | 15 | 8 | 8640 | 3840 |
| HONO | negative-ion proton-transfer chemical ionization mass spectrometry (NI-PT-CIMS) ^{44 b} | 30 | 3 | 1 | 12 | 8 | 1856 | 1301 |
| HONO | incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) ⁴⁶ | 15 | 10 | 10 | 8 | 4 | 266 | 148 |
| HONO | long-path differential optical absorption spectroscopy (LP-DOAS) ¹³ | 8 | various ^c | ~60 ^d | 12–17 | 7–10 | 31–109 | 28–57 |

^aSee references for details. ^bThe acetate CIMS is now recognized to have an interference as a result of HO₂NO₂. The levels of HO₂NO₂ expected under the conditions in Pasadena are 20 pptv at most, not enough to account for the weekday–weekend variability reported in this paper. ^cMeasurements were made along light paths from 33 m agl to retroreflectors at four heights (m agl): low, 78 m; mid, 121 m; high, 255 m; and highest, 556 m. ^dResolution for each profile.

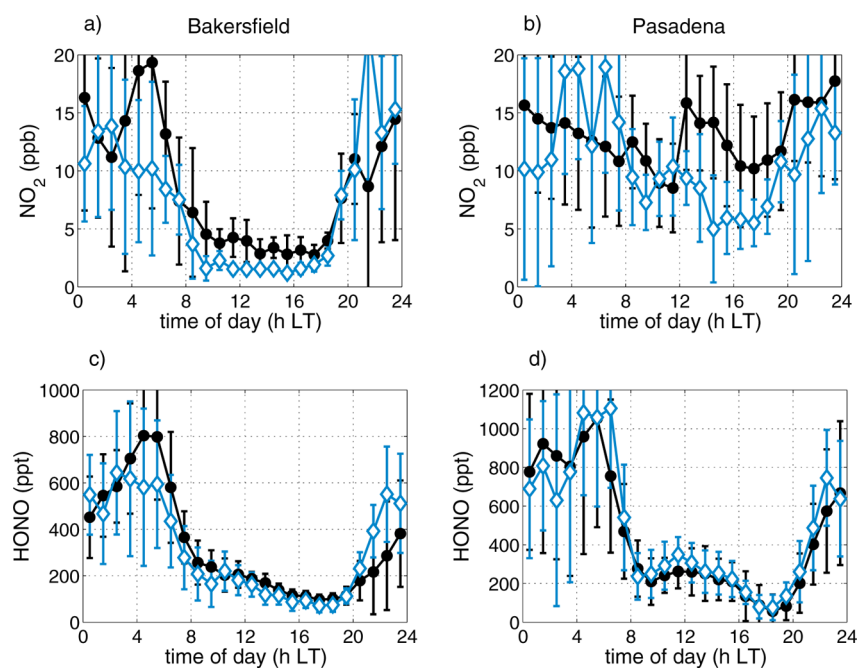


Figure 1. (a) Hourly medians of NO₂, measured by laser-induced fluorescence, as a function of time of day on weekdays (black closed circles) and weekends (blue open diamonds) in Bakersfield, CA. (b) Hourly medians of NO₂, measured by cavity ring down, on weekdays and weekends in Pasadena, CA. NO₂ data are only included in the averaging when HONO data also exist. Error bars show the 1σ variability. (c) Hourly medians of AIM-IC HONO on weekdays and weekends in Bakersfield, CA. (d) Hourly medians of HONO NI-PT-CIMS measurements on weekdays and weekends in Pasadena, CA. HONO data are only included in the averaging when NO₂ data also exist. All y axes are truncated to highlight daytime differences.



Report of the nighttime ambient ratio of HONO/NO₂ is canonical and consistently ~0.03–0.05.^{10–13} Increases in relative humidity (RH) and presumably H₂O_(surface) have been observed to correlate with maximum HONO/NO₂¹⁰ and decreased HONO uptake onto surfaces.¹⁴ Measurements of vertical HONO gradients point to the ground as the dominant reaction surface.^{6,8,13,15–18} Chemical models that include M1 reproduce observed HONO at night and in the early morning but are unable to do so during the day when photolytic losses are large and NO_x (NO_x ≡ NO + NO₂) is more dilute.^{4,5}

Sufficiently fast source chemistry consistent with daytime HONO and NO_x observations is lacking.

A variety of daytime HONO sources have been proposed with many hypotheses centered on chemistry that reduces NO₂ or on primary sources that are expected to co-vary with NO_x in unique ways. These include NO₂ conversion to HONO on photoactive surfaces,¹⁹ for example, soot,²⁰ humic acid,²¹ and organic surfaces,²² direct HONO emissions, by either vehicles²³ or soils with active ammonia-oxidizing bacteria or archaea,^{24–30} photolysis of NO₃[−] on surfaces,^{31–33} in acidic aqueous solutions,³⁴ and snow,^{35,36} and release from NO₂[−] surface reservoirs by acid displacement, with HONO having been

produced by nocturnal chemistry and deposited to the surface as the original NO_2^- source.^{6,37,38}

In the U.S., NO_x emissions have a well-known day-of-week dependence as a result of reduced heavy-duty diesel truck traffic on weekends.³⁹ As a result, NO_x concentrations are 30–60% lower on weekends than weekdays,⁴⁰ and these steep weekend decreases occur in the absence of equivalent changes in other gas-phase emissions, of which heavy-duty diesel engines are not major emitters.⁴¹ Arguably, this is as close as we come to a controlled experiment in the atmosphere. To examine the NO_2 dependence of daytime HONO, we compare weekday–weekend relationships of NO_2 and HONO in two U.S. cities: Bakersfield and Pasadena, CA.

■ OBSERVATIONS

The California at the Nexus of Air Quality and Climate Change (CalNex) experiment took place in the late spring and early summer of 2010 (<http://esrl.noaa.gov/csd/groups/csd7/measurements/2010calnex/>).⁴² Here, we present NO_2 and HONO observations, along with OH, NO, j_{HONO} , HNO_3 , organic acids, and meteorological data, collected in the polluted cities of Bakersfield (May 18–June 29, six weekends) and Pasadena, a suburb of Los Angeles (May 15–June 16, four weekends).

CalNex provided an ideal opportunity to study daytime HONO because it featured a variety of HONO instruments with independent operating principles. NO_2 and HONO measurement techniques along with weekday–weekend sampling statistics are listed in Table 1.

■ RESULTS

Diurnal patterns in NO_2 and HONO on weekdays and weekends in Bakersfield and Pasadena are shown in Figure 1 (and Figures S1–S3). Weekdays include Tuesdays–Fridays; weekends include Saturdays and Sundays. Mondays and Saturdays are considered transition days because they are influenced by carryover from previous days. We omit Mondays for this reason but keep Saturdays to improve weekend statistics (see the Supporting Information). NO_2 and HONO data were averaged to the same time base and only included in the calculation of the 1 h medians when simultaneous measurements existed. Data in panels c and d of Figure 1 were collected by ambient ion monitor ion chromatography (AIM-IC)^{37,43} and negative-ion proton-transfer chemical ionization mass spectrometry (NI-PT-CIMS),⁴⁴ respectively. These measurements were selected for the main text because they were closest to one another in height above the ground, as significant vertical gradients in daytime HONO were observed in both cities (see the Supporting Information).^{8,37} Observations from stripping-coil visible absorption photometry (SC-AP),⁴⁵ incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS),⁴⁶ and long-path differential optical absorption spectroscopy (LP-DOAS)⁴³ are presented in the Supporting Information. We interpret consistency in weekday–weekend patterns across all HONO instruments as evidence that the NO_2 dependence is not the result of measurement biases.

In both cities, daytime (8 am–4 pm LT) HONO concentrations did not correspond to either the absolute amount of NO_2 or the atmospheric variability in NO_2 when data were organized by hour of day separately for weekdays and weekends. Median daytime (8 am–4 pm LT) NO_2 was 55%

greater in Bakersfield⁴⁷ and 35% greater in Pasadena⁴⁸ on weekdays than on weekends. There was a visible shift in the timing of the daytime NO_x profile in Pasadena (see the Supporting Information for an extended description of NO_2 weekday–weekend patterns). Weekday–weekend differences in daytime NO_2 for all data sets were found to be significant at the 1% level with $p < 0.01$ using the Wilcoxon rank sum test, a non-parametric test of two independent data populations.⁴⁹ Median daytime HONO was observed to be only 10–15% (from 9 ± 1 to 27 ± 10 pptv) greater on weekdays than weekends in Bakersfield, depending upon the HONO data set (SC-AP or AIM-IC, respectively). Listed precision is the standard error. Differences are 6–10% between means. In Pasadena, median daytime HONO measured by NI-PT-CIMS was 10% (25 ± 4 pptv) lower on weekdays than on weekends. We compute the statistical significance of daytime HONO differences with respect to inferred daytime HONO production rates rather than HONO concentrations (see the Discussion).

In addition to weekday–weekend differences in mean NO_2 , the variability (1σ) in NO_2 in Bakersfield was 35–50% ($1\text{--}1.5$ ppbv) greater on weekdays than on weekends, but only small differences in the 1σ variability in HONO were observed. With the longer SC-AP data set, the 1σ variability was nearly equal on weekdays and weekends at <5% (3 pptv) higher on weekdays. The 1σ variability of the AIM-IC measurements was 15% (10 pptv) larger on weekends than weekdays. Large differences in NO_2 variability in Pasadena by weekday–weekend were not observed.

■ DISCUSSION

The absence of a pronounced weekday–weekend difference in daytime HONO implies the total HONO source does not increase proportionally to increases in same-day NO_2 . In what follows, we discuss several published mechanisms in this weekday–weekend context.

The median midday photolytic loss rate of HONO is rapid, occurring on time scales of tens of minutes and corresponding to >1 ppbv h^{-1} near the surface in both cities (details in the Supporting Information). This lifetime is short enough that the source must nearly equal the photolytic sink, with regional transport too slow to have a major effect. Thus, if weekday–weekend differences in HONO concentrations are small, weekday–weekend differences in the local source term must also be small. Our thinking about sources includes processes occurring at the ground or other interfaces, with HONO then transported to near-surface atmosphere; therefore, vertical transport is an important but weekday–weekend-independent term.

The gas-phase reaction of NO with OH is an established daytime HONO source. This source varies weekday to weekend: NO decreases on weekends, and OH is a nonlinear function of NO_x . During the CalNex study period, median daytime (8 am–4 pm LT) OH was slightly higher on weekdays than on weekends in Bakersfield and Pasadena. The median midday NO + OH source in Bakersfield was 0.2 ppbv h^{-1} on weekdays and 0.1 ppbv h^{-1} on weekends, and the median midday NO + OH source in Pasadena was 0.3 ppbv h^{-1} on weekdays and 0.1 ppbv h^{-1} on weekends. This is $\sim 15\%$ of total daytime (8 am–4 pm LT) loss rate in Bakersfield and $\sim 20\%$ in Pasadena.

The inferred production rate of the remaining source when steady-state conditions apply, as defined by eq 1, is shown in Figure 2. $P(\text{HONO})_{\text{inferred}}$ is a sum over all processes producing

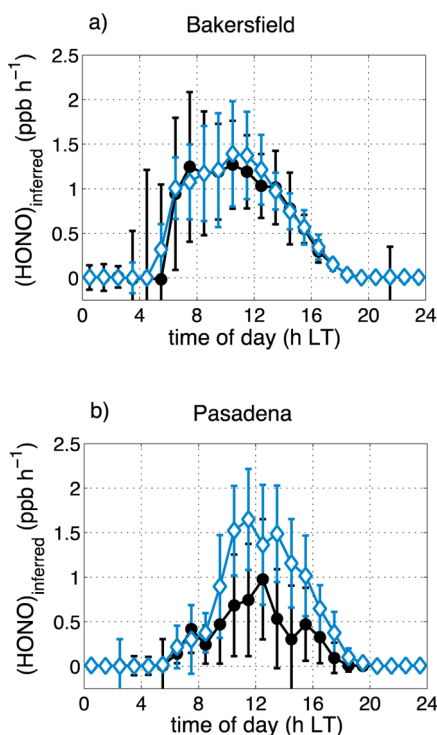


Figure 2. (a) Medians of $P(\text{HONO})_{\text{inferred}}$, as defined by eq 1, in Bakersfield, CA, using AIM-IC HONO data on weekdays (black closed circles) and weekends (blue open diamonds). (b) Medians of $P(\text{HONO})_{\text{inferred}}$ in Pasadena, CA, using PT-CIMS HONO data on weekdays and weekends. $P(\text{HONO})_{\text{inferred}}$ was computed prior to diurnal hourly averaging (see the Supporting Information for details). Deriving $P(\text{HONO})_{\text{inferred}}$ in this way gives the source term at that measurement height and not the boundary layer average.

HONO and is not observed to increase with NO_2 on weekdays compared to weekends. Rather, daytime $P(\text{HONO})_{\text{inferred}}$ is found to be greater on weekends than on weekdays, and while differences in Bakersfield are small, as evident in Figure 2a, they are statistically significant by the Wilcoxon rank sum test at the 1% level ($p < 0.01$) in both cities. In the presence of steep vertical gradients, the correct formulation of eq 1 also includes a vertical transport term, which is likely large in comparison to the chemical terms but day-of-week-independent. Instead, eq 1 is an apparent production rate, representative of an instantaneous OH production rate at a particular height above ground; it is not applicable to the entire boundary layer. Changes in environmental variables, especially sunlight, RH, and temperature, influence OH chemistry⁵⁰ and, hence, $P(\text{HONO})_{\text{inferred}}$. In Bakersfield, the daytime (8 am–4 pm LT) median solar radiation and RH were comparable on weekends and weekdays, although the temperature was slightly higher on weekends (0.5–2 °C) (Figures S4 and S5). However, during the shorter 4 week Pasadena experiment, significant differences in meteorological conditions by weekday–weekend were observed (Figures S6 and S7). On weekends compared to weekdays, daytime median solar radiation was 25% higher, temperatures were >3 °C hotter, and RHs were 20% lower. Because solar radiation and, hence, j_{HONO} were 25% greater on weekends but concentrations were similar weekday to weekend, the data imply a larger weekend source, opposite the variation in NO_2 .

$$P(\text{HONO})_{\text{inferred}} = j_{\text{HONO}}[\text{HONO}] + k_{\text{HONO}+\text{OH}}[\text{HONO}][\text{OH}] - k_{\text{NO}+\text{OH}}[\text{NO}][\text{OH}] \quad (1)$$

Laboratory experiments have shown that NO_2 is reduced to gas-phase HONO by heterogeneous chemistry at many different types of illuminated substrates.^{19–22} Models including such chemistry still require large unidentified HONO sources to reconcile daytime HONO measurements.^{4,5} That said, the atmosphere interfaces with a complex patchwork of surfaces, especially in cities, leaving open the possibility that unexamined substrates are large sources of daytime HONO. Weekday–weekend HONO observations suggest, however, that the reduction of NO_2 at photoactive surfaces is not a large HONO source to the atmosphere if rate limited by NO_2 . One study has found that NO_2 binding sites are in excess; i.e., NO_2 is the limiting reagent, until gas-phase NO_2 concentrations are orders of magnitude higher than typical of ambient daytime conditions.²¹ Weekday–weekend observations are also evidence against a large HONO source associated with diesel emissions, such as from reactions on surfaces of airborne soot,^{20,51,52} other primary diesel aerosols,⁵³ and direct HONO diesel emissions.

Contributions to $P(\text{HONO})_{\text{inferred}}$ that would be consistent with the observation that HONO concentrations do not increase with weekday increases in NO_2 are (a) emission sources that are associated with gasoline-powered vehicles or that are biogenic or agricultural in origin and (b) production mechanisms for which the relevant NO_x dependence takes place on time scales longer than seconds to hours.

HONO is a primary emission of gasoline-powered vehicles. Emission factors have been measured to be ~ 0.008 HONO/ NO_x for vehicles without catalytic converters⁵⁴ and ~ 0.001 for those with well-maintained catalysts.⁵⁵ A tunnel study in California reported on-road average HONO/ NO_x from vehicle emissions equal to ~ 0.003 .²³ Assuming the number of vehicles on the road in 2010 without well-maintained catalysts is 50% lower than when this tunnel study was performed, we predict HONO/ NO_x equal to 0.002 during CalNex. Referenced to gasoline-powered vehicle NO_x , i.e., weekend levels, the noontime median weekend HONO/ NO_x is 0.028 (AIM-IC) and 0.025 (NI-PT-CIMS), which are each more than 10 times larger than attributable to emissions even if the entire surface was equal to the tailpipe.

Secondary chemistry associated with gasoline-powered vehicle emissions may also align with weekday–weekend HONO observations. Examples are the photolysis of *o*-nitrophenols⁵⁶ and the reduction of gas-phase HNO_3 catalyzed by exhausted hydrocarbons and/or organic aerosol.^{57,58} The latter is consistent with weekday–weekend HONO observations if hydrocarbons rather than HNO_3 are rate-limiting or if HNO_3 is weekday–weekend-independent and with observed vertical gradients if chemistry occurs at motor-oil-coated road surfaces.³³

One proposed biogenic source of HONO is release by ammonia-oxidizing bacteria and archaea in soils.^{24–28,30} These microorganisms produce NO_2^- during nitrification, and while a portion of this NO_2^- is reduced to NO or nitrous oxide on soil surfaces,⁵⁹ another portion partitions to the atmosphere as HONO, the conjugate acid of NO_2^- . Laboratory experiments using collected soil samples found significant HONO fluxes, often greater than microbial NO emissions in soils from

cultivated fields, where fluxes of both HONO and NO were shown to maximize at the same soil wetness, a function of the temperature and precipitation rather than ambient gas-phase NO_x .²⁷ The acidity of the soil environment, particularly of soil surfaces rather than the bulk soil pH, has been found to be important as well.^{14,25,29} In non-cultivated soils, nitrogen availability to microorganisms was also shown to be a factor.²⁶ To our knowledge, field observations of HONO soil fluxes unambiguously attributed to this mechanism have not been reported.

Recent work in the laboratory³⁸ and the atmosphere^{6,37} has described large HONO emissions from ground reservoirs of NO_2^- following protonation by deposited acids, where NO_2^- is thought to be accumulated HONO, produced on previous nights by M1 that has deposited to the surface. Gas-phase acids are photochemical products, and as a result, this HONO source may also appear to be photochemical, although the NO_2^- reservoir may be deep enough to blur weekday-weekend differences. Emission of HONO produced by M1 as a result of changes in the pH of dew droplets containing NO_2^- has also been suggested.⁶⁰ Of the common atmospheric acids, the strong acid HNO_3 may vary by weekday-weekend, because it is formed by the reaction of NO_2 and OH. In Bakersfield and Pasadena, daytime (8 am–4 pm LT) median OH varied little weekday to weekend. At constant OH, HNO_3 production increases with increasing NO_2 at low NO_x (typical of rural atmospheres) and is independent of NO_2 at high NO_x (typical of the urban core). At moderate NO_x , the NO_2 dependence of HNO_3 production is complicated by the formation of organic nitrates.⁶¹ HNO_3 is also formed through nighttime chemistry, which in the summertime in these two cities is proportional to NO_2 , but also depends upon ambient ozone, unsaturated hydrocarbons, aerosol surface area, and aerosol NO_3^- . The nocturnal HNO_3 source will not appear to be photochemical. In Bakersfield, none of the acids important to this mechanism that were measured varied weekday to weekend: gas-phase daytime (8 am–4 pm LT) median HNO_3 was ~ 0.5 ppbv; formic acid was 1–4 ppbv; and acetic acid was ~ 1 ppbv, in each case, independent of weekday-weekend. VandenBoer et al.^{37,38} used AIM-IC observations of both HONO and airborne NO_2^- to attribute at least 0.4 ppbv h^{-1} (30%) of the unknown midday source to this pathway in Bakersfield during CalNex. The same analysis has not been performed in Pasadena, where median daytime HNO_3 varied from 1.9 ppbv on weekdays to 3.0 ppbv on weekends (means were 3.7 ppbv on weekdays and 4.2 ppbv on weekends).

It has been proposed that the photolysis of NO_3^- yields HONO. Laboratory studies indicate that the photolysis rate of surface-adsorbed NO_3^- is $\sim 10^{-3}$ – 10^{-5} s^{-1} , which is 2 (on Pyrex)³¹ to 4 (on urban grime surfaces)³³ orders of magnitude faster compared to liquid-phase NO_3^- or gaseous HNO_3 . However, recent work in the lab that directly monitored the change in the gas-phase HONO concentration upon surface-adsorbed nitrate photolysis at 308 nm found no evidence that HONO was formed but rather that the OH + ground-state NO_2 product channel was dominant.⁶² The photolysis of aqueous-phase NO_3^- ($\lambda > 290$ nm) has been observed to yield more gaseous HONO than is predicted by known quantum efficiencies. Laboratory evidence suggests that, in the presence of OH scavengers, solvated NO_2 produced in irradiated acidic aqueous NO_3^- solutions hydrolyzes efficiently to produce NO_2^- . Mass-transfer rates prevent significant hydrolysis of atmospheric NO_2 at liquid surfaces, and therefore, the NO_2

dependence of the NO_3^- photolytic HONO source follows the NO_2 dependence of HNO_3 production but shifted in time according to the fate of HNO_3 . At least two field studies have reported gas-phase HONO fluxes at the forest location correlated with leaf-surface NO_3^- and not ambient NO_x .^{30,32} While gas-phase HNO_3 deposition is rapid, incorporation into aerosol as ammonium nitrate can extend the atmospheric lifetime of HNO_3 by days and deposition to the surface in the evening has its largest impact on HONO concentrations the following day. Thus, multiday and variable hysteresis in the rate-limiting NO_2 concentration may be possible.

The purpose of this paper is to report that weekday-weekend analysis provides an atmospheric constraint on the NO_2 dependence of daytime HONO formation chemistry. In this way, we find that weekday-weekend HONO observations challenge current assumptions about relationships between HONO and NO_2 . In summary, the total steady-state inferred daytime HONO production rate, $P(\text{HONO})_{\text{inferred}}$, as defined by eq 1, is not observed to increase on weekdays compared to weekends alongside increases in NO_2 of 35–55% in two U.S. cities. Future atmospheric daytime HONO experiments would benefit from being long enough that average meteorological variables are equal weekday to weekend, because differences in these variables during CalNex add uncertainty to our conclusions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02511.

NO_2 weekday-weekend patterns, calculating $P(\text{HONO})_{\text{inferred}}$, Figures S1–S8, and references (PDF)

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Notes

The authors declare no competing financial interest.

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