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Validating HONO as an intermediate tracer of the external cycling of reactive nitrogen in the background atmosphere

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7 1 Validating HONO as an intermediate tracer of the
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11 2 external cycling of reactive nitrogen in the
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33
34 9 ABSTRACT
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38 10 In the urban atmosphere, nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$)-related reactions dominate the
39
40 11 formation of nitrous acid (HONO). Here, we validated an external cycling route of HONO and
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42 12 NO_x , i.e., formation of HONO resulting from precursors other than NO_x , in the background
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44 13 atmosphere. A chemical budget closure experiment of HONO and NO_x was conducted at a
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46 14 background site on the Tibetan Plateau and provided direct evidence of the external cycling. An
47
48 15 external daytime HONO source of 100 pptv h^{-1} was determined. Both soil emissions and photolysis
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50 16 of nitrate on ambient surfaces constituted likely candidate mechanisms characterizing this external
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52 17 source. The external source dominated the chemical production of NO_x with HONO as an
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3 18 intermediate tracer. The OH production was doubled as a result of the external cycling. A high
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5 19 HONO/NO_x ratio (0.31±0.06) during the daytime was deduced as a sufficient condition for the
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8 20 external cycling. Literature review suggested the prevalence of high HONO/NO_x ratios in various
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10 21 background environments, e.g., polar regions, pristine mountains and forests. Our analysis
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12 22 validates the prevalence of the external cycling route in general background atmosphere and
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15 23 highlight the promotional role of external cycling regarding the atmospheric oxidative capacity.
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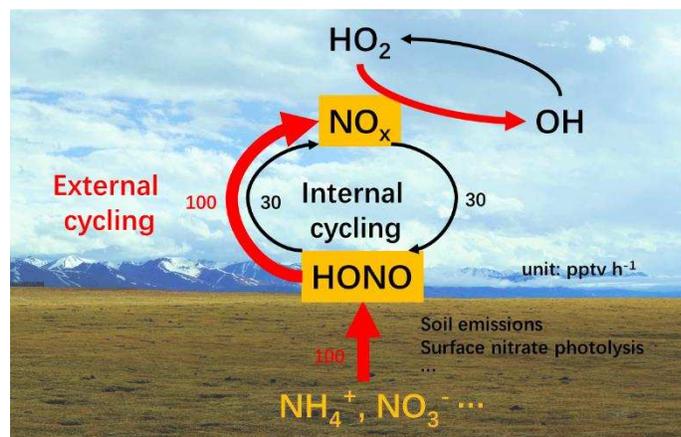
20 25 **KEYWORD**
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23 26 nitrous acid (HONO), reactive nitrogen, budget analysis, photochemistry, atmospheric oxidative
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25 27 capacity, the Tibetan Plateau
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32 29 **SYNOPSIS**
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35 30 Our data suggests a revision of reactive nitrogen chemistry and the oxidative capacity of the
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37 31 atmosphere.
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36 Introduction

37 In the urban atmosphere, nitrous acid (HONO) is distributed at concentrations ranging from
38 hundreds of pptv to several ppbv. Solar radiation extending to up to 400 nm photolyzes HONO to
39 produce OH radicals and NO (R1). The HONO photolysis frequency can reach $1.6 \times 10^{-3} \text{ s}^{-1}$ (ca.
40 HONO lifetime of 10.4 min) at solar noon (solar zenith angle = 0°). HONO is therefore a primary
41 precursor of OH radicals and greatly impacts the atmospheric oxidative capacity in such
42 environments¹⁻³.



46 The primary HONO emissions from vehicles can be characterized by a HONO/NO_x emission
47 ratio of 0.008⁴. However, a typical daytime HONO/NO_x ratio of 0.02 is accompanied by a high
48 abundance of HONO in the urban atmosphere⁵. This underlines the dominating role of chemical
49 production in the HONO budget and in raising the HONO/NO_x ratio. NO_x-related reactions, i.e.,
50 homogeneous reactions of NO with OH radicals (R2) and the heterogeneous conversion of NO₂
51 on environmental surfaces (R3), are generally accepted HONO formation mechanisms in such
52 environments^{6,7}. Under the photo-stationary state assumption (PSS) of HONO, equilibrium is
53 established between HONO photolysis (R1) and HONO production from NO_x-related reactions.
54 Assuming a pseudo-first-order R2 reaction rate of $1.16 \times 10^{-5} \text{ s}^{-1}$ (at an OH radical concentration of
55 $10^6 \text{ molecule/cm}^3$ and temperature of 273 K)⁸ and a HONO photolysis frequency of $1.6 \times 10^{-3} \text{ s}^{-1}$
56 under solar zenith angle $\Theta = 0^\circ$, the PSS HONO/NO ratio is calculated as 0.007. The pseudo-first-
57 order reaction rate of R3 on the ground surface is observed within the range of 0.004-0.033 h⁻¹
58 without light enhancement⁹, resulting in a corresponding PSS HONO/NO₂ ratio range of 0.0007-
59 0.006. The slow turnover rate of NO_x to HONO compared to that of HONO to NO_x characterizes

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3 60 a PSS HONO/NO_x ratio that is not significantly higher than the primary emission ratio. Solar
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5 61 radiation enhances heterogeneous NO₂ conversion (R3, hv) by one order of magnitude¹⁰ and
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7 62 promotes the PSS HONO/NO_x ratio by the same magnitude, which could account for the typical
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9 63 PSS HONO/NO_x ratio of 0.02 in the urban atmosphere. The R1-R3 reactions are referred to as the
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11 64 internal cycling routes of HONO and NO_x, and there is no net production of HONO or NO_x in the
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13 65 internal cycling under the photo-stationary state of HONO.
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17 66 Compared to the urban atmosphere where internal cycling chemistry dominates, substantially
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19 67 higher PSS HONO/NO_x ratios have been observed with lower HONO and NO_x levels in polar
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21 68 areas¹¹⁻¹⁵. External sources, i.e., formation mechanisms with HONO precursors other than NO_x,
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23 69 are proposed in such environments. Upward HONO and NO_x fluxes from ice and snow surfaces
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25 70 point to enhanced photolysis of nitrate deposited on ice and snow surfaces as one external source
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27 71 of HONO and NO_x^{11,16}. The concept of a quasi-liquid layer on snow and ice surfaces has been
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29 72 further constructed to account for the surface-catalyzed photolysis of nitrate, which occurs nearly
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31 73 one order of magnitude faster than the photolysis of gaseous nitric acid¹⁷. Such an external source
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33 74 dominates the HONO source budget and naturally also serves as a source of NO_x via external
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35 75 HONO photolysis in polar areas where primary NO_x emissions are negligible. OH production is
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37 76 greatly promoted as a result of the presence of external sources of HONO and NO_x^{15,16}. Compared
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39 77 to internal cycling, which is initialized and accelerated by primary anthropogenic NO_x emissions
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41 78 in the urban atmosphere, external cycling in polar regions is driven by natural conditions, i.e.,
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43 79 ubiquitous ambient surface and solar radiation conditions, implying its universal significance in
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45 80 the atmosphere.
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51 81 Herein, we raise scientific questions regarding whether such external cycling of reactive
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53 82 nitrogen is prevalent in general background atmosphere and how external cycling perturbs the
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3 83 oxidative capacity of these environments. The Tibetan Plateau is referred to as the third pole of
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5 84 the world, representing the global background of the atmosphere. With an average altitude of over
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8 85 4000 m, the Tibetan Plateau features high solar radiation and notably intense photochemistry. The
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10 86 natural conditions of the Tibetan Plateau facilitate external cycling of reactive nitrogen analogous
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12 87 to the process prevailing in polar regions. During the in-depth study of atmospheric chemistry
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14
15 88 performed over the Tibetan Plateau in 2019, referred to as the @Tibet 2019 field campaign, we
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17 89 collected a comprehensive dataset related to HONO and NO_x budgets, the first dataset of its kind
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19 90 available for a background site on the Tibetan Plateau. This dataset allows direct validation of the
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22 91 external cycling of reactive nitrogen with HONO as an intermediate tracer and its role in promoting
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24 92 the atmospheric oxidative capacity via a near-explicit chemical model. A HONO/NO_x ratio that is
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26 93 unreasonably higher than the internal cycling mechanism permits is summarized as a sufficient
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28 94 condition for external cycling. A literature review suggests the prevalence of such unreasonably
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31 95 high ratios and, therefore, of an external cycling route present in general background atmosphere.
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34 96 **Materials and Methods**

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36 97 **Measurements.** Under the umbrella of the second Tibetan Plateau Scientific Expedition and
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38 98 Research Program (STEP), the field campaigns “In-depth Study of the Atmospheric Chemistry
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41 99 over the Tibetan Plateau: Measurement, Processing and the Impacts on Climate and Air Quality”
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43 100 (referred to herein as @Tibet 2019) was carried out at the Nam Co Multisphere Observation and
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45 101 Research Station (30°46.44'N, 90°59.31'E, 4730 m a.s.l.) from 28 April to 10 July 2019. The site
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47
48 102 was covered by alpine steppe with sparse vegetation during the measurement period. With very
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50 103 limited anthropogenic emissions, including visiting vehicles and pasture activities around the
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52 104 station, the Nam Co site is considered a background site.
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3 105 Container measurements included HONO, NO₂, OH radicals, peroxyacetyl nitrate (PAN), O₃,
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5 106 CO, volatile organic compounds (VOCs), oxygenated VOCs (OVOCs), photolysis frequency of
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7 107 HONO, NO₂, and O₃, meteorological parameters, and the HONO flux, satisfying the calculation
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9
10 108 of HONO and NO_x budgets. The measurement methods are briefly described below.

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12 109 HONO was measured by a commercial LOnG-Path Absorption Photometer (LOPAP-03,
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14 110 QUMA), characterizing a wet chemical sampling and photometric detection technique¹⁸. In this
15
16 111 study, 0.05 M sulfanilamide (SA) in a 0.1 M HCl was used as the scrubbing solution for gaseous
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18 112 HONO and 0.5 mM N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA) was used for
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20 113 derivatization. The HONO was sampled with a two-channel coil, and HONO concentration was
21
22 114 calculated by subtracting the signal in the second channel from that in the first channel to minimize
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24 115 possible interference (e.g., from PAN or NO₂). Zero air measurements were measured every 2 h
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26 116 for 30 min to correct for the instrument baseline fluctuations. A liquid nitrite standard calibration
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30 117 was performed to renew the calibration curve every week. The detection limit of the LOPAP was
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32 118 5 pptv ($\pm 3 \sigma$) with a time resolution of 3 min. The uncertainty of the LOPAP measurements mainly
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34 119 came from variations in the liquid flow rate and changes in the purities of the reagents, with a final
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36 120 uncertainty of 25%¹⁸. In this campaign, gaseous HONO was sampled at a tower at heights of 1.8
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39 121 m and 6.8 m with a time cycle of 15 min to satisfy the measurement of HONO flux.

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42 122 HONO flux was obtained by integrating the eddy covariance method (EC) and the Atmospheric
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44 123 gradients method (AG). The turbulent diffusion coefficient (k) was derived from the H₂O flux
45
46 124 measured with eddy covariance method and water vapor density gradient, thus providing the real-
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48 125 time k required in the HONO flux calculation. The continuous HONO mixing ratio was obtained
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50 126 via interpolation, and the HONO gradients between 1.8 m and 6.8 m were then calculated. The
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53 127 HONO flux was then calculated using the k value and HONO gradients.

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3 128 NO₂ was measured by an incoherent broadband cavity-enhanced absorption spectrometer
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5 129 (BBCES)¹⁹. Briefly, incoherent light centered at 460 nm was emitted from a blue light-emitting
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7 130 diode (LED), coupled in a light fiber and collimated with a SMA collimator before entering a 1-m
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9 131 Teflon optical cavity with highly reflective mirrors ($R > 99.9\%$) on both ends. The light was
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11 132 reflected multiple times before being transmitted and detected by a spectrometer (Ocean Optics,
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13 133 QE65000). The NO₂ mixing ratio was obtained by applying a least-squares fitting to the optical
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15 134 extinction coefficient and reference absorption cross-section of NO₂ over the wavelength range of
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17 135 446-466 nm. The wavelength-dependent reflectivity of mirrors was determined weekly to calibrate
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19 136 the optical extinction coefficient of NO₂ in this system. The detection limit of NO₂ was 25 pptv
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21 137 (1σ) with a time resolution of 36 s. The uncertainty of the system was estimated to be 4%.

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24 138 OH radicals were measured with a fluorescence assay by gas expansion (FAGE) instrument as
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26 139 described elsewhere²⁰. Nonmethane VOCs and OVOCs were measured by online gas
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28 140 chromatography-mass spectrometry (GC-MS/FID, TH-PKU 300B, Wuhan Tianhong Instrument
29
30 141 Co. Ltd., China) with a measurement method described elsewhere²⁰. PAN was detected by a
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32 142 commercial analyzer (Metcon, Germany) consisting of an automated gas chromatograph equipped
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34 143 with an electron capture detector and a calibration unit. O₃ was measured by a commercial Ultra-
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36 144 Visible photometer (49C, Thermo Scientific™, MA, USA). CO and CH₄ were measured by a
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38 145 commercial analyzer based on wavelength-scanned cavity ring-down spectroscopy (PICARRO
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40 146 G2401). Photolysis frequencies were measured with a spectroradiometer (Metcon CCD-
41
42 147 Spectrograph). Meteorological parameters, including temperature, pressure, precipitation, and
43
44 148 water vapor pressure, were measured by the DZZ4 Automatic Weather Station.

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47 149 Data observed from 2 – 20 May were averaged to the hourly resolution and used for analysis
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49 150 and model constraints in this study, as these parameters related to the HONO and NO_x budgets,
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3 151 and OH radical production were most complete during this period. The list and time series of these
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5 152 parameters are shown in Table. S1 & Figure S1.
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8 153 **Budget calculation.** Calculations of HONO and NO_x budgets, and OH radicals production were
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10 154 conducted by relying on field-measured parameters, published chemical kinetic data and model-
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12 155 calculated concentrations. The budget of each species was calculated with Eqs. 1-5 below.
13

$$156 \quad P_{HONO} = k_{NOOH}[NO]_{mod}[OH] + k_{het}[NO_2] + \frac{HONO \text{ flux}}{MLH} + j_{pNO_3}[pNO_3^-] + External_{unaccounted}$$

17
18 157 Eq.1
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$$21 \quad D_{HONO} = j_{HONO}[HONO] - \frac{v_{HONO}}{BLH}[HONO] \quad \text{Eq.2}$$

$$24 \quad P_{NO_x} = j_{HONO}[HONO] + k_{bpan}[PAN] \quad \text{Eq.3}$$

$$28 \quad D_{NO_x} = k_{NOOH}[NO]_{mod}[OH] + k_{het}[NO_2] + k_{fpan}[NO_2][CH_3(O)O_2] + k_{NORO_2}[NO][RO_2] +$$

$$30 \quad k_{NO_2OH}[NO_2][OH] \quad \text{Eq.4}$$

$$34 \quad P_{OH} = j_{HONO}[HONO] + f \times j_{O^1D}[O_3] + k_{NOHO_2}[NO][HO_2] + k_{O_3HO_2}[O_3][HO_2] +$$

$$36 \quad j_{H_2O_2}[H_2O_2] + \sum i \{ j_{ROOH}^i [ROOH]_i \} \quad \text{Eq. 5}$$

39 164 The HONO budget (Eq. 1 & Eq. 2) was constrained by the measured mixing ratio of NO₂,
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41 165 HONO, OH radicals, the photolysis frequency of HONO, and the HONO flux. The mixing ratio
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43 166 of particulate nitrate ([pNO₃⁻]) was derived as the nitrate concentration in the particulate matter
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45 167 PM_{2.5} samples collected during the campaign and measured via ion chromatography, and the
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47 168 mixing ratio of particulate nitrate can be calculated with Eq. 6, as follows:
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$$51 \quad pNO_3^- = \frac{nNO_3^-}{V} \times 10^{-12} \quad \text{Eq. 6}$$

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3 170 where nNO_3^- (mol) is the amount of nitrate in the PM_{2.5} samples, V is the sampling volume, and
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5 171 10^{-12} is a unit conversion factor. Due to measurement failures, the mixing ratio of NO had to be
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7 172 calculated in the “Mea.” model run as described in model setup section. The previously published
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9 173 reaction rate constant of NO with OH radicals (k_1) and the photolysis frequency of particulate
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11 174 nitrate (j_{pNO_3}) were applied^{8,21}. The HONO deposition rate was parameterized with the HONO
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13 175 deposition velocity (v_{HONO}) and boundary layer height (BLH). We took the relatively high HONO
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15 176 deposition velocity of 2 cm/s due to the strong turbulence at the NMC site^{6,22,23}. The BLH was
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17 177 calculated with the Nozaki method by measuring meteorological parameters of temperature, dew
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19 178 point, and wind speed at 2 m above the ground. The heterogeneous reaction rate of NO₂ (k_{het}) was
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21 179 parameterized using Eq. 7 and Eq. 8 at nighttime (20:00-8:00 (+1 day)) and daytime (8:00-20:00),
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23 180 respectively.

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$$k_{het_N} = \frac{[HONO]_{t2} - [HONO]_{t1}}{\Delta t \times [NO_2]} \quad \text{Eq. 7}$$

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$$k_{het_D} = \frac{1}{4} \times \frac{1}{MLH} \times \sqrt{\frac{8RT}{\pi M}} \times \gamma \times \frac{j_{NO_2}}{j_{NO_2_noon}} \quad \text{Eq. 8}$$

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38 183 For nighttime, the NO₂ conversion rate constant was calculated according to the method
39
40 184 described previously², obtaining an average value of 2.1% [NO₂] h⁻¹; this value is comparable with
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42 185 previous observations of 1.4-2.4% [NO₂] h⁻¹ recorded at rural and subrural sites²⁴⁻²⁶. In the daytime,
43
44 186 the NO₂ conversion rate constant or uptake coefficient of NO₂ was scaled with the photolysis
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46 187 frequency of NO₂ (j_{NO_2}). The term γ is defined as the uptake coefficient of NO₂ under the j_{NO_2}
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48 188 reference at noon, $j_{NO_2_noon}$, with an upper-limit value of 6×10^{-5} derived in a previous study²⁷. The
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50 189 term $\sqrt{\frac{8RT}{\pi M}}$ (m s⁻¹) is the mean molecular speed of NO₂. MLH is the mixed layer height of HONO;
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3 190 this value was determined with the photolysis frequency of HONO and turbulent diffusion
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5 191 coefficient(k) with Eq. 9, as follows:

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$$MLH = \sqrt{\frac{2k}{j_{HONO}}} \text{ Eq. 9}$$

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11 193 MLH was calculated at ~ 50 m with an observed HONO lifetime of 10-20 min and k value varying
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13 194 from 1 to 2 m^2/s as determined from flux tower measurements.

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16 195 Regarding the NO_x budget (Eq. 3 & Eq. 4), HONO-related reactions were calculated with the
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18 196 method described above. PAN-related budget items were calculated with the measured mixing
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20 197 ratio of NO_2 , PAN, and the model-generated concentration of peroxyacetyl radicals ($[CH_3CO_3]$).
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22 198 The reaction rate of NO with RO_2 radicals producing organic nitrates ($RONO_2$) was derived as the
23
24 199 sum of reactions rates of the model-generated NO with 208 RO_2 species. The reaction rate of NO_2
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26 200 with OH radicals producing gaseous nitric acid (HNO_3) was constrained with the field-measured
27
28 201 concentrations of NO_2 and OH radicals. The photolysis and oxidation of gaseous HNO_3 and
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30 202 $RONO_2$ back to NO_x were minor budget items and thus were not included in this work. All reaction
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32 203 rate constants considered herein were previously published data extracted from the model.
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36 204 OH radical production (Eq. 5) was calculated to evaluate the perturbation of the external HONO
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38 205 source on the atmospheric oxidative capacity. The budget items were constrained with the field-
39
40 206 measured mixing ratio of HONO, O_3 , and their photolysis frequencies (j_{HONO} , j_{O^1D}). The reaction
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42 207 rates of HO_2 radicals with NO ($k_{NOHO_2}[NO][HO_2]$) and O_3 ($k_{O_3HO_2}[O_3][HO_2]$), as well as the
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44 208 photolysis of peroxides ($j_{H_2O_2}[H_2O_2] + \sum_i \{j_{ROOH}^i [ROOH]_i\}$), were calculated with model-
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46 209 generated mixing ratio of NO , HO_2 , H_2O_2 and peroxides and were extracted from the model.
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51 210 **Model description.** A zero-dimensional photochemical box model based on the Master
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53 211 Chemical Mechanism (MCM)²⁹ was used to help calculate the budgets of HONO, NO_x and OH
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55 212 and evaluate the impact of external cycling on HONO, NO_x and OH radicals with HONO as the
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3 213 intermediate tracer. The mechanism consisted of 11152 gas-phase reactions extracted from the
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5 214 website (MCM v3.3.1, <http://mcm.leeds.ac.uk/MCM>), including all inorganic chemistry reactions
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8 215 and organic chemistry reactions related to VOCs and OVOCs measurements. The heterogeneous
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10 216 conversion of NO₂ and deposition of HONO were also included in the chemical mechanism with
11
12 217 the parameterization methods described above.

14 218 Two model runs were designed and conducted. The control model run (referred to herein as
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16
17 219 “Mea.”) was constrained by the diurnal variations of parameters listed in Table S2. The sensitive
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19 220 model run (“Base”) was constrained with all parameters as in “Mea.” model except HONO, NO₂
20
21 221 and OH radicals. The model setup was fully described in Table S2. The comparison of these two
22
23 222 model runs provided evidence for the perturbation of external HONO on NO_x and OH radicals.
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26 223 Each model was initialized with inputs from the first measurement day and spun up for days, before
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28 224 the concentrations and budgets of HONO, NO_x and OH radicals were extracted and analyzed on
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31 225 the third day.

32 33 226 **Results and Discussion**

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35 227 To identify the external cycling in polar areas, several key arguments, such as the distributions
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37 228 and budgets of HONO and NO_x, mechanism analyses and atmospheric perturbations of external
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39 229 cycling, have been comprehensively discussed in various studies lasting from the 1990s to the
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41 230 present^{11–16,28–31}. The polar scenario suggests a revision of atmospheric photochemistry by the
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43 231 external cycling mechanism within the snowpack^{11,16}. Specifically, an external source of nitrate
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45 232 photolysis on snow/ice surfaces promotes HONO and NO_x abundances and increases HO_x to levels
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47 233 even exceeding those found in tropical marine boundaries¹⁵. Herein, we follow this lead to explore
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49 234 the scientific questions raised above.

50 51 235 **Distributions of HONO, NO_x and the PSS HONO/NO_x ratio**

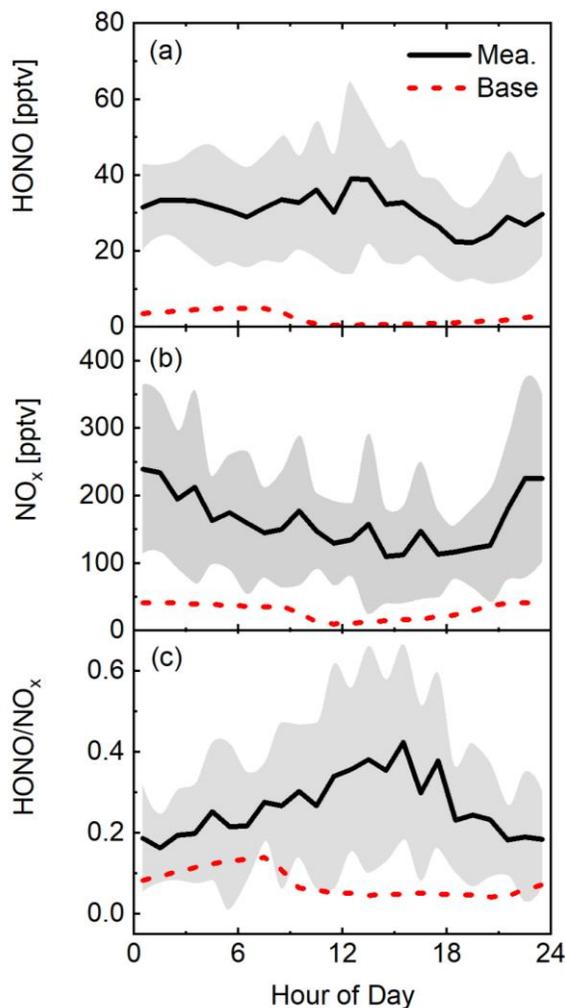
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3 236 The hourly mixing ratio of HONO ranged from 7 to 94 pptv from 2 – 20 May (Figure. S1 (a)).
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5 237 The average mixing ratio of HONO at this pristine alpine site was 30 (± 13 , 1σ) pptv. Our HONO
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7 238 observations are comparable with other measurements recorded in terrestrial background
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9 239 environments, such as the value of 46 pptv observed at the summit of Whiteface Mountain³², that
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11 240 of 32 pptv measured in a boreal forest³³, and that of 35 pptv measured at a background coastal site
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13 241 in Cyprus³⁴, while it is slightly higher than the measurements of 8-35 pptv recorded in polar
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15 242 areas^{11,13,31,35,36}. Higher HONO mixing ratio values were frequently found in the daytime
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17 243 observations compared to those in the nighttime observations, in contrast to the relatively fast
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19 244 photolysis with a photolysis rate constant of $1-1.6 \times 10^{-3} \text{ s}^{-1}$. Occasionally, spikes occurred on
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21 245 several nights along with spikes in the NO₂ mixing ratio, suggesting the influence of the local
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23 246 combustion of cow dung cakes and emissions from visiting vehicles.

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25 247 The mixing ratios of NO₂ ranged from 20 to 620 pptv, with high values occurring in narrow
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27 248 spikes (Figure. S1 (b)). The time durations comprising these NO₂ spike occurrences consisted of
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29 249 ~7.5% of the whole measurement period. A small discrepancy between the average mixing ratio
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31 250 of 143 (± 100 , 1σ) pptv and the median value of 119 pptv was also observed. We therefore
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33 251 concluded that occasional emissions do not significantly raise the pollution level of this pristine
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35 252 site. For the mixing ratio of NO, we projected a daytime average value of 34 (± 26 , 1σ) pptv and a
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37 253 nighttime value near zero due to titration by ca. 50 ppb of O₃. These mixing ratios of NO_x were
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39 254 comparable with those measured at 100-300 pptv in terrestrial background sites³²⁻³⁴ but were
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41 255 slightly higher than the tens of pptv observed in polar regions^{12,15,35}.

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43 256 The HONO/NO_x ratios varied from 0.03 to 1 during this field campaign, with mean and median
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45 257 values of 0.26 (± 0.18 , 1σ) and 0.20, respectively (Figure S1 (c)). The HONO/NO_x ratio was
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47 258 substantially higher than the 0.006-0.05 ratios observed in urban sites⁵ but was comparable with
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3 259 the 0.06-0.53 values observed in polar areas and terrestrial background sites^{11-14,16,33-35,37,38}.
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5 260 Relatively high HONO/NO_x ratios were frequently observed in daytime than nighttime, with peak
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8 261 values mostly occurring around noon.

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10 262 The measured diurnal patterns of HONO, NO_x and the HONO/NO_x ratio are shown in black line
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12 263 in Figure 1. A bridge-shaped diurnal pattern of HONO was characterized with a noontime (12:00-
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14 264 13:00) maximum of 40 pptv and a nighttime (20:00-8:00) minimum of 22 pptv; this pattern was
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17 265 consistent with the corresponding time-series observations on most days. The diurnal pattern of
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19 266 NO_x was characterized with relatively high values of 190 (± 38 , 1σ) pptv at night and slightly lower
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21 267 values of 135 (± 21 , 1σ) pptv during the day on average. Bridge-shaped diurnal pattern was also
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24 268 observed for the HONO/NO_x ratio. The average HONO/NO_x ratio was 0.20(± 0.03 , 1σ) throughout
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26 269 the night while averaged at 0.31(± 0.06 , 1σ) in the daytime. Contradictory to the measurements,
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29 270 obvious U-shape diurnal patterns of HONO, NO_x and HONO/NO_x ratio were predicted with the
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31 271 “Base” model run, the chemical model simulations performed with a simple internal cycling
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33 272 mechanism (Figure 1., red dash line). The predicted HONO concentration was averaged at 3.5
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35 273 (± 1.2 , 1σ) pptv in the nighttime and 1 (± 0.9 , 1σ) pptv in the daytime. NO_x concentrations were
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38 274 projected at 17 (± 8 , 1σ) pptv in the daytime and 38 (± 2 , 1σ) pptv at night on average. HONO/NO_x
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40 275 ratio was averaged at 0.07 (± 0.03 , 1σ) throughout the day, and at 0.05 (± 0.007 , 1σ) in the daytime.
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277 **Figure 1.** Diurnal patterns of (a) HONO, (b) NO_x, and (c) HONO/NO_x ratio. The “Mea.” model
278 results are shown as a black line, with the gray shaded area representing the variation ($\pm 1\sigma$). The
279 “Base” model predictions are shown as red dashed lines.

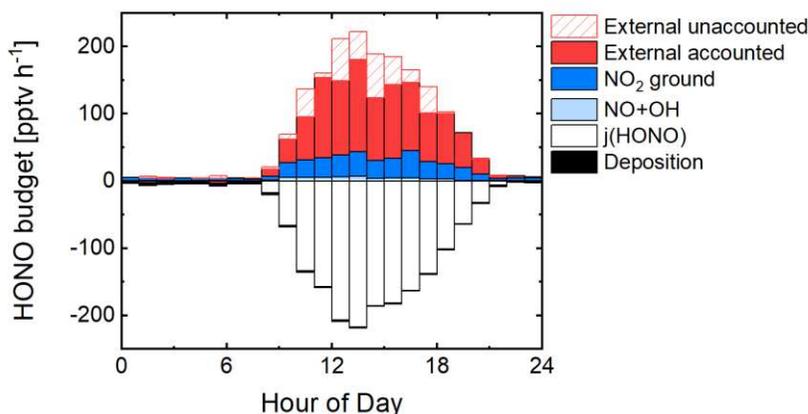
280 Here, we conclude that external cycling prevails and dominates at the background site based on
281 the distribution patterns of HONO, NO_x and the HONO/NO_x ratio. First, the “Base” model run
282 underestimates the HONO and NO_x observations by 90% and 80%, respectively (Figure 1(a) &
283 (b)), suggesting that the internal cycling mechanisms could only explain a minor part of HONO
284 and NO_x abundance. Second, a PSS HONO/NO_x ratio, i.e. HONO/NO_x ratio in the daytime, of

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3 285 0.05 was predicted in the “Base” model run in the daytime; this value was substantially lower than
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5 286 the observed PSS HONO/NO_x ratio of 0.31(±0.06, 1σ). The high HONO/NO_x ratio further
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7 287 suggested that internal cycling was not sufficiently strong to sustain daytime HONO
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9 288 concentrations. Elevated HONO/NO_x ratio was attributed to the photosensitization of NO₂
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11 289 recorded on the ground surface in previous field measurements³⁵. However, here, we took the
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13 290 upper-limit NO₂ heterogenous conversion rate of 6×10⁻⁵ derived in previous field campaigns,
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15 291 though this value could still not explain the observed HONO/NO_x ratio, suggesting a missing
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17 292 source of HONO from non-NO_x precursors, i.e., an external source. In addition, no correlation
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19 293 between the mixing ratios of HONO and NO₂ was observed (R²<0.1), implying that the
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21 294 distributions of HONO and NO_x are not controlled by their internal cycling. Third, the bridge-
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23 295 shaped diurnal pattern of HONO and the relatively stable diurnal pattern of NO_x against their
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25 296 photolysis and oxidative losses could only be reconciled by a mutual source of HONO and NO_x,
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27 297 i.e., an external source. This external source should be scaled by temperature or solar radiation to
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29 298 sustain the noontime HONO and NO₂ observations. Last but not least, the proxy mechanisms of
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31 299 external sources discussed in previous literature are reasonable, as they produce HONO and NO_x
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33 300 at a high production ratio and are scaled with either temperature or solar radiation. First, nitrate
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35 301 photolysis has been extrapolated to ambient surfaces, such as tree leaves, urban grimes, and aerosol
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37 302 surfaces, with a HONO/NO_x production ratio range of 0.4-33^{21,39-41}. The light-related and surface-
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39 303 catalyzed characteristics of this process make it a potential mechanism at this background site on
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41 304 the Tibetan Plateau. Nitrification and/or denitrification processes in surface soils where nitrate or
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43 305 ammonium is available as a HONO precursor are another proven external source^{42,43}. Soil
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45 306 emissions of HONO have been observed in both fertile and barren soils, such as those in forests,
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47 307 grasslands, and deserts, both in the field and laboratory, supporting such an external HONO source
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3 308 as a universal source⁴². Overall, the distribution patterns of HONO, NO_x and HONO/NO_x indicate
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5 309 the dominant role of this external source on the HONO budget.
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8 310 **Chemical budget of HONO**

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10 311 Our measurement constraint on the HONO budget allowed us to quantify the internal and
11
12 312 external cycling routes of HONO and NO_x. The HONO budget is shown in Figure 2. At night,
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14 313 HONO was produced at a rate of 4 pptv h⁻¹ through the heterogeneous conversion of NO₂. This
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16 314 rate was not only small but may also have been offset by HONO deposition at a magnitude of 3
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18 315 pptv h⁻¹. The nighttime budget calculation was in line with our observation of stable HONO
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20 316 throughout the night, suggesting that no or only minor nighttime accumulation occurs from
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22 317 heterogeneous reactions of NO₂ on the ground surface. In the daytime, the homogeneous reaction
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24 318 between NO and OH radicals produces HONO at an average rate of 3 pptv h⁻¹; this rate is negligible
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26 319 compared to the overall HONO source budget of 130 pptv h⁻¹. The heterogeneous conversion of
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28 320 NO₂ on the ground is accelerated by solar radiation. Given an upper limit of the noontime uptake
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30 321 coefficient of 6×10^{-5} , the daytime average rate of 25 pptv h⁻¹ was calculated. Although the upper
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32 322 limit of the uptake coefficient was taken into consideration here^{10,27,44}, the conversion of NO₂ was
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34 323 still only one-sixth of the daytime HONO source budget. Here, we evaluated the 30 pptv h⁻¹ rate
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36 324 produced by internal sources in the daytime and projected its contribution to the overall HONO
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38 325 budget to be ca. 23%. The external HONO source thus accounted for at least 77% of the HONO
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40 326 source budget in the daytime and an average daytime HONO production rate of 100 pptv h⁻¹.
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328 **Figure 2.** Chemical budget terms of HONO as evaluated by the “Mea.” model. HONO
329 deposition is shown with the black bar; photolysis ($j(\text{HONO})$) is shown with the white bar; the
330 reaction of NO with OH radicals (NO+OH) is shown with the light blue bar; and the heterogenous
331 conversion of NO₂ on ground surfaces (NO₂ ground) is shown with the blue bar. The external
332 sources accounted for by surface fluxes and particulate nitrate photolysis (External accounted) are
333 shown with red bars. The remaining external source (External unaccounted) is shown with the red
334 line bars.

335 Surface flux measurements of HONO provided a constraint on external cycling. During the field
336 campaign, an average daytime HONO flux of $0.02 \text{ nmol m}^{-2} \text{ s}^{-1}$ was measured (Figure S1 (g)).
337 Assuming an MLH of 50 m described in Materials and Methods, the surface HONO flux was
338 converted into an in situ HONO source rate of ca. 65 pptv h^{-1} . The upper limit of photo-enhanced
339 heterogeneous conversion of NO₂ on the ground surface was estimated to be 25 pptv h^{-1} , suggesting
340 an external source accounting for at least the remainder of 40 pptv h^{-1} . Both soil emissions and the
341 surface-catalytic photolysis of nitrate on ground surfaces are candidates for this external source.

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3 342 The response of the HONO flux peak to precipitation with a delay of one day might be attributed
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5 343 to the soil activation mechanism, implying the dominating role of soil emissions (Figure S1 (g)).
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8 344 An in situ external HONO source from the photolysis of particulate nitrate cannot be ruled out.
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10 345 The photolysis of particulate nitrate has been found to be enhanced by 1-3 orders of magnitude
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12 346 compared to that of gaseous nitric acid^{21,40}. We took the photolysis frequency of $1.3 \times 10^{-4} \text{ s}^{-1}$ to
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14 347 estimate the HONO production rate via particulate nitrate photolysis in this study, which is the
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16 348 mean value derived from HONO production via particulate nitrate photolysis experiments with
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18 349 particulates collected over a variety of various environments²¹. The mean nitrate concentration of
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20 350 $\text{PM}_{2.5}$ samples collected during the campaign was 110 pptv. We therefore estimated an in situ
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22 351 HONO production rate of approximately 35 pptv h^{-1} in the daytime.
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26 352 All these external sources summed up to 75 pptv h^{-1} , 25% less than the total external source of
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28 353 100 pptv h^{-1} derived from the HONO budget analysis. This discrepancy was, however, within the
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30 354 measurement uncertainties. Specifically, the measurement uncertainties were determined to be 25%
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32 355 for HONO and 35% for the HONO flux. Uncertainties also arose from the evaluation of external
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34 356 HONO source candidates, but these uncertainties are difficult to quantify. First, to evaluate the
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36 357 HONO source from the flux measurements, we assumed a uniform distribution of HONO in the
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38 358 50-m mixed layer. However, with a noontime solar radiation measurement of 1700 W m^{-2} and an
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40 359 average wind speed of 4 m s^{-1} , rapid vertical mixing of HONO should be expected. Therefore, the
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42 360 HONO budget item would be very sensitive to the MLH evaluation. Second, in situ HONO
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44 361 production from particulate nitrate photolysis is heavily dependent on the photolysis frequencies
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46 362 observed in different environments²¹, which might also vary in the pristine environment of the
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48 363 NMC site.
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3 364 Despite these uncertainties, our HONO budget evaluation provides evidence that both soil
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5 365 emissions and the surface-catalytic photolysis of nitrate are potential proxy mechanisms
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8 366 representing the unidentified external source. However, the large uncertainties hinder the
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10 367 separation of the contributions of these two proxy mechanisms. Further precise quantification
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12 368 measurements of the two external source candidates in the mixed layer, combined with a chemical
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15 369 transport model analysis, are thus encouraged.

16 17 370 **Perturbation of NO_x and OH radicals**

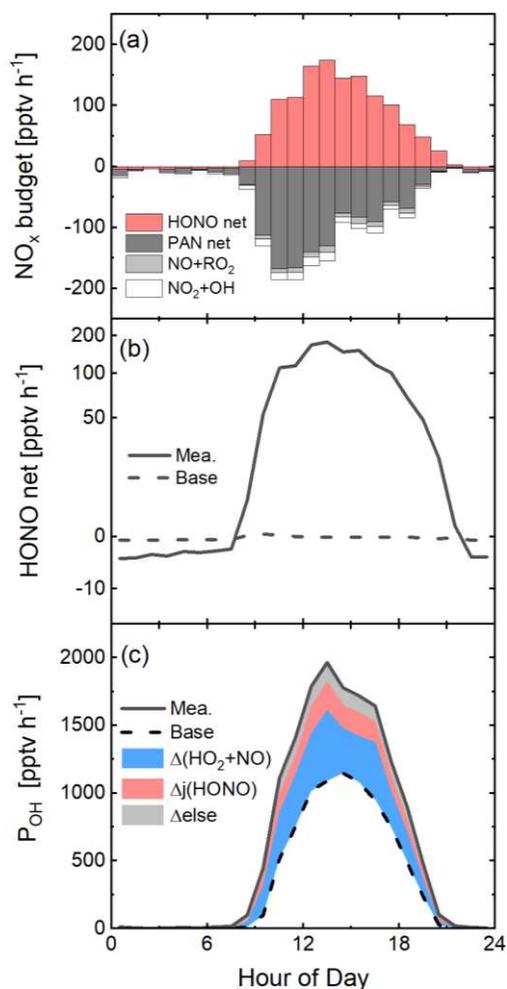
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19 371 External sources of HONO are also sources of NO_x because HONO quickly photolyzes,
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21 372 producing NO. Therefore, we propose the occurrence of external cycling routes of NO_x with
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24 373 HONO as an intermediate tracer. External cycling further promotes OH radical production directly
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26 374 via HONO photolysis and indirectly via OH recycling routes, such as the reaction of NO with HO₂
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28 375 radicals. Our model evaluates the perturbation of this external source on the distributions and
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31 376 budgets of NO_x and OH radicals.

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33 377 The model results underline HONO as a critical intermediate to NO_x. Specifically, in the “Mea.”
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35 378 model run constrained by our measurements, 100 pptv h⁻¹ of net NO_x production ($\text{HONO net} =$
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38 379 $j_{\text{HONO}}[\text{HONO}] - k_1[\text{NO}]_{\text{mod}}[\text{OH}] - k_{\text{het}}[\text{NO}_2]$) was determined to occur via the photolysis of
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40 380 external HONO. The photolysis of external HONO dominated the chemical production of NO_x in
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42 381 this pristine environment. Nevertheless, the formation of PAN, HNO₃ and RONO₂ provide NO_x
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45 382 sinks at this site. A net loss of NO_x to PAN ($\text{PAN net} = k_{\text{bpan}}[\text{PAN}] - k_{\text{fpan}}[\text{NO}_2][\text{CH}_3\text{CO}_3 \cdot]$) at
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47 383 a rate of 90 pptv h⁻¹ was predicted in the model. High abundances of NO₂ and CH₃CO₃ radicals
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49 384 promote the reaction of NO₂ with CH₃CO₃ radicals to a rate of 110 pptv h⁻¹, while the low
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51 385 temperatures in this alpine site suppress the thermal decomposition of PAN to a rate of 20 pptv h⁻¹
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54 386 ¹. When further seeking the precursors of CH₃CO₃ radicals, we found acetaldehyde at a

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3 387 concentration of 1 ppb at this site; however, the source of this acetaldehyde is not yet clear.
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5 388 Relatively slow losses of NO_x to RONO_2 and HNO_3 were projected in the model at rates of 6 pptv
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7 389 h^{-1} and 9 pptv h^{-1} , respectively. The chemical budget of NO_x is imbalanced, with an unaccounted
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9 390 source in early morning and unaccounted sink in the afternoon. There are two possible
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11 391 explanations for the imbalance. First, direct production of NO_x in external cycling was not included
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13 392 in our budget analyses. Second, as discussed for HONO above, vertical mixing of NO_x into a
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15 393 higher layer of air masses is a potential sink of NO_x . However, with the mechanisms currently
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17 394 considered, we still conclude external HONO as a precursor to NO_x and HONO as the intermediate
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19 395 tracer of the external cycling, by the discrepancy between the “Mea” and “Base” model results
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21 396 (Figure 3(b)). In the “Base” model run in which only internal cycling was included, “HONO net”
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23 397 was nearly zero in the daytime because HONO photolysis was offset by NO_x -related reactions and
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25 398 no net NO_x was produced.

30 399 OH production is greatly promoted as a result of external cycling. As shown in Figure 3 (c), the
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32 400 OH production rate was doubled in the daytime in the “Mea.” model run compared to that in the
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34 401 “Base” run. Of the enhancements, 54% and 23% could be attributed to the reaction of NO with
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36 402 HO_2 radicals and to the photolysis of HONO, respectively. The enhancement of OH production
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38 403 resulted in an elevated mixing ratio of OH radicals. The measured mixing ratio of OH radicals was
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40 404 2.25 times higher than that predicted in the “Base” model run in the daytime, with average values
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42 405 of 2.67×10^6 molecule/ cm^3 and 1.49×10^6 molecule/ cm^3 , respectively (Figure S2). These results
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44 406 imply an underestimation of the atmospheric oxidative capacity at this background site if only the
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46 407 internal cycling of HONO and NO_x is considered.

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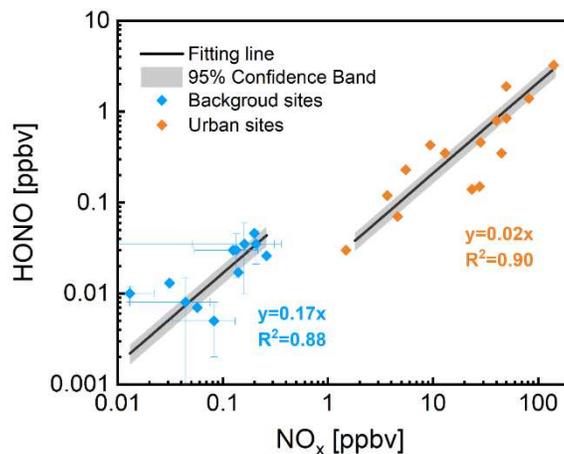


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410 **Figure 3.** (a) NO_x budget calculated in the “Mea.” model run. $\text{HONO net} = j_{\text{HONO}}[\text{HONO}] -$
 411 $k_1[\text{NO}]_{\text{mod}}[\text{OH}] - k_{\text{het}}[\text{NO}_2]$ and $\text{PAN net} = k_{\text{bpan}}[\text{PAN}] - k_{\text{fpan}}[\text{NO}_2][\text{CH}_3\text{CO}_3 \cdot]$; (b)
 412 “HONO net” calculated in two model runs. The rate predicted with the “Mea.” model is shown as
 413 a solid line, while that predicted with the “Base” model is shown as a dashed line. (c) OH
 414 production rates calculated in two model runs. The rate predicted with the “Mea.” model is shown
 415 as a solid line, while that predicted with the “Base” model is shown as a dashed line. The blue, red,
 416 and gray shaded areas represent the enhancement of the OH production rate via the reaction of NO
 417 with HO_2 radicals, HONO photolysis and the reactions of the model-generated species.

418 Environmental implications

419 High PSS HONO/NO_x ratios are prevalently observed in pristine areas^{15,32,33,38}. Here, we
420 summarize the daytime HONO and NO_x concentrations measured in the background atmosphere
421 and compare them with those measured in the urban atmosphere (Figure 4 & Table S3). In the
422 urban atmosphere, the PSS HONO/NO_x ratio values are scattered around approximately 0.02, thus
423 strengthening that the internal cycling chemistry of HONO and NO_x dominates in such
424 environments⁵. However, the PSS HONO/NO_x ratios measured in the background environments
425 range from 0.06 to 0.77. The fitting PSS HONO/NO_x ratio of 0.17 was derived for the background
426 atmosphere; this ratio is significantly higher than that obtained for urban observations. This finding
427 is indicative of external cycling having taken over in pristine atmosphere, while internal cycling
428 was still inclusive.



429
430 **Figure 4.** Distributions of HONO against NO_x observed in the daytime in background (blue) and
431 urban (orange) sites. The solid lines and gray shaded areas are the fitting lines and 95% confidence
432 bands, respectively, for the two scenarios. The linear fitting results are shown in blue and orange
433 for background and urban sites, respectively, with the slope representing PSS HONO/NO_x.

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3 434 By deducing a high HONO/NO_x ratio as a sufficient condition for external cycling, we validate
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5 435 the prevalence of external cycling in general background atmosphere. The great perturbation of
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7 436 external cycling on the budgets of NO_x and OH radicals was also validated. Underappreciating the
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9 437 external cycling mechanism is therefore a major flaw of our current understanding of the reactive
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11 438 nitrogen cycling process and atmospheric oxidative capacity in background terrestrial
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13 439 environments.
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19 441 ASSOCIATED CONTENT
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22 442 **Supporting Information.**
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26 443 The following files are available free of charge.
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28 444 HONO _ intermediate tracer _ SI .pdf
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31 445 AUTHOR INFORMATION
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54 492 Author Contributions
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3 493 J.W. and C.Y. design the research, interpreted the data, and wrote the manuscript. J.W., Y.Z., C.Z.,
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5 494 Y.W., J.Z., L.K.W., E.J.S., J.E.D., W.X., and P.C. conducted the measurements. J.W., Y.W., and
6
7 495 R.W.M conducted the model simulations. The manuscript was written through contributions of all
8
9 496 authors. All authors have given approval to the final version of the manuscript.
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23 501 Notes

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