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Impact of HONO on global atmospheric chemistry calculated with an empirical parameterization in the EMAC model

Y. F. Elshorbany¹, B. Steil¹, C. Brühl¹, and J. Lelieveld^{1,2}

¹Max-Plank Institute for Chemistry, Atmospheric Chemistry Department, Mainz, Germany ²The Cyprus Institute, Nicosia, Cyprus, and King Saud University, Riyadh, Saudi Arabia

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Correspondence to: Y. F. Elshorbany (yasin.elshorbany@mpic.de)

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Abstract

The photolysis of HONO is important for the atmospheric HO_{v} (OH + HO₂) radical budget and ozone formation, especially in polluted air. Nevertheless, owing to the incomplete knowledge of HONO sources, realistic HONO mechanisms have not yet been implemented in global models. We investigated measurement data sets from 15 field 5 measurement campaigns conducted in different countries worldwide. It appears that the HONO/NO_x ratio is a good proxy predictor for HONO mixing ratios under different atmospheric conditions. From the robust relationship between HONO and NO_v, a representative mean HONO/NO_x ratio of 0.02 has been derived. Using a global chemistry-climate model and employing this HONO/NO_x ratio, realistic HONO levels 10 are simulated, being about one order of magnitude higher than the reference calculations, which only consider the reaction $OH + NO \rightarrow HONO$. The resulting enhancement of HONO significantly impacts HO_x levels and photo-oxidation products (e.g. O_3 , PAN), mainly in polluted regions. Furthermore, the relative enhancements in OH and secondary products were higher in winter than in summer, thus enhancing the oxidation 15

capacity in polluted regions, especially in winter, when the other photolytic OH sources are of minor importance. Our results underscore the need to improve the understanding of HONO chemistry and its representation in atmospheric models.

1 Introduction

Since three decades, nitrous acid (HONO) photolysis has been shown to be an important source of OH radicals, especially during the early morning, when other sources are of minor importance (Perner and Platt, 1979; Harris et al., 1982). Recently, HONO photolysis was reported to contribute more strongly to daytime primary OH production than O₃ photolysis, both under urban and rural conditions (Elshorbany et al., 2009a; Sörgel et al., 2011a, respectively). It has been demonstrated that HONO photolysis can be a major OH initiation source under high NO_x (e.g., Kleffmann et al., 2007; Elshorbany



et al., 2009a, 2010a; Ren et al., 2006; Dusanter et al, 2009) as well as low NO_x conditions (e.g., Kleffmann et al., 2005; Elshorbany et al., 2012, Sörgel et al., 2011a). OH radicals constitute the major oxidant of the atmosphere, initiating the removal of most reactive gases (i.e. regulating the self-cleaning capacity of the atmosphere), though

- ⁵ also lead to the formation of secondary products such as O₃ and PAN, which can be harmful for human health. The OH oxidation of volatile organic compound (VOC) contributes to the formation of aerosol particles, affecting air quality and climate. HONO is also an important ingredient of the strongly anthropogenically perturbed global nitrogen cycle, which indirectly influences climate change (Kumala and Petäjä, 2011).
- ¹⁰ Owing to the thus far incomplete knowledge of HONO sources, in particular during daytime, it was not yet possible to simulate realistic HONO levels using global models. Li et al. (2010), Zhang et al. (2011) and Czader et al. (2012) have shown that additional HONO sources are required to match measured HONO mixing ratios; for some regions tenfold mismatches have been found based on the known gas phase HONO formation
- ¹⁵ only (i.e., OH + NO \rightarrow HONO). Li et al. (2011) and Goncalves et al. (2012) showed that modelled HONO was consistently lower than observations, even when the most effective recently suggested formation mechanisms were considered. This underestimation of HONO by models may be expected to impact the simulated HO_x and O₃ budgets as well as other secondary products.

Several HONO sources have been identified in the laboratory (e.g., Zhou et al., 2003; George et al., 2005; Stemmler et al., 2006, 2007; Bejan et al., 2006; Li et al., 2008; Gustafsson et al., 2006; Ndour et al., 2008; Su et al., 2011), yet these sources cannot account for the HONO levels observed during daytime (Elshorbany et al., 2010b; Su et al., 2011; Czader et al., 2012). While the heterogeneous conversion of NO₂ on humid surfaces (Finlayson-Pitts et al., 2003) in the dark is commonly accepted as the dominant HONO source during the night (Alicke et al., 2002), the exact mechanism is still unclear. For daytime HONO sources, five photochemical mechanisms were recently identified. Three of them dominate under high-NO_x urban conditions, i.e., heterogeneous conversion of gaseous NO₂ on photosensitized solid surface



organic compounds (George et al., 2005; Stemmler et al., 2006), photocatalytic conversion of NO₂ on TiO₂ (Gustafsson et al., 2006; Ndour et al., 2008) and the photolysis of gaseous nitro-aromatic compounds (Bejan et al., 2006), which are expected to correlate well with $j(NO_2)$. Under low-NO_x rural conditions, the photolysis of nitric acid

- ⁵ (Zhou et al., 2003, 2011) adsorbed on solid surfaces (including vegetation) may dominate and is expected to primarily correlate with $j(O^1D)$, related to the much lower wavelength range of nitric acid photolysis than $j(NO_2)$. Su et al. (2011) showed that HONO can also be emitted from soils, being a function of temperature (i.e, light independent). This source may be important in tropical forested regions. Sörgel et al. (2011a) showed
- ¹⁰ that unknown HONO daytime sources, normalized with NO₂ mixing ratios have a clear dependency on $j(NO_2)$. Recently, Czader et al. (2012) also showed that photo-induced conversion of NO₂ on organic surfaces is a strong daytime HONO source.

In addition to the incomplete knowledge about daytime HONO chemistry, most of the thus far identified HONO sources are generally also associated with large uncertainty

- ¹⁵ as the mechanisms and controlling parameters are only partly understood (Kleffmann, 2007; Li et al., 2010; Czader et al., 2012; Goncalves et al., 2012). Consequently, several recent attempts to simulate HONO formation were based on the modulation of the model parameters (i.e., via several assumptions and simplifications) to match the measurements in individual studies (e.g., Li et al., 2010; Czader et al., 2012; Goncalves
- et al., 2012). For example, Czader et al. (2012) simulated HONO using an approach adopted by Li et al. (2010), for which a daytime HONO source with a relatively large uptake coefficient was employed based on variable threshold values of light intensity. However, Czader et al. (2012) obtained unrealistically high HONO concentrations and therefore used the same uptake coefficient but scaled by a different and constant fac-
- ²⁵ tor to match the measured HONO. In contrast, Goncalves et al. (2012) obtained about three orders of magnitude lower production rates of HONO when using the approach adopted by Li et al. (2010) and reverted to another approach, more suitable to the studied area. Unfortunately, this approach to match measurements cannot be implemented



in global models, as each region would need its specific parameterization. Thus, a more general approach is needed to calculate more realistic HONO levels on a global scale.

A common factor between the known major day- and nighttime sources is that they are generally surface-based (except the gas phase photolysis of nitro-aromatic com-

- ⁵ pounds). Indeed, such HONO sources contribute a major fraction of measured HONO levels (Harrison and Kitto, 1994; Stutz et al., 2002; Veitel, 2002; Kleffmann et al., 2003; Zhang et al., 2009; Sörgel et al., 2011b; Wong et al., 2011) and consequently the dispersion into the atmosphere is a function of turbulent mixing (Sörgel et al. 2011b). This was first proposed by Febo et al. (1996) based on radon measurements, a species
- emitted exclusively from the ground. Veitel (2002) also showed that HONO correlates linearly with radon with highest values reported in winter. In addition, both, groundand aircraft-based gradient measurements showed that HONO mixing ratios near to the ground follow a steep gradient during stable conditions (Veitel, 2002; Zhang et al., 2009, respectively). Thus, HONO mixing ratios appear to be controlled by the sur-
- face area in a mixed volume of air (s/v), and the changes can often be accounted for by scaling HONO to NO₂ or NO_x (Sörgel et al. 2011b, and references therein). Similarly, Zhang et al. (2011) showed that the spatial distribution of simulated HONO during day- and nighttime is generally consistent with the NO_x emission pattern. Kleffmann (2007) concluded that the HONO/NO_x ratio is a reasonable measure of HONO
- as it takes into account the dilution of trace gases during transport, after being emitted or formed at the ground. Several previous studies indicated the HONO/NO_x ratio as a proxy for HONO formation under rural (e.g., Acker et al., 2006; Elshorbany et al., 2012; Sörgel et al., 2011b), remote (e.g., Kleffmann and Wiesen, 2008) and urban conditions (e.g., Elshorbany et al., 2009a, 2010a). Furthermore, Villena et al. (2011)
 showed that the HONO/NO_x ratio and its daytime maximum are independent of altitude. Thus, the HONO/NO_x ratio may be a practicable metric to help predict HONO in the atmosphere.

In this study, data sets from 15 different field measurement campaigns around the globe are investigated, confirming that the $HONO/NO_x$ ratio is a good proxy predictor of



the HONO mixing ratio for use in global models. The impacts of simulated HONO levels on the levels of oxidants (OH, O_3 , PAN, etc.) are determined using an atmospheric chemistry-climate model.

2 Methodology

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5 2.1 Model description

The applied modelling system is based on the ECHAM5 general circulation model (Roeckner et al., 2006) and the Modular Earth Submodel System (MESSy, Jöckel et al., 2005) to simulate the meteorology and atmospheric chemistry. The ECHAM5/MESSy Atmospheric Chemistry (EMAC) system is a coupled lower-middle atmospheric chemistry general circulation model (AC-GCM), which has been extensively evaluated (e.g., Jöckel et al., 2006; Lelieveld et al., 2007; Tost et al., 2007; Pozzer et al., 2008, 2010, 2012; Brühl et al., 2012). The model structure and setup have been described by Jöckel

et al. (2006) and only a brief description is given here.

Atmospheric chemical reactions are incorporated in the model through the module ¹⁵ MECCA1 (Sander et al., 2005), including the Mainz Isoprene Mechanism, version 2 (MIM2, Pöschl et al., 2000; von Kuhlmann et al., 2004; Taraborrelli et al., 2009). To study the effects of changes in the chemistry while avoiding possible feedbacks of radiatively active gases and aerosols through the meteorology, the radiation scheme has been decoupled, and the model is used in the atmospheric chemistry-transport mode.

- ²⁰ The radiation code in EMAC therefore uses an ozone climatology (Fortuin and Kelder, 1998), fixed vertical profiles for CH_4 , N_2O and CFCs and constant mixing ratios of CO_2 . The reference run (base) has been performed for the year 2005 in T42L31 resolution (i.e., with a triangular truncation at wave number 42 for the spectral core of ECHAM5, and with 31 levels on a hybrid-pressure grid in the vertical, reaching up to 10 hPa). The
- T42 resolution corresponds to a quadratic Gaussian grid of approximately $2.8^{\circ} \times 2.8^{\circ}$ in latitude and longitude. To simulate realistic synoptic conditions, we applied a weak



"nudging" towards actual meteorology by the assimilation of analysis data from the European Centre for Medium-range Weather Forecasting (ECMWF) through the Newtonian relaxation of four prognostic model variables: temperature, divergence, vorticity and the logarithm of surface pressure (van Aalst et al., 2004). The first 5 months of the simulation are regarded as spin up period and these results are not considered in our analysis.

Output has been archived as 1-hourly instantaneous fields to capture an hourly resolved diurnal cycle. In the sensitivity runs S1, S2 and S3, HONO levels were parameterized such that the HONO/NO_x ratio is fixed at 0.01, 0.02 and 0.04, respectively (see Sect. 3.3). This was achieved by an iterative correction of HONO and NO_x (i.e., without

¹⁰ Sect. 3.3). This was achieved by an iterative correction of HONO and NO_x (i.e., without disturbing the reactive nitrogen budget), which was applied every minute, thus limiting deviations in the HONO/NO_x ratio to within ± 0.005 .

2.2 Field measurements

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Average diurnally resolved data sets from eight different field measurement campaigns
(see Table 1) were used to analyse the day- and nighttime HONO chemistry. HOx-Comp took place at the Jülich Research Centre, Germany during 9–11 July, 2005 (we used only the diurnal profile of the cloud free day, 10 July, Elshorbany et al., 2012); the Santiago de Chile campaigns took place during 8–20 March 2005 (Santiago_S, Elshorbany et al., 2009a) and during 25 May to 7 June 2005 (Santiago_W, diurnal average of cloud free days only, Elshorbany et al., 2010a); the PMTACS-NY campaign took place from 10 July to 2 August 2001 in New York (New York, Ren et al., 2003); the Mexico City Metropolitan Area campaign took place during 14–31 March 2006 (MCMA-2006, Dusanter et al., 2009); the DOMINO campaign took place in Southwest-

ern Spain during November–December, 2008 (DOMINO, diurnal average of cloud free days only, Sörgel et al., 2011a) and we used two gradient measurement data sets obtained during a field measurement campaign at a 55 m tall building in Santiago de Chile from 17–29 November 2009 at the altitudes of 6 m (3rd floor, Santiago_3) and 53 m (21st floor, Santiago_21) above the ground (Villena et al., 2011). In addition, measured



average concentrations of HONO and NO_x from 7 other field measurement campaigns, adopted from Li et al. (2012), were also investigated (see Table 1). These measurement campaigns were performed in three different continents (from 52° N to 37° S and from 116° E to 99° W) under a range of meteorological conditions. These measurements also encompass a wide range of different NO_x conditions, typically from NO sensitive conditions (e.g., HOxComp) to VOC sensitive conditions (e.g., Santiago and New York). Furthermore , the results obtained from the analysis of these data are compared with other field campaigns reported in the literature. The range of HONO mixing ratios obtained from these data sets represents the minimum and maximum HONO levels measured during the last decade and therefore, represent an optimal global overview of HONO measurements.

2.3 Intercomparison of field measurements

The average measured diurnal profiles of HONO, HONO/NO_x and *j*(NO₂) for the first 8 data sets in Table 1 are shown in Figs. 1 and 2. The HONO diurnal profiles typically show increasing mixing ratios after sunset due to HONO formation by heterogeneous reactions, direct emissions and the absence of photolytic loss processes, in addition to the decrease in boundary layer height (i.e. the mixing volume). Owing to its short lifetime of about 10–30 min and the increased vertical mixing, HONO decreases after sunrise, reaching its minimum levels during the afternoon. Influenced by relatively high nighttime values, 24 h average HONO levels range from about 0.1 to 5 ppbv (see Table

- ²⁰ nighttime values, 24 h average HONO levels range from about 0.1 to 5 ppbv (see Table 1). Average daytime HONO mixing ratio range from about 3.25 ppbv in Santiago de Chile (winter) to about 0.03 ppbv during the DOMINO campaign in Southern Spain (autumn). Daytime HONO/NO_x ratios range from about 0.01 during the MCMA-2006 to about 0.05 during the Santiago_S with average and median values of about 0.02
- for all campaigns. The very low values of the HONO/NO_x ratio during MCMA-2006 in comparison to the other campaigns is partly due to the different spatial measurement of HONO by LP-DOAS (Long-Path Differential Optical Absorption Spectroscopy) and NO_x by a local standard instrument (see also Sect. 3.2.2).



Average diurnal profiles of gradient HONO measurements in Santiago de Chile at 6 and 53 m altitude are shown in Fig. 2. The diurnal profiles show a clear vertical gradient with HONO mixing ratios at 53 m of about 60 % of those at 6 m during daytime. Similar HONO gradient were observed previously in the Mexico City metropolitan area during the MCMA-2003 at 70 and 16 m altitude (Volkamer et al., 2010). Both NO and NO₂ 5 show similar gradients while O₃ increases with height owing to the inter-conversion of NO/NO₂ through reactions of NO (emitted at ground level) with RO₂ and HO₂ (Villena et al., 2011). Due to the stronger absolute gradient of NO₂, HONO/NO₂ ratios show an opposite strong gradient during daytime while HONO/NOx ratios appear to be almost unaffected. Similarly, Kleffmann (2007) also showed that the HONO/NO_x ratio 10 decreases only little with altitude from about 2.5% at 10 m to about 2% at 190 m. The photolysis of HONO releasing OH and NO, enhances photochemical oxidation processes, which subsequently catalytically convert NO into NO₂ which in turn photolyses to form O_3 . Consequently, the relative change of HONO as a result of its photolysis is also reflected in the O_3 and NO_x levels resulting in a nearly constant HONO/NO_x 15 ratio. Therefore, the HONO/NO₂ ratio may be considered a good measure of HONO during the night (see also Sörgel et al., 2011b) while during daytime the HONO/NO_x ratio seems to be more suited (see Sect. 3.3).

3 Results and discussion

20 3.1 Average HONO/NO_x ratio

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To obtain an overview of measured HONO/NO_x ratios, daytime and 24 h average mixing ratios of HONO and NO_x based on all available data sets are plotted in Fig. 3. A high correlation ($R^2 = 0.87$) is obtained between HONO and NO_x during daytime with a linear regression slope of 0.02 ± 0.002 (Fig. 3, upper panel). Similarly, a high correlation ($R^2 = 0.90$) is obtained for the 24 h average values with a linear regression slope of 0.02 ± 0.001. However, for the DOMINO, BERLIOZ, HOxCOMP, PRIDE-PRD2006



(Back Garden), Yufa and Kathmandu campaigns, a slightly different regression slope of 0.05 (\pm 0.004) was found (Fig. 3, lower panel). This is likely due to the relatively high NO_2/NO_x ratio during these campaigns (see Table 1), especially during night when the influence of direct NO emissions in these regions is small. These measurement campaigns were characterised by a high NO morning peak, decreasing to less than 5 1 ppbv during the rest of the day due to a change in wind direction as mentioned in the respective references (Sörgel et al., 2011a; Alicke et al., 2003; Elshorbany et al., 2012; Li et al., 2012; Yu et al., 2009, respectively, except for the Yufa campaign, for which the data were obtained from Li et al. (2012)). The higher NO₂ fraction during the night leads to higher HONO via its heterogeneous formation in the dark, resulting 10 in higher HONO/NO, ratios compared to other measurement campaigns. This influence is less pronounced during daytime as the NO₂/NO_x ratios for all campaigns are much closer (see Table 1). Since HONO photolysis only influences HO_x, O₃ and other oxidants during daytime, the HONO/NO_x regression slope of 0.02 ± 0.001 determined above appears to be representative and may be used to investigate the impact on HO_v 15 and oxidant chemistry. Detailed analyses of the factors controlling the HONO diurnal profile as a function of NO_x are presented in the next section.

3.2 HONO diurnal profile

To determine the factors controlling the HONO mixing ratio as a function of NO_x, the aforementioned 8 field measurement data sets (HOxComp, Santiago_S, Santiago_W, Santiago_3, Santiago_21, DOMINO, MCMA-2006 and New York) have been investigated. During the first 6 measurement campaigns, HONO was measured by the sensitive LOPAP (Long Path Absorption Photometer) technique (Heland et al., 2001; Kleffmann et al., 2002). During MCMA-2006, HONO was measured using LP-DOAS (Dussanter et al., 2009 and references therein), while during the New York campaign HONO was measured by aqueous-phase scrubbing and HPLC analysis (Ren et al., 2003 and references therein). To analyse the factors influencing the HONO diurnal profile, we distinguish 4 time sectors, midnight to sunrise (sector A), sunrise to mid-noon (sector)



B), mid-noon to sunset (sector C) and from sunset to midnight (sector D), grouped into two main sectors, nighttime (A and D) and daytime (B and C). The onset of sunrise and sunset is defined at 30 % of the maximum measured $j(NO_2)$ values. The duration of each sector period varies based on the $j(NO_2)$ values measured in each study. The obtained linear regression expression is then used to calculate HONO mixing ratios in each sector in terms of NO_x and the other related parameters.

3.2.1 Nighttime HONO levels

In contrast to daytime HONO levels, which are generally higher than expected based on model calculations (e.g., Kleffmann et al., 2005; Acker et al., 2006; Li et al., 2010; Sörgel et al., 2011a; Su et al., 2011; Elshorbany et al., 2012), HONO concentrations 10 during nighttime can be largely explained by known sources, i.e., the heterogeneous reaction on humid surfaces (Alicke et al., 2002) and direct emissions (Vogel et al., 2003). All measurement campaigns are included in this analysis except MCMA-2006, for which no nighttime HONO data are available. Though the correlation between HONO and NO_x during both night sectors, A and D, reveal a similar slope of about 15 0.02 (see Fig. 4), the HONO/NO_x ratio itself is found to to be logarithmically related to NO_x, which can be explained by the nighttime heterogeneous formation of HONO (Kleffmann et al., 2003). This is confirmed by the HONO/NO_x dependency on wind speed (ws) (see Fig. 4). In addition, the slope of the HONO/NO, ratio versus NO, was found to be about two times higher in sector A compared to sector D (see Fig. 4), 20

resulting in the following two regression equations:

 $[HONO]A = ((-0.011 \pm 0.002) \ln([NO_x]) + (0.078 \pm 0.009)) \times [NO_x]$ [HONO]D = ((-0.005 \pm 0.001) \ln([NO_x]) + (0.043 \pm 0.004)) \times [NO_x]

Similarly, anti-correlation between HONO/NO_x ratio and NO_x was previously reported (Sörgel et al., 2011b). Again, for the correlation between HONO/NO_x ratio and ws, the slope in sector A is higher than that in sector D, albeit with a higher correlation coefficient in sector D (see Fig. 4). Nevertheless, as shown in Fig. 5, simulated HONO



(1)

(2)

using Eqs. (1) and (2) (sector A and D, respectively) is only improved for measurement campaigns with a nighttime HONO/NO_x ratio > 0.02, i.e., HOxComp, Santiago_S and DOMINO, compared to that using the mean HONO/NO_x ratio of 0.02, while for other campaigns, measured HONO was reasonably well simulated based on the mean HONO/NO_x ratio of 0.02.

3.2.2 Daytime HONO mixing ratio

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During daytime, a similar regression slope of 0.02 ± 0.002 between measured HONO and NO_x mixing ratio was obtained for all measurement campaigns (see Fig. 6), albeit with a lower correlation coefficient in comparison to nighttime values, which is mainly due to the low correlation between HONO and NO_x during the afternoon (sector C, see below). However, in contrast to nighttime, the HONO/NO_x ratio during daytime is independent of HONO and NO_x mixing ratios while it has a light dependency (given by $j(NO_2)$, though with a low correlation coefficient ($R^2 = 0.23$). These results are in agreement with Zhang et al. (2012), who showed that the daytime HONO flux does not

- ¹⁵ correlate significantly with measured NO_x mixing ratios, suggesting that under these conditions NO_x is not an important precursor of HONO daytime formation. In addition, using the Community Multiscale Air Quality (CMAQ) model, Czader et al. (2012) demonstrated that photochemical HONO formation can be a strong source during daytime, which directly impacts HO_x and ozone levels.
- ²⁰ During daytime, HONO mixing ratios are controlled by the photostationary state concentration of HONO, [HONO]pss, calculated from the known gas phase chemistry by the following equation:

[HONO]pss=
$$\frac{k_{OH+NO}[OH][NO]}{j(HONO) + k_{OH+HONO}[OH]}$$

plus other sources that are not known or not accounted for, henceforth denoted as "unidentified". Owing to their negligible contributions during daytime, heterogeneous formation of HONO and its deposition on the ground (e.g., Elshorbany et al., 2009;



(3)

Sörgel et al., 2011a) are ignored. Given the reported low HONO/NO_x ratio of 0.3–0.8% for directly emitted HONO estimated at a NO/NO_x ratio of > 0.9 (Kurtenbach et al., 2001), and considering the variable low NO/NO_x ratios (0.2 to 0.6) and the much higher measured HONO/NO_x ratios for the investigated campaigns, emitted HONO contributions are not expected to contribute significantly to measured HONO levels (Su

- ⁵ contributions are not expected to contribute significantly to measured HONO levels (Su et al., 2008) during the investigated campaigns and are therefore not considered in the following calculation. For the estimation of [HONO]pss the OH concentration and the HONO photolysis frequency (j(HONO)) in addition to measurements of NO and HONO mixing ratios are required, which were available only for four measurement campaigns,
- HOxComp, Santiago_S, Santiago_W and DOMINO. For all campaigns [HONO]pss was calculated using the IUPAC recommendations (Atkinson et al., 2004). During daytime [HONO]pss constituted 29, 72, 55 and 50% of measured HONO levels during HOx-Comp, Santiago_S, Santiago_W and DOMINO, respectively. Unidentified HONO mixing ratios were calculated by subtracting the calculated [HONO]pss from the measured HONO mixing ratios. The largest contributions of [HONO]pss are typically obtained
- during the early morning (sector B, from sunrise to mid-noon) reaching a maximum during the rush hour.

As shown in Fig. 7, high correlations were obtained between average HONO, [HONO]pss and unidentified HONO mixing ratios versus NO_x levels for the investigated ²⁰ measurement campaigns during both, sector B and daytime (sectors B + C). However, the regression slopes for the measured HONO and unidentified HONO levels versus NO_x were higher during daytime in comparison to that of sector B, showing that unidentified sources contribute most during the afternoon, again in good agreement with previous studies, which showed that the high afternoon HONO/NO_x ratio points towards

an unknown HONO daytime sources (e.g., Kleffmann et al., 2005; Elshorbany et al., 2009a, 2010b, 2012). Consequently, a higher correlation coefficient was obtained for the relationship between HONO, [HONO]pss and NO_x during sector B in comparison to the average daytime values. In contrast, for [HONO]pss, similar slopes were obtained during daytime as well as sector B, implying similar average contributions (i.e.,



of [HONO]pss to HONO measured mixing ratios) during both sectors, B and C. For sector B, the following linear regression expressions were obtained:

 $[HONO]pss = (0.014 \pm 0.001) \times [NO_x]$ $[HONO]B = (0.021 \pm 0.001) \times [NO_x]$

- As shown in Fig. 5, HONO mixing ratios in sector B calculated by Eq. (5) and by the global mean of 0.02 are similar and in very good agreement with that measured, related to the similar slope of HONO/NO_x in sector B and the mean HONO/NO_x ratio of 0.02, except for Santiago_3, Santiago_21 and MCMA-2006. In fact, measured HONO during sector B for Santiago_21 and Santiago_3 could have been accurately simulated based
- on Eq. (4) alone, which shows that measured HONO during sector B in these data sets can be largely explained by [HONO]pss. However, for consistency we used Eq. (5) for sector B in all data sets. For MCMA-2006, the overestimation of HONO mixing ratios in sector B is due to the very high measured NO_x mixing ratio, which is not related to that of HONO (see below).
- The noon to sunset time period (sector C) is the most important one in the HONO diurnal profile, during which unidentified daytime HONO sources contribute most significantly. The linear regression analysis for this time period was found to result in two different slopes as shown in Fig. 8 (middle panel). For measurement campaigns with a HONO/NO_x ratio of ≤ 0.02 , i.e., DOMINO, Santiago_3, Santiago_21, New York and
- ²⁰ MCMA-2006, a high correlation is obtained with a regression slope of 0.017 ± 0.003, while measurement campaigns with a HONO/NO_x ratio > 0.02, i.e., HOxComp, Santiago_S, Santiago_W indicate a regression slope of 0.042 ± 0.01 (Fig. 8, middle panel). The regression slope for measurement campaigns with HONO/NO_x ratios \leq 0.02 is quite comparable to that of [HONO]pss vs. NO_x (see Fig. 7), which shows that HONO
- ²⁵ mixing ratios during this time period for these measurement campaigns can be described accurately by [HONO]pss, with an additional small contribution from unidentified sources. Interestingly, a very high correlation ($R^2 = 0.99$) between the HONO/NO_x ratio and *j*(NO₂) has been obtained only for measurement campaigns with HONO/NO_x



(4)

(5)

ratios > 0.02 (see Fig. 8), from which HONO mixing ratios during sector C can be calculated as:

 $[HONO]C = (9.42 \pm 0.16) \times j(NO_2) \times [NO_x]$

For those with a HONO/NO_x ratio ≤ 0.02 , a much worse correlation ($R^2 = 0.44$), even with a negative slope was obtained. Consequently, for measurement campaigns with HONO/NO_x ratios > 0.02, calculated HONO mixing ratios based on the above Eq. (6) match the measurements well (see Fig. 5), while for those with a HONO/NO_x ratio ≤ 0.02 , measured HONO mixing ratios are better simulated using the average of 0.02. One potential explanation for this different $j(NO_2)$ dependency is that for measurement campaigns with a HONO/NO_x ratio ≤ 0.02 , unknown daytime HONO sources that are $j(NO_2)$ dependent do not contribute significantly to the measured HONO mixing ratios. Indeed, for two of these measurement campaigns, DOMINO and New York, unidentified daytime HONO source strengths of about 100 and 150 pptvh⁻¹, respectively were reported, which is very low compared to that of about 0.33, 1.7 and 2.5 ppbvh⁻¹ for HOxComp, Santiago_S and Santiago_W, respectively. Similarly, the unknown source

- HOxComp, Santiago_S and Santiago_W, respectively. Similarly, the unknown source strengths for other campaigns reported in the literature are also in the range of 200– 500 pptv h⁻¹, 500 pptv h⁻¹ and up to 2 ppbv h⁻¹ calculated for rural, semi-urban and urban conditions, respectively (Kleffmann et al., 2007). For MCMA-2006, an additional daytime HONO source was reported (Dusanter et al., 2009) despite the low average
- ²⁰ daytime HONO/NO_x ratio of about 0.01. However, as mentioned above (Sect. 2.2), this is due to the different spatial account of HONO and NO_x (i.e., measuring different air masses of HONO and NO_x). During MCMA-2006 HONO was measured using an LP-DOAS system over an optical path length of 5285 m while NO_x was measured using a local commercial standard instrument, which is known to be affected by inter-
- ²⁵ ferences from other NO_y components (e.g., HNO₃, PAN, RNO₃, etc.). Therefore, the low HONO/NO_x ratio of 0.01 is likely to be caused by higher measured NO_x levels in different air masses. Unfortunately, no strict method or correlation could be found to predict the HONO/NO_x ratio (i.e., > 0.02 or \leq 0.02). Therefore the different dependency



(6)

of HONO/NO_x on $j(NO_2)$ can only be used as an indicator of the presence of significant unknown HONO sources, rather than to predict the HONO concentration.

3.2.3 Unidentified HONO sources

The contribution of unidentified HONO sources to measured HONO during the afternoon (sector C, from noon to sunset) was largest during HOxComp (~ 91 %) followed by Santiago_W (~ 69 %) and Santiago_S (~ 25 %). As shown in Fig. 9, high correlations are obtained between unidentified HONO mixing ratios and their derived source strength (ppb h⁻¹) with *j*(NO₂), *j*(O¹D) and temperature for sector C. The good agreement for both *j*(NO₂) and *j*(O¹D) relates to the onsets of sunrise and sunset being defined at 30 % of the maximum *j*(NO₂) values, when the *j*(O¹D) values correspond to about 10 % of their daytime maximum. This method allows investigating the dependency of unidentified daytime HONO sources on both, *j*(NO₂) and *j*(O¹D). In previous studies (e.g., Elshorbany et al., 2009a, 2012), better agreement was obtained for the correlation between unidentified HONO sources and *j*(NO₂) in comparison to *j*(O¹D)
by considering the full photolysis frequency range of these photolysis rates, and the latter produces an intercept due to the smaller span of *j*(O¹D). However, the good

- correlation between unidentified HONO sources (see Fig. 9) and temperature (in addition to $j(NO_2)$ and $j(O^1D)$) implies that photolytic sources active at longer wavelengths (e.g., photosensitized conversion of NO₂ on organic surfaces, Stemmler et al., 2006)
- or photolysis of nitro aromatic compounds (Bejan et al., 2006) or those that are *j*(O¹D) dependent, e.g., the photolysis of HNO₃ (Zhou et al., 2003, 2011) or those that are temperature dependent (Su et al., 2011), are all of significance. Despite that these results leave the question of unknown HONO daytime sources open, they offer linear regression equations that can be used as an indicator for unknown HONO production
 within the range of conditions investigated (i.e., at a HONO/NO_x ratio > 0.02).
 - Interestingly, the unidentified HONO sources were found to correlate inversely with $j(NO_2)$, $j(O^1D)$ and temperature (see Fig. 9), which is not surprising. Veitel (2002)



showed that nocturnal HONO mixing ratios directly correlate to radon, especially in winter. He also measured the highest HONO mixing ratios of 2.4 ppb at night in January (1999) coinciding with very high radon levels. Thus, Veitel (2002) concluded that surfaces at or near the ground form the most prominent HONO source both by day and night. Similarly, Febo et al. (1999) stated that especially trace gases emitted or formed near the ground show a direct and strong correlation with radon. The correlations in Fig. 9 are also quite interesting because they show that unidentified HONO sources during afternoon can be directly calculated as a function of $j(NO_2)$ or $j(O^1D)$ (also vs.

temperature but with less accuracy) as follows:

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¹⁰ Unidentified HONO (ppbv h⁻¹) =
$$(-838 \pm 360)j(NO_2) + (6.65 \pm 2.15)$$
, (7)
Unidentified HONO (ppbv h⁻¹) = $(-1.78 \pm 0.94) \times 10^5 j(O^1 D)$ (8)

Indeed, considering an estimated daytime average $j(NO_2)$ for Xinken, China (PRIDE_PRD2004) and Back Garden, China (PRIDE-PRD2006) of about 0.005 and 0.007 s⁻¹, the approximate unidentified HONO source strength based on the relation-

¹⁵ ship Eq. (7) would be about 2.5 ± 1.1 and 0.78 ± 0.34 ppb h⁻¹, respectively which is in good agreement with those reported by Li et al. (2012). Nevertheless, since the above correlations were derived based on a limited number of measurement campaigns, further evaluation is required.

3.2.4 Measured vs. simulated HONO levels

- Figure 10 shows the correlations between measured and simulated HONO mixing ratios based on Eqs. (1) to (6) and the mean HONO/NO_x ratio of 0.02 for all investigated measurement campaigns. It appears that measured HONO diurnal profiles for all campaigns can be simulated quite well for both 24 h and daytime averages with a linear measured/simulated regression slope of 1.10 ± 0.05 and 0.91 ± 0.07 , respectively.
- tively. Similar agreement is also obtained between measured and calculated HONO mixing ratios using the mean HONO/NO_x ratios of 0.02 with slopes of 1.02 ± 0.05 and 1.06 ± 0.13 , respectively, albeit with lower correlation coefficients, which is due to the



underestimation of measured HONO mixing ratios during the afternoon for measurement campaigns with HONO/NO_x ratios > 0.02 (see Sect. 3.2.2). This can only be accounted for by Eq. (6). However, the calculation of afternoon HONO mixing ratios using Eq. (6) requires the prior knowledge of the HONO/NO_x ratio (see Sect. 3.2.2), which s is not feasible for a prognostic method. In addition, during daytime the slope of the re-

⁵ Is not feasible for a prognostic method. In addition, during daytime the slope of the relationship between HONO and NO_x for all measurement campaigns is 0.022 ± 0.002 , which is quite similar to the overall mean HONO/NO_x ratio. Therefore, the overall mean HONO/NO_x ratio of 0.02 is considered to be most suitable to approximate the HONO mixing ratios and investigate the global impact of HONO photolysis during daytime on HO_x and O₃ chemistry.

3.3 Global impact

In global models HONO is typically simulated based on the known gas phase chemistry, thus only accounting for [HONO]pss (see Sect. 3.2.2) rather than observed HONO, thus significantly underestimating ambient concentrations. Consequently, HO_x ,

- $_{15}$ O₃ and other secondary oxidation products from HONO photolysis during daytime are also expected to be significantly underestimated. Since most polluted regions with high NO_x levels are located in the Northern Hemisphere, the impact of using more realistic HONO levels should be most pronounced in this part of the world, where NO levels are often sufficient for efficient radical recycling (Lelieveld et al., 2002; Elshorbany et al.,
- ²⁰ 2010b). To investigate the impacts by HONO photolysis, including the seasonal dependency, we focus on model output for the months June and December. The global mean HONO/NO_x ratio of 0.02, empirically derived from the correlation between HONO and NO_x has been implemented in the EMAC model. In addition, the sensitivity runs S1 and S3 apply differences by a factor of two, thus using a HONO/NO_x ratios of 0.01 and 25 0.04, respectively.

As shown in Fig. 11, simulated HONO levels based on a HONO/NO_x ratio of 0.02 (S2) are typically more than order of magnitude higher than those simulated by the base run, which considers only gas phase HONO formation (i.e., $OH + NO \rightarrow HONO$).



These results are in agreement with Li et al. (2010), Zhang et al. (2011) and Czader et al. (2012) who showed that measured HONO mixing ratios are about tenfold of those calculated when this reaction is the only formation mechanism. The simulated HONO levels in the S2 run in December are higher than those during June, which is also

- ⁵ good agreement with previous studies, showing that HONO levels in winter are higher than in summer (e.g., Elshorbany et al., 2010a). The simulated HONO levels in June in South Korea and in December in East China compare well to those measured during May–July 2005 in Seoul (Korea) and during October–January 2004/2005 in Shanghai (China) (Li et al., 2012, and references therein).
- Figure 12 shows that the shape of the simulated diurnal HONO profile on 10 July, 2005, in North-West Germany (50.93° N, 6.36° E) using the base model, differs strongly from the observations during the HOxComp and other campaigns presented in Fig. 1. Owing to the coarse spatial resolution of the model the profiles in Fig. 12 represent larger areas than the measurements, though the agreement is rather good, probably
- ¹⁵ indicating that HOxComp is representative of this area. In contrast to the base scenario, the shape of the simulated HONO diurnal profiles, S1, S2 and S3 based on the HONO/NO_x ratios of 0.01, 0.02 and 0.04, respectively match the measurements much better with maximum HONO mixing ratios during the early morning and minimum values during afternoon. The simulated HONO by the S2 run (based on a HONO/NO_x ratio
- of 0.02) agrees best with the measurements. These results corroborate our earlier conclusion that simulating HONO based on a mean HONO/NO_x ratio of 0.02 provides a realistic representation of HONO, rather than considering only the gas phase formation of HONO. Therefore, the S2 run is used hereafter to investigate the impact of implementing this more realistic HONO profile. As also shown in Fig. 12, enhancements in
- OH, HO₂, O₃, PAN, H₂O₂, NO_x and HNO₃ are calculated only at NO levels of about 1 ppbv (marked by the dashed line in the diurnal NO profile). When NO levels are below 1 ppbv, enhancements are typically small or negligible. This is due to the low recycling efficiency (under NO sensitive conditions), under which any increase in the OH levels as a result of HONO photolysis does not lead to a significant increase in the HO₂ levels



from reaction (RO₂ + NO \rightarrow HO₂) or H₂O₂ from the reaction of (HO₂ + HO₂ \rightarrow H₂O₂) or O₃ from the reaction of (RO₂/HO₂ + NO \rightarrow O₃). These results show that an increase in the HO_x levels as well as in the secondary oxidation products only occurs under conditions of efficient recycling of OH through RO₂/HO₂, in agreement with the sensitivity analysis performed for HOxComp (Elshorbany et al., 2012). The enhancement of HO_x as a result of applying higher HONO values also leads to a redistribution of model calculated reactive nitrogen compounds. For example, the increased levels of OH, HO₂ and other secondary oxidation products (e.g., acyl peroxy radicals (RC(O)O₂)) may reduce NO₂ (e.g., OH + NO₂ \rightarrow HNO₃, RC(O)O₂ + NO₂ \rightarrow PAN) and NO (e.g., HO₂ + NO \rightarrow OH + NO₂) forming HNO₃ and PAN. As shown in Fig. 12, the additional daytime HONO leads to a decrease in NO and NO₂, while HNO₃ and PAN increase during the high NO_x period. During daytime (6:00 – 18:00 UTC), NO, NO₂, OH, HO₂, O₃, PAN, H₂O₂ and HNO₃ change by –19, –9, 36, 45, 10, 26, 2 and 19 %, respectively

in the S2 run compared to the base model, in agreement with previous studies (e.g., Li

¹⁵ et al., 2011).

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To further investigate the impact of the more realistic HONO levels in relatively polluted areas (high-NO_x, VOC-limited conditions), Fig. 13 compares the simulated diurnal profiles in the Eastern USA and downwind on 1 June 2005. It appears that the shape of the simulated diurnal HONO profiles from the runs S1, S2 and S3 match very well those measured in field campaigns (see Fig. 1), in contrast to that simulated using the base scenario. As shown in Fig. 13, significant increases in HO_x and the secondary oxidation products result from the more realistic HONO levels (simulated by S2). Unfortunately, no HONO field measurements are available for comparison in this area for 2005. The simulated maximum O₃ levels (S2) agree with the reported levels in New

²⁵ York State in 2005 (New York State Department of Environmental Conservation). Similar to the HOxComp case, NO and NO₂ decrease while HO_x, O₃, PAN, H₂O₂ and HNO₃ increase, with higher relative enhancements compared to HOxComp, owing to the relatively high NO_x conditions during daytime (see Fig. 13).



These results underscore that the more realistic representation of HONO in a global model leads to an enhancement in simulated HO_x and oxidation products, predominantly under high NO_x conditions.

- Figures 14 and 15 show the absolute and relative enhancements, respectively, in
 OH and O₃ together with simulated NO levels. As shown in Fig. 14, in the relatively polluted Northern Hemisphere average monthly NO mixing ratios in December are typically two times higher than in June. In addition, in June NO levels are relatively high in the Northeastern USA and in Northern Europe, e.g., in comparison to Eastern China. Consequently, the enhancements of OH and O₃ levels are relatively strong in these high-NO_x regions. Also, over Eastern China in December where NO levels are
- higher than in the USA and Europe, the enhancements of OH and O_3 levels are larger. In addition, the relative enhancements of OH and O_3 are significantly higher in the winter hemispheres compared to summer (see Fig. 15). Similarly, previous studies showed that the impact of HONO photolysis on OH is higher in winter than in summer
- ¹⁵ (Aumont, 2003; Elshorbany et al., 2010a), owing to the relatively minor importance of the other photochemical sources such as O_3 and HCHO (Elshorbany et al., 2010b), in addition to the higher NO levels in winter. Thus, the increased HONO levels in the model significantly enhance the oxidation capacity in polluted regions, especially in winter, when other photolytic OH sources are of minor importance.
- Figures 16 and 17 show some details of the model calculated enhancement in OH, O_3 , NO_x , HNO_3 and PAN over the Eastern USA in June and Eastern China in December, together with the NO mixing ratios (top panels in Fig. 16). It is evident that the relative enhancements in these species follow the relative changes in NO. In these high- NO_x regions, monthly average OH enhancements up to about 1.5×10^6 and
- $_{25}$ 0.6 × 10⁶ mol cm⁻³ are calculated for June and December 2005, respectively, while O₃ is calculated to increase up to 12 and 8.5 ppbv, respectively. These increases are highly significant, corresponding to relative OH and O₃ enhancements of about 80 and 30 % in June and about 90 and 40 % in December, respectively. These results are quite similar to those of previous studies for specific locations applying local models. For



example, model simulations of daytime HONO in Mexico City, which could only achieve about 30–50 % of the observed HONO, indicate an average midday O_3 enhancement of 6 ppbv (Li et al., 2010). Similarly, Li et al. (2011) reported an average O_3 enhancement of 12 ppbv (~50%) compared to the base case considering only gas phase HONO

- ⁵ formation. These results are also in good agreement with Elshorbany et al. (2009b) who compared box model calculations constrained by measured HONO to those only considering OH + NO → HONO. In the latter case, O₃ levels decreased on average by 30 % during daytime. Similarly, Harris et al. (1982) and Clapp and Jenkin (2001), employing photochemical trajectory models, showed that HONO photolysis may have an
- ¹⁰ important impact on the level of oxidants mostly under polluted high-NO_x conditions. Jorba et al. (2012) also showed that O_3 levels are enhanced in response to additional OH production only in high-NO_x regions though can be decreased in regions with low-NO_x conditions.

These results illustrate that because of the buffering effect by NO_x the mean HONO/NO_x ratio is a reasonable proxy to simulate HONO levels in global models, thus avoiding severe underestimation of HONO concentrations, with consequences for simulated HO_x and secondary oxidation products. In the view of the many unknowns and uncertainties about daytime HONO sources, global models could apply this method until the chemistry of HONO is resolved in greater detail.

20 4 Conclusions

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HONO, NO_x and auxiliary atmospheric chemistry parameters have been investigated using data from 15 field measurement campaigns around the globe (from 52° N to 37° S and from 116° E to 99° W). The high correlation between HONO and NO_x in all data sets reveals a robust and consistent linear regression slope of 0.02 ± 0.002 . Our analysis indicates that, given the ambient NO_x mixing ratio, the HONO/NO_x ratio is a robust proxy of HONO mixing ratios both during night and daytime.



For nighttime conditions, we derive a linear regression slope of 0.02 ± 0.001 based on all investigated campaigns. The HONO/NO_x ratio itself was appear to have a logarithmic relationship with NO_x, which can be explained by the nighttime heterogenous formation of HONO. This is corroborated by the HONO/NO_x dependence on wind ⁵ speed. In addition, the regression slope of the HONO/NO_x ratio versus NO_x is different during both nighttime sectors A (midnight to sunrise) and D (sunset to midnight), from which the HONO concentration can be calculated as a function of NO_x levels.

During daytime, a similar regression slope of 0.02 ± 0.002 between measured HONO and NO_x mixing ratios is obtained for all investigated measurement campaigns. However, in contrast to nighttime conditions, the HONO/NO_x ratio is independent of HONO and NO_x mixing ratios, in agreement with previous studies. The correlations between [HONO]pss and NO_x during time sector B (sunrise to noon) as well as during daytime (time sectors B + C) reveal a similar correlation slope of 0.014, implying comparable contributions during both time sectors B and C. In contrast, the correlations between

- ¹⁵ unidentified HONO and NO_x mixing ratios during the time sector B reveal a regression slope of 0.007, much lower than the 0.011 obtained for daytime, implying higher contributions by unidentified sources during the afternoon, also in agreement with previous studies. In contrast to time sector B, the correlation between HONO and NO_x during sector C (noon to sunset) results in two different correlation slopes. For measurement
- ²⁰ campaigns with HONO/NO_x ratios ≤ 0.02 , a regression slope of 0.017 ± 0.003 is obtained, while measurement campaigns with HONO/NO_x ratios > 0.02 follow a regression slope of 0.042 ± 0.01 . These results imply that for conditions with HONO/NO_x ratios ≤ 0.02 , HONO mixing ratios during time sector C can be largely represented by [HONO]pss, with small additional contributions by unidentified sources. A very high cor-
- ²⁵ relation ($R^2 = 0.99$) between the HONO/NO_x ratio and $j(NO_2)$ is obtained only for conditions with a HONO/NO_x ratio > 0.02, while for those with HONO/NO_x ratios ≤ 0.02 , a much worse correlation ($R^2 = 0.44$), even a negative slope is obtained. A potential explanation for this different $j(NO_2)$ dependency is that during measurement campaigns



with HONO/NO_x ratios ≤ 0.02 , unknown daytime HONO sources that are $j(NO_2)$ dependent do not contribute significantly.

High correlations are also obtained between unidentified HONO and its source strength (ppb h⁻¹), and $j(NO_2)$, $j(O^1D)$ and temperature for time sector C (noon to sunset). These results imply that photolytic sources active at longer wavelengths or those that are $j(O^1D)$ dependent are of significance. In fact these results suggest that sources that are solely temperature dependent may also be important, as predicted by Su et al. (2011). Interestingly, we also find that unidentified HONO sources correlate inversely with $j(NO_2)$, $j(O^1D)$ and temperature, from which they can be estimated.

- ¹⁰ The mean HONO/NO_x ratio of 0.02, derived from all measurement campaigns investigated, has been implemented into the EMAC chemistry-climate model to calculate the global HONO distribution. Strong HONO enhancements are predicted relative to the base model, which only accounts for the gas phase reaction of OH with NO. Reasonable agreement is obtained between simulated and measured HONO mixing ratios
- ¹⁵ during both summer and winter. The simulated HONO mixing ratios appear to have a significant impact on HO_x , O_3 and other oxidants, however, predominantly under polluted high- NO_x conditions. Furthermore, the relative enhancements in OH and secondary products were higher in winter than in summer, thus enhancing the oxidation capacity in polluted regions, especially in winter, when the other photolytic OH sources
- ²⁰ are of minor importance. The results of the current study suggest that realistic HONO levels should be accounted for by global models and that simulated HO_x , O_3 and secondary oxidation products should be revised accordingly.

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Table 1. Summary of the field measurement data sets used.

campaign	location	global dimensions	measurements period	HON	O [ppbv]	NO ₂	[ppbv]	NOx	[ppbv]	reference
				24 h	daytime	24 h	daytime	24 h	daytime	
HOxComp	Jülich, Germany	50°54' N, 06°24' E	Jun–Jul 2005	0.22	0.12	4.26	2.89	4.79	3.66	Elshorbany et al. (2012)
Santiago_S	Santiago de Chile	33°26' S, 70°40' W	8–20 Mar 2005	2.39	1.90	23.84	18.53	80.63	49.73	Elshorbany et al. (2009)
Santiago_W	Santiago de Chile	33°26' S, 70°40' W	25 May–6 Jun 2005	5.17	3.25	48.33	69.59	262.72	140.22	Elshorbany et al. (2010b)
Santiago_3 (6 m)	Santiago de Chile	33°26' S, 70°40' W	Nov 2009	1.44	1.40	35.98	39.50	74.24	81.49	Villena et al. (2011)
Santiago_21 (53 m)	Santiago de Chile	33°26' S, 70°40' W	Nov 2009	1.00	0.85	31.01	31.93	46.82	49.80	
DOMINO	El Arenosillo, Spain	37°05' N, 06°44' W	Nov–Dec 2008	0.08	0.03	1.80	1.09	1.88	1.48	Sörgel et al. (2011)
PMTACS-NY	New York, USA	40°44' N, 73°49' W	Jul–Aug 2001	0.66	0.46	26.44	21.51	31.06	28.29	Ren et al. (2003)
MCMA-2006	New Mexico, USA	19°25' N, 99°8' W	14–31 Mar 2006	1.03	0.35	n/a	28.40	n/a	44.80	Dusanter et al. (2009)
LOOP/PIPAPO	Milan, Italy	45°32' N, 09°12' E	May–Jun 1998	0.53	0.14	25.75	18.30	70.45	23.40	Alicke et al. (2002)
NITROCAT	Rome, Italy	22°36' N, 113°35' E	May–Jun 2001	0.58	0.15	15.60	4.00	27.70	4.20	Acker et al. (2006)
PRIDE_PRD2004	Xinken, China	41°55' N, 12°30' E	13 Oct-2 Nov	1.05	0.80	32.40	30.00	38.90	40.00	Su et al. (2008)
Kathmandu	Kathmandu, Nepal	27°43' N, 85°21' E	Jan–Feb 2003	1.05	0.35	13.25	8.60	16.55	13.00	Yu et al. (2009)
BERLIOZ	Pabstthum, Geremany	52°51' N, 12°56' E	Jul–Aug 1998	0.20	0.07	3.25	3.60	3.95	4.60	Alicke et al. (2003)
Yufa	Yufa, China	39°30' N, 116°17' E	Jul–Aug 2006	0.66	0.43	11.10	8.00	13.85	9.40	Li et al. (2012)*
PRIDE-PRD2006	Back Garden, China	23°30' N, 113°1' E	Jun 2006	0.60	0.24	10.50	4.50	13.20	5.50	Li et al. (2012)

*no reference could be found and data were adopted from Li et al. (2012)



Fig. 1. Diurnal cycles of the HONO/NO_x ratio, HONO and $j(NO_2)$ observed in different field measurement campaigns. For abbreviations and references, see the text.





Fig. 2. Average diurnal cycles of HONO measurements at 6 and 53 m altitude in Santiago de Chile, 2009, adopted from Villena et al. (2011).











Fig. 4. Correlation of nighttime average HONO and NO_x mixing ratios as well as wind speed (ws) for sector A (right panel, from midnight to sunrise) and sector D (left panel, from sunset to midnight). Error bars represent 1 σ of the mean.





Fig. 5. Simulated diurnal HONO cycles based on the Eqs. (1) to (6) for the different sectors (simulated) and those based on the mean HONO/NO_x ratio of 0.02 (global mean), compared to measurements in different campaigns. Small spikes appear between sectors due to the different parameterizations applied.











Fig. 7. Correlation between HONO, [HONO]pss, unidentified HONO and NO_x during sector B (left, sunrise to 12:00 UTC) and during daytime (right, sunrise to sunset). Error bars represent 1σ of the mean.





Fig. 8. Correlations between average afternoon (sector C, mid-noon to sunset) HONO mixing ratios versus the corresponding NO_x and $j(NO_2)$ values observed in different measurement campaigns. Error bars represent 1σ of the mean.





Fig. 9. Correlation between unidentified HONO mixing ratios and their source strength versus $j(NO_2)$, $j(O^1D)$ and temperature observed in field measurement campaigns with a HONO/NO_x ratio of > 0.02. Error bars represent 1 σ of the mean.





Fig. 10. Correlations between measured and calculated HONO mixing ratios for 24 h (upper panel) and daytime averages (lower panel) based on the HONO/NO_x dependency (simulated, left panel, see text for details) and that calculated using the mean HONO/NO_x ratio of 0.02 (global mean, right panel) for the different measurement campaigns. Error bars represent 1 σ of the mean.





Fig. 11. Simulated monthly average HONO mixing ratio near the surface in ppbv for the base (upper panel) and S2 (lower panel) scenarios in June (left) and December (right).





Fig. 12. Simulated diurnal cycles for 10 July 2005, in Northwest Germany (50.93° N, 6.36° E) compared to the measured HONO diurnal profile during the HOxComp campaign near Jülich in Germany (50.91° N, 6.41° E, from Elshorbany et al., 2012).





Fig. 13. Simulated diurnal cycles in the Eastern USA (40.5° N, 73.1° W) on 1 June 2005.





Fig. 14. Simulated monthly average enhancement of OH (middle panel, 10⁶ mol cm⁻³) and ozone (lower panel, ppbv) near the surface, indicating the difference between the S2 and base scenarios as a function of NO (base scenario, upper panel, ppbv) in June (left panels) and December (right panels).





Fig. 15. Monthly average relative enhancements (in %) in OH (top panels) and ozone (lower panels) near the surface, indicating the difference between the S2 and base scenarios (relative to the latter) in June (left panels) and December (right panels).





Fig. 16. Simulated monthly average enhancement of OH (middle, 10^6 mol cm^{-3}) and O₃ (lower, ppbv) near the surface as a function of NO (base scenario, upper panels) in June over the Eastern USA (left panels) and December over Eastern China (right panels).







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