



Airborne remote sensing of nitrous acid in the troposphere: potential sources of excess HONO

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Abstract. The photolysis of nitrous acid (HONO) produces hydroxyl radicals (OH), the most important cleaning agent of the troposphere. For decades, HONO has been measured in concentrations which exceed the photo-stationary concentration arising from its gas phase formation via the reaction $\text{NO} + \text{OH}$ and destruction by photolysis. Several heterogeneous formation mechanisms as well as the photolysis of particulate nitrate have been proposed which may explain this excess HONO. This study reports on airborne remote sensing measurements of the mini-DOAS instrument over continental Europe, Southeast Asia, and the tropical Atlantic. The observations form a C-shaped profile in the troposphere with maximum volume mixing ratios of approximately 150 ppt in the planetary boundary layer, about 10 ppt in the free troposphere and up to 100 ppt in the tropical upper troposphere. These measurements of HONO throughout the troposphere exceed model predictions by up to an order of magnitude. Together with a host of other measured species and parameters, various formation mechanisms are explored to investigate in situ HONO sources. Although a precise formation mechanism in the polluted boundary layer remains elusive, the photolysis of particulate nitrate may explain excess HONO in the marine boundary layer. The excess HONO observed in the upper troposphere requires a gas phase source with a formation rate of up to 300 ppt h^{-1} . The possible role of peroxyxynitrous



acid (HOONO), formed by the reactions $\text{NO} + \text{HO}_2 + \text{M}$ and $\text{NO}_2 + \text{OH} + \text{M}$, and further oxidation by reactions with NO or O_3 , is explored.

15 1 Introduction

Since its discovery in the planetary boundary layer (PBL), the tropospheric sources and sinks of nitrous acid (HONO) have been a matter of intense debate (Perner and Platt, 1979). HONO is a key species in atmospheric photochemistry, in particular in the polluted environment, due to its effects on the formation of hydroxyl radicals (OH) and its potential to recycle reactive nitrogen (e.g., Perner and Platt (1979); Platt et al. (1980); Jacob (2000); Zhou et al. (2001); Alicke et al. (2003); Kleffmann et al. (2005); Acker et al. (2006); Zhang et al. (2009); Li et al. (2014); Ye et al. (2016a, 2017, 2018), and others). In the polluted boundary layer, the rate of production of OH from the photolysis of HONO may outpace OH production from the reaction of $\text{O}(^1\text{D})$ with H_2O , especially in the morning.

However, past studies — mainly performed at the ground — revealed much larger HONO volume mixing ratios (VMR) (up to some ppb) and source strengths (up to several ppb h^{-1}) than the well known gas phase formation reaction (R1), destruction by photolysis (R2), and reaction with the OH radical (R3) can explain (e.g., (Acker et al., 2006; Villena et al., 2011; Kleffmann et al., 2005; Wang et al., 2015; Tong et al., 2016), and others).



During the daytime, reactions R1 to R3 result in a photo-stationary state (PSS) from which the HONO concentration can be calculated:

$$[\text{HONO}]_{\text{PSS}} = \frac{k_{\text{R1}}[\text{NO}][\text{OH}]}{J_{\text{HONO}} + k_{\text{R3}}[\text{OH}]} \quad (1)$$

Daytime HONO measurements can then be compared to $[\text{HONO}]_{\text{PSS}}$ to quantify sources that exceed reaction R1 (further on called excess HONO). Since in near-surface measurements in the polluted environment reaction R1 was often found to be insufficient to explain measured HONO, a large set of homogeneous and heterogeneous reactions as well as the photolysis of particulate nitrate were investigated, mainly in laboratory studies, which are discussed in the following and tabulated in the appendix (see Table A1).



40 There is some consensus that in the polluted boundary layer and lower atmosphere, in addition to reaction R1, HONO is produced mainly by heterogeneous reactions involving NO_x on macroscopic surfaces (e.g., infrastructure and vegetation), and/or on the surface and/or in the bulk of atmospheric aerosols (e.g., Lammel and Cape (1996); Ammann et al. (1998); Reisinger (2000); Kleffmann et al. (2003); Monge et al. (2010); Ma et al. (2013b); Cheng et al. (2016); Tong et al. (2016); Lu et al. (2018), and many others). It has also been recognized that its production is greatly enhanced by the presence of organics
45 attached to surfaces and potentially within the aerosol when exposed to sunlight (e.g., George et al. (2005); Stemmler et al. (2006); Scharko et al. (2014); Wang et al. (2015); Laufs and Kleffmann (2016); Benedict et al. (2017); Ye et al. (2017), and others).

In addition, photolysis of HNO₃ adsorbed to surfaces, including those of vegetation (Zhou et al., 2003, 2007) and snowpack (Zhou et al., 2001), has also been suggested as a major source of daytime HONO in low-NO_x environments. Moreover,
50 different HONO sources in the topsoil have also recently been identified, which are mostly mediated by nitrate to nitrite reducing soil bacteria (e.g., Su et al. (2011); Oswald et al. (2013); Wu et al. (2019); Song et al. (2023b)). The photolysis of particulate nitrate has also been frequently discussed in the literature (Ye et al., 2016a; Reed et al., 2017; Andersen et al., 2023). These HONO formation mechanisms have been summarized in several review papers (Kleffmann, 2007; Ma et al., 2013a; Spataro and Ianniello, 2014; Wang et al., 2025).

55 In previous studies HONO in near surface air was typically investigated. There, the formation of HONO in the gas phase (reactions R1 to R3), by heterogeneous reactions on and within the aerosol, on macroscopic surfaces and within the topsoil occurs simultaneously and therefore are difficult to distinguish. To date only a few studies investigated the sources and sinks of HONO in air from the upper regions of the PBL and free troposphere. In this case, the sources of HONO from the ground heterogeneous inorganic chemistry, from the soil and macroscopic surfaces can largely be excluded, at least during the day
60 because the HONO lifetime of approximately 10 minutes (Eq. R2 and Eq. R3) is significantly shorter than the timescale for vertical transport from the surface (e.g., Ye et al. (2018)).

Previous airborne studies of HONO include those of Zhang et al. (2009); Li et al. (2014); Neuman et al. (2016); Ye et al. (2016b, 2018) and Andersen et al. (2023). In airborne investigations, the techniques most commonly used to measure HONO are wet chemical techniques such as long-path absorption photometry (e.g., by Li et al. (2014); Ye et al. (2016b, 2018))
65 and high performance liquid chromatography (described by Huang et al. (2002); Zhang et al. (2009)). Recently, chemical ionization mass spectrometry (CIMS) (e.g. Neuman et al. (2016)) and differential optical absorption spectroscopy (DOAS) (e.g. Heue et al. (2014) and this study) measurements have also been employed in airborne HONO studies. Each technique has specific strengths and weaknesses, but nevertheless recent comparisons indicated a reasonable agreement among the different instruments and retrieval techniques used for the detection of HONO, at least for large HONO VMRs (in the ppb range) such
70 as those met in polluted environments (Wang et al., 2017; Crilley et al., 2019).

Despite decades of research, the mechanism and rate of formation of HONO in the atmosphere remains poorly quantified. This study reports measurements of HONO in different regions and at different altitudes in the troposphere and aims to reconcile the observed HONO with the potential HONO formation mechanisms. Airborne measurements of a variety of precursors of HONO and aerosols were also made. Due to the short photolytic lifetime of HONO in the atmosphere, airborne



75 observations should not be strongly influenced by HONO emissions from or near the surface. Consequently, we assume
that these sources are negligible for our study performed in the upper part of the boundary layer, and in the free and upper
troposphere. HONO found there needs to be produced in-situ rather transported from elsewhere. An overview of previously
proposed HONO formation mechanisms potentially relevant for the present study (i.e. excluding ground processes) is given
in Table A1. Some mechanisms (in particular the Mechanisms 1, 2, 3, 4, and 6) have been shown to be insufficient to explain
80 daytime observations of HONO (for details see the comments at the bottom of Table A1).

This study investigates the presence and potential formation mechanisms of HONO throughout the troposphere in different
photochemical environments over Europe, East Asia, and the tropical Atlantic. Using an airborne DOAS instrument (Hüneke
et al., 2017; Stutz et al., 2017), remote sensing measurements of nitrous acid, formaldehyde, and nitrogen dioxide are reported
from 25 scientific flights of the high altitude and long range research aircraft HALO (operated by the German Aerospace
85 Center (DLR)). DOAS measurements are complemented by simultaneous in situ measurements of photochemically related
trace gases, as well as measurements of relevant atmospheric parameters performed by other instruments on board the HALO
aircraft. For the research missions, EMeRGe (2017/2018) and CAFE-Africa (2018), EMAC (ECHAM/MESSy Atmospheric
Chemistry) and MECO(n) (MESSy-fied ECHAM and COSMO) model data is also available for comparison.

The paper is structured as follows: In Sect. 2, we provide some information on how HONO and other UV/Vis absorbing
90 species are measured. Section 3 describes the measurements, Sect. 4 contextualizes those measurements within three regimes
of the troposphere, and Sect. 5 concludes the study.

2 Methods

This study employs measurements of several instruments operated on board the HALO aircraft, including the remote sensing
mini-DOAS instrument, and in situ instruments. It also utilizes simulations of the EMAC and MECO(n) models for comparison
95 and interpretation.

2.1 The mini-DOAS instrument

The mini-DOAS instrument records scattered skylight in the ultraviolet/visible/near-infrared wavelength ranges in nadir and
limb direction (Stutz et al., 2017; Hüneke et al., 2017; Werner et al., 2017; Rotermund et al., 2021; Kluge et al., 2020, 2023).
Here, solely the data collected in limb direction (telescope elevation angle 0°) are reported.

100 The interpretation of air-borne mini-DOAS observations requires the DOAS analysis of the measured skylight spectra, ra-
diative transfer modeling of the observation conditions with a Monte Carlo model such as McArtim (Deutschmann et al.,
2011), and the conversion of inferred differential slant column densities (dSCDs) retrieved with the DOAS technique into
VMRs using the scaling method (Stutz et al., 2017; Hüneke et al., 2017). In this study, the focus is on limb geometry
measurements of NO_2 , HCHO and HONO, which were performed during 25 scientific flights of the EMeRGe (e.g. https://acp.copernicus.org/articles/special_issue1074.html, Andrés Hernández et al. (2022); Lin et al. (2023); Förster et al. (2023))
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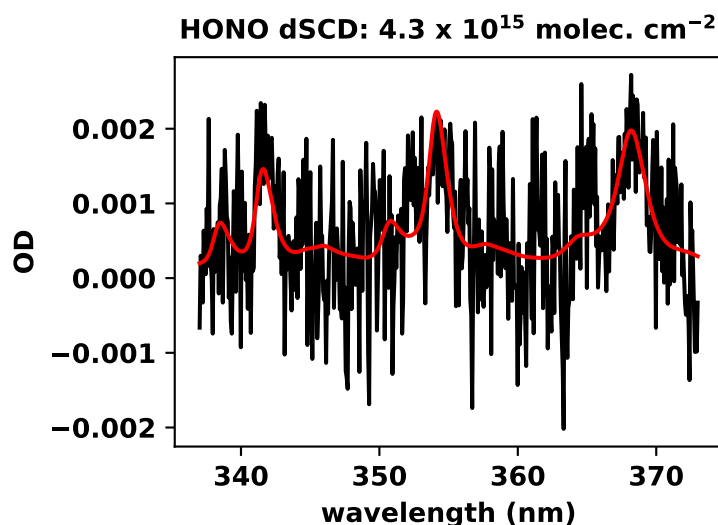


Figure 1. Example of a HONO spectral retrieval in the UV-A wavelength range for a limb spectrum recorded at 14 km altitude, at 17:17 on the 24th of August, 2018 (i.e. during the CAFE-Africa campaign). Optical depth (OD) shown as a function of wavelength. The scaled absorption cross-section of HONO is plotted in red; the fit including the residual is plotted in black. The differential slant column density (dSCD) is the quotient of the OD and the absorption cross-section.

and CAFE-Africa (e.g. Tadic et al. (2021); Nussbaumer et al. (2021b); Hamryszczak et al. (2023)) missions during 2017 and 2018.

2.1.1 HONO retrievals

HONO is retrieved in the UV-A range 337–373 nm according to the recommendations by Wang et al. (2017, 2019), with slight
 110 modifications. For example, the Taylor terms for NO₂ at 298 K as described by Pukite et al. (2010) and recommended by Wang
 et al. (2017, 2019) are not included. While they are recommended for spectral retrievals in the UV, the low optical densities
 (ODs) arising from NO₂ absorption (several 10^{−3}) measured by the air-borne optical instrumentation in limb direction does
 not necessitate the inclusion of these Taylor terms. This was investigated in a sensitivity study (not shown here) which indicates
 the inclusion of the Taylor terms only has a minor impact on the retrieved HONO dSCDs (in the range of about 1–2 %).
 115 Here, the HONO absorption cross-section from Stutz et al. (2000) is used, though a recent study by Li et al. (2024) reveals
 that it is overestimated by over 20 %. A smaller HONO absorption cross-section would accordingly increase the DOAS
 retrieved HONO VMRs and at the same time would reduce the HONO photolysis frequencies. In effect, it would not affect
 the major conclusion of our study that HONO_{meas} often exceeds HONO_{PSS} (see equation 1).



Table 1. For each absorbing gas, the absorption cross-sections used for the spectral retrievals, their temperatures and uncertainties are listed.

No.	Absorber	Temperature [K]	Reference	Uncertainty
1	O ₃	223, 293	Serdyuchenko et al. (2014)	3 %
2	O ₄	293	Thalman and Volkamer (2013)	4 %
3	NO ₂	223, 293	Bogumil et al. (2003)	3 %
4	H ₂ O	296	Polyansky et al. (2018)	1 %
4b	H ₂ O	293	Rothman et al. (2009)	8 %
5	HCHO	293	Chance and Orphal (2011)	10 %
6	HONO	298	Stutz et al. (2000)	5 %

Moreover, no low temperature absorption cross-sections of HONO have been published to date. The absorption cross-section
 120 (T = 298 K) is reported for the wavelength range 292 to 404 nm (Stutz et al., 2000). For the retrieval parameters shown in
 Table 1, one example of a retrieved HONO spectrum is shown in Fig. 1.

To convert dSCDs into SCDs, the absorption already present in the Fraunhofer reference spectrum (SCD_{ref}) must be deter-
 mined. This is most often accomplished using a priori information from the EMAC and MECO(n) models, in combination with
 the radiative transfer (RT) model McArtim. SCD_{ref} s are determined at altitudes where modeled SCDs approximate measured
 125 dSCDs well (in the absence of clouds), and can otherwise be assumed to be zero at high enough altitudes for gases which do
 not absorb much light overhead (i.e in the stratosphere, e.g. HONO).

2.2 The scaling method

The attribution of the determined SCDs to VMRs of the targeted gases in space and time in the atmosphere is performed
 using the scaling method (e.g. Hüneke et al. (2017); Stutz et al. (2017); Kluge et al. (2020); Rotermund et al. (2021); Kluge
 130 et al. (2023)). The scaling method relies on information about the radiative transfer inferred from co-measured or calculated
 absorption of a gas with a known concentration or extinction $[P]_i$ in an atmospheric layer i .

Weighting factors i.e., relative detection sensitivities of the targeted gas $[X]_i$ and the scaling gas $[Y]_i$ (further on called α
 factors), are determined by combining air mass factors calculated by the radiative transfer model McArtim (Deutschmann et al.,
 2011) and the chosen a priori profiles for both gases.

135 The radiative transfer model is provided the time and the geolocation of the measurements and in-situ temperatures and
 pressures provided by the aircraft's navigation and monitoring system, climatological aerosol profiles as well as a priori profiles
 of the target and scaling gas.

Climatological aerosol profiles are determined from the stratospheric aerosol and gas experiment (384 nm and 520 nm)
 instrument from the international space station and the lidar climatology of vertical aerosol structure (355 nm and 532 nm)
 140 light detection and ranging instrument, while parameterization of the single scattering albedo (Heintzenberg et al., 1997) and
 Henyey-Greenstein phase function (Toublanc, 1996) are also included.



The a priori extinction profiles of the O_4 collisional complex are calculated from the oxygen concentration and the collisional absorption cross-section. The a priori profile of ozone is determined from in situ ozone measurements and ozone mapping and profiler suite satellite data. The a priori profiles of the target gases are taken from the EMAC or MECO(n) models, where
145 available.

Previously, the sensitivity of inferred VMRs with respect to uncertainties related to the a priori profile was studied (Kluge et al., 2023) (Figure 1), and it was found that after a few iteration steps (i.e. the inferred profile of the targeted gas in step i are used as a priori for the retrieval of step $i+1$), a priori profiles converge to a final profile. This is corroborated by another sensitivity study, an investigation of the erroneous retrieval of HONO VMRs in the free troposphere above a layer of intense
150 air pollution in the boundary layer. It was found that the scaling method robustly avoids mis-attributing absorption from the boundary layer to higher altitudes as long as the a priori information captures the general shape of the trace gas profile (see Fig. 2).

Furthermore, the scaling method converts a detection limit defined by the DOAS retrieval error into VMRs which vary with altitude. The detection limit for HONO for example ranges from 1 to 15 ppt from the boundary layer to the upper troposphere.

155 The precision of the scaling method is primarily limited by the signal to noise ratio of the DOAS retrieval of the target gas. Other sources of error include the determination of the SCD_{ref} of the scaling gas, differences between a priori and measured profiles, and misalignment of the telescopes during flight. For details see Hüneke et al. (2017); Stutz et al. (2017).

The integration of spectra in the UV lasts 30 s on average - during which the aircraft moves at 100 ms^{-1} - while the mean path length at 360 nm increases with altitude. The retrievals of the mini-DOAS instrument represent averages over a volume,
160 the horizontal area of which ranges from dozens to hundreds of square kilometers.

2.3 Ancillary instruments on board the HALO aircraft

The interpretation and contextualization of the measurements of the mini-DOAS instrument require observations of complementary instrumentation operated on board the HALO aircraft, although the package of instruments varied between the different missions. Those instruments which were present for the EMERGE mission as well as the CAFE-Africa mission are
165 listed in Table 2, as well as those instruments which were present only for one mission or the other. Further details of the instruments are provided in the respective publications listed in the last column of Table 2.

2.4 Atmospheric chemistry models

In the absence of an in situ instrument which measures HONO, or satellite measurements thereof, the VMRs of HONO observed by the mini-DOAS instrument are compared to the simulations of atmospheric chemistry models. Model outputs are
170 also compared to the measured HCHO and NO_2 VMRs. These simulations are used to construct a priori profiles of the target gases for the scaling method. The two models used in this study are the EMAC and MECO(n) chemistry climate models. Neither model is suited for fine spatial (and temporal) scale comparison of parameters measured from the aircraft, in particular with the VMR ratios measured by our instrument near emissions or around the boundaries of air masses with different trace gas concentrations. This is not due to a deficiency of either model per se, but rather that the concentrations of the investigated

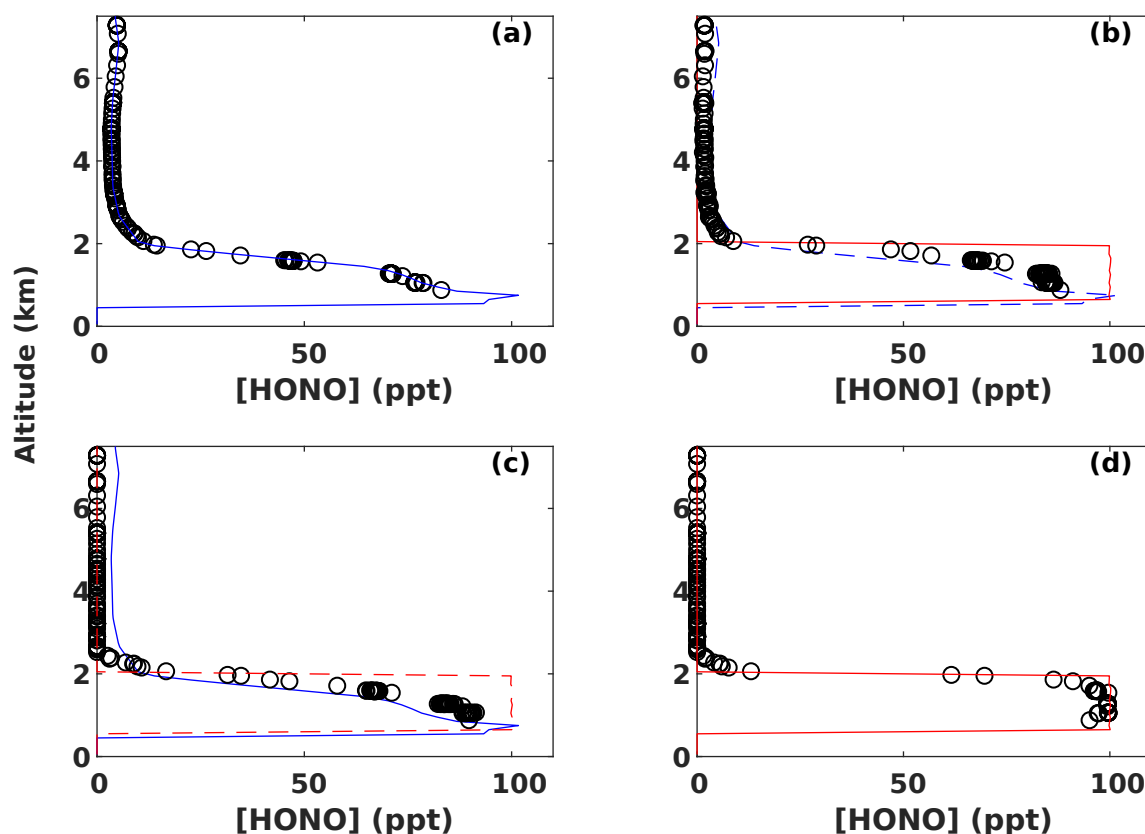


Figure 2. HONO VMRs retrieved by the scaling method using virtual measurements. In each panel, virtual measurements are created from the profiles shown as solid lines. Those virtual measurements are then scaled according to an a priori profile shown as dashed lines. The blue lines are a representative HONO profile, the red lines are a Heaviside function representing a loaded boundary layer. For example, in panel b, scaling measurements which were produced by a loaded boundary layer with a smoother profile results in an underestimation of HONO within the boundary layer, as well as an overestimation of HONO of some 10 % — decreasing with increasing altitude — up to 1 km above the boundary layer.



Table 2. The instruments, missions, institutions, measured parameters, precision and resolution thereof (if specified).

Instrument	Mission	Institute	Measured Parameter(s)	Precision	Resolution	Reference
BAHAMAS	EMeRGe/CAFE	DLR FX	aircraft, ambient data		1 s	Mallaun et al. (2015)
C-ToF-AMS	EMeRGe/CAFE	MPIC	NO_3^- , SO_4^{2-} , NH_4^+		30 s	Schulz et al. (2018)
HALO-SR-A	EMeRGe/CAFE	FZJ	photolysis frequencies			Bohn and Lohse (2017)
Sky-OPC	EMeRGe/CAFE	MPIC	aerosol surface area and volume		60 s	Heintzenberg (1994)
FAIRO	EMeRGe/CAFE	KIT IMK	O_3	2 %, 1 ppb		Zahn et al. (2012)
SP2	EMeRGe/CAFE	MPIC	black carbon		1 s	Holanda et al. (2020)
AENEAS	EMeRGe	DLR IPA	NO , NO_Y		1 s	Ziereis et al. (2004)
HKMS	EMeRGe	KIT IMK	HCHO , VOCs	18 %, 90 ppt	60 s	Brito and Zahn (2011)
PeRCEAS	EMeRGe	IUP Bremen	RO_2^*		60 s	George et al. (2020)
NOAH	CAFE	MPIC	NO	6 %	1 s	Tadic et al. (2020)
HORUS	CAFE	MPIC	OH , HO_2			Marno et al. (2020)
CIMS	CAFE	MPIC	HNO_3			Dörich et al. (2021)
MMS	CAFE	MPIC	acetonitrile		60 s	Wang et al. (2020)

gases may vary near strong sources of pollution on spatial and temporal scales which in these cases neither model resolves (see below). However, model predictions should still be broadly representative of atmospheric composition, and capture the general spatial distribution of the target gases in the free and upper troposphere.

2.4.1 EMAC

The ECHAM/MESSy Atmospheric Chemistry (EMAC) model is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2010). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5 Roeckner et al., 2006). The physics subroutines of the original ECHAM code have been modularized and re-implemented as MESSy submodels and have continuously been further developed. Only the spectral transform core, the flux-form semi-Lagrangian large scale advection scheme, and the nudging routines for Newtonian relaxation are remaining from ECHAM. We applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.54.0) in the T42L90MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approx. 2.8 by 2.8 degrees in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. Anthropogenic emissions are prescribed monthly average values following the IPCC RCP8.5 scenario. For the longer-lived greenhouse gases, pseudo emissions are applied by prescribing zonally and monthly averaged mixing ratios at the surface. To facilitate a comparison with the observations, EMAC is nudged (by Newtonian relaxation) against ECMWF ERA-Interim data. The chemical mechanism considers the basic gas-phase chemistry of ozone, methane and odd nitrogen. Alkanes and alkenes are included up to C4. Halogen chemistry includes bromine and



chlorine species. For the chemistry of isoprene plus a few selected non-methane hydrocarbons (NMHCs), we used version 1 of the Mainz Isoprene Mechanism (MIM1). Further details of the model set-up as well as the considered chemical processes are described by (Jöckel et al., 2016).

EMAC model data is available for both phases of the EMeRGe mission and for the CAFE-Africa mission.

2.4.2 MECO(n)

MECO(n) is a global-regional chemistry-climate model, which couples EMAC and the regional chemistry-climate model COSMO-CLM/MESSy online (Kerkweg and Jöckel, 2012a, b). The dynamics of EMAC, in the simulation of which the results are analyzed here, was nudged towards ECMWF ERA-Interim as described above. The dynamics in COSMO-CLM/MESSy is not nudged, the forcing at the lateral boundaries of the regional model domains are on-line provided by the global EMAC model (first nested COSMO-CLM/MESSy instance), or from the next coarser resolved COSMO-CLM/MESSy instance, respectively.

The simulations for EMeRGe-Europe features 40 vertical levels and three refinements with the finest resolution of 7 km which has been used for analyses. The simulations for EMeRGe-Asia feature 45 vertical levels and 2 refinements with the finest resolution of 12 km, which has been used for the analyses. The simulations for Europe used EDGAR 4.3.2 anthropogenic emissions. For Asia the EDGAR 5.0 emissions have been used. In MECO(n) the same chemistry scheme as for EMAC has been applied (see above). The overall set-up is very similar to the one described by Mertens et al. (2016).

In both cases, EMAC and MECO(n), the analyzed model data has been sampled on-line along the flight-tracks of the research aircraft(s) with the S4D submodel (Jöckel et al., 2010) at a frequency corresponding to the model time step length, i.e. every 12 minutes in EMAC, every 60 seconds in the 7 km instance of MECO(n) and every 120 seconds in the 12 km instance of MECO(n).

3 Measurements

The mini-DOAS instrument was deployed on several missions between 2017 and 2019. This study focuses on the analysis of data collected during three missions: EMeRGe-EU (July 2017), EMeRGe-Asia (March & April 2018) — which are two phases of the same broader mission (EMeRGe) — and CAFE-Africa (August & September 2018). The missions are chosen according to the flight patterns, and the presence of complementary instruments on board the HALO aircraft during those missions which are used to augment the investigations of the trace gases measured with the mini-DOAS instrument. The geographical areas and flight altitudes probed during these missions vary significantly, providing a broad overview of the concentrations of the trace gases studied in different seasons, layers of the troposphere and regions of the globe.

3.1 EMeRGe

The EMeRGe mission investigated the composition, transport and transformation of pollution plumes from mega-cities and major population centers. Airborne measurements of relevant atmospheric parameters, trace gases, and aerosols were made on board the HALO aircraft at different altitudes over Europe in July 2017 and the East China and South China Seas between



the Philippines and Japan in spring 2018 (during the inter-monsoon period, which favors the outflow of pollutants from East Asia). These airborne observations were complemented by a suite of ground- and satellite-based measurements, as well as photochemical transport and chemistry climate modeling (e.g. EMAC, MECO(n), ...) (Andrés Hernández et al., 2022). The field observations concentrated on the characterization of different air mass types downwind from various emission sources (e.g., those of anthropogenic, biogenic, and biomass burning origin as well as background air). The transformation of the suite of trace gases and radicals as well as aerosol parameters (e.g., particle number, size distribution, and chemical composition) has been used to provide insights into chemical processing (and mixing) of these air masses during their atmospheric transport (Förster et al., 2023). Of particular importance are the measurements of peroxy radicals RO_2^* , which are strongly influenced by the OH produced from the photolysis of HONO (George et al., 2023). A detailed description of the objectives, instrument payload, and findings of the EMeRGe mission is found in publications of the ACP/AMT inter-journal EMeRGe special issue (https://acp.copernicus.org/articles/special_issue1074.html), specifically in the EMeRGe-EU overview paper by Andrés Hernández et al. (2022).

During both EMeRGe phases, the measurement flights had a duration of eight hours on average. The take off was typically in the mornings and landings occurred in the afternoon, i.e. flights were exclusively during daylight. While the flight levels spanned measurement altitudes from a few dozen meters above sea level to up to 12500 m, 72 % of the air masses analyzed were within the lowermost four kilometers of the atmosphere, i.e. in the boundary layer and free troposphere. As a consequence of the altitude range and season, the ambient temperatures were mostly above 0 °C; the high ambient temperatures and associated cabin temperatures reduced the data coverage of the DOAS instrument during some flights. The measurement flights sampled large geographical areas, spanning continental Europe and East Asia.

Detailed flight tracks together with air mass tags (see Sect. 3.3) are shown in Fig. 3. During the European deployments, most of the flight time was spent over land, in contrast with deployments in Asia, where much of the flight time was spent over the East China Sea and South China Sea. Various atmospheric conditions characterized each flight, such as the occurrence of thunderstorms in Southern Europe, as well as the presence of anthropogenic pollution plumes.

3.2 CAFE-Africa

The CAFE-Africa (<https://mpic.de/4130589/cafe-africa>) mission was based in Sal, Cape Verde and took place in August and September of 2018. The area of study was the tropical troposphere over the Atlantic Ocean and western Africa. Of the 14 scientific flights, 12 are analyzed here since the transfer flights are excluded. The scientific objectives of CAFE-Africa included the study of oxidation chemistry, thunderstorm effects, radiative forcing, and long-range transport of pollutants from biomass burning. The investigated region overlaps with the inter-tropical convergence zone, while the maximum flight altitude was around 15 km. The flight tracks are shown in Fig. 4.

The measurement flights took off in the mornings, landed in the evenings and were primarily conducted during daylight (except for the flight on 26.08.2018, which continued past sunset). Most of the flight time was spent at high altitudes, over the Atlantic Ocean. The ambient temperature was therefore usually well below 0 °C, enhancing the temperature stability of the mini-DOAS instrument.

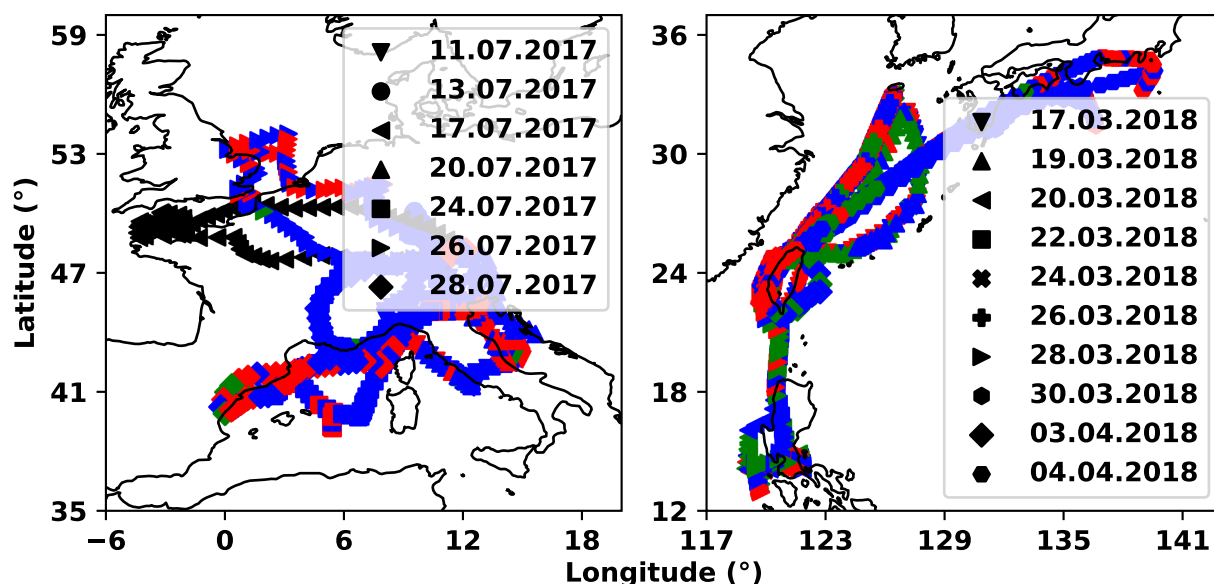


Figure 3. The flight tracks of the seventeen scientific flights of the two phases of the EMeRGe mission during July 2017 and March/April 2018. The operational base of EMeRGe-EU (left panel) was Oberpfaffenhofen, Germany; EMeRGe-Asia (right panel) was based out of Tainan, Taiwan. Transfer flights to and from Tainan during EMeRGe-Asia are excluded. The coordinates of the flight tracks are colored by air mass tags inferred from VOC measurements of the HKMS instrument (Förster et al., 2023) (see Sect. 3.3), except for the flight on 17.07.2017 due to an instrument failure (shown in black). Red coloring indicates primarily anthropogenic emissions, green indicates biomass burning, while blue indicates neither, and is assumed to be aged background air.

During the CAFE-Africa mission, simultaneous measurements of OH, NO, and J_{HONO} allow the quantification of gas phase HONO formation. Airborne measurements of HONO within the same region (and at similar altitudes) the following year, reported by Andersen et al. (2023), largely corroborate the HONO reported by this study.

3.3 Air mass characterization

The origin and composition of an air mass may determine the concentrations of trace gases sampled from the HALO aircraft. In keeping with the scientific objectives of the EMeRGe mission, the air masses probed are characterized with plume tags, which are interpolated from the volatile organic compound (VOC) measurements of the HKMS instrument (Förster et al., 2023). Elevated VMRs of acetonitrile (above 145 ppt) are indicative of biomass burning influence, whereas VMRs of benzene (above 19 ppt) are indicative of anthropogenic pollution. Across all flights, 34 % of air masses observed during the EMeRGe missions are tagged with anthropogenic influence, 14 % contain signatures of biomass burning, and the remaining 51 % are assumed to be otherwise aged background air. These percentages vary from flight to flight and across mission phases. As expected, less

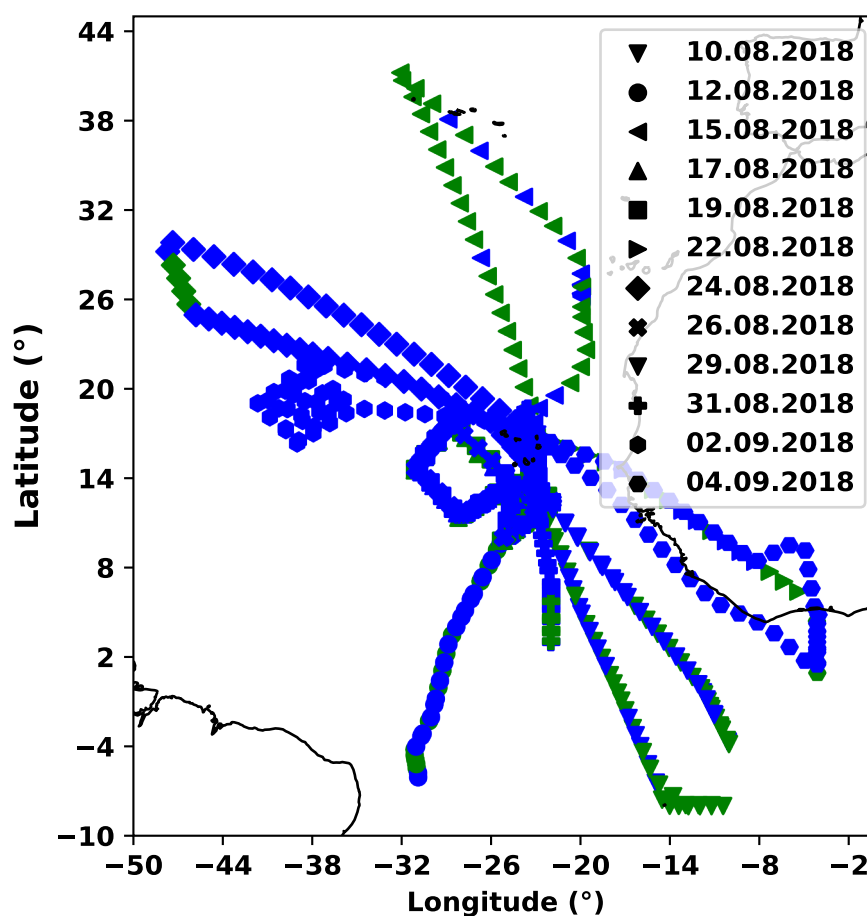


Figure 4. The flight tracks of the 12 scientific flights of the CAFE-Africa mission in August and September of 2018 (the transfer flights are excluded). The operational base was Sal, Cape Verde. As in Fig. 3, the coordinates of the flight tracks are colored according to the air mass tags described in Sect. 3.3. Green indicates biomass burning, blue indicates background air.



biomass burning influenced air was found during the deployments in Europe, compared to those probed over Asia (Förster
et al., 2023). Since the HKMS instrument was not part of the CAFE-Africa mission, the same thresholds were applied to the
acetonitrile measurements of the MMS instrument to differentiate biomass burning (BB) air masses accordingly Crowley et al.
(2025). Fine and coarse aerosol surface area (SA) and volume (V) data calculated from the measurements of the Sky-OPC
instrument may also be used to identify dust events (Weger et al., 2018).

3.4 Availability of measurements

The measurements reported here are derived from several thousand limb spectra successfully recorded with the mini-DOAS
instrument. Rarely, there are periods during some flights when skylight could not be collected, or when measured skylight
spectra cannot be analyzed. The former includes highly variable cloud conditions, when the aircraft flew inside or next to bright
clouds, since then the spectrometers tend to become over-saturated (in the post-flight analysis such periods are identified by
inspecting images captured with the IDS uEye camera). Otherwise, night flights do not provide sufficient light for the collection
of spectra. The latter occurs when the detector and/or spectrometer temperature increase beyond approximately 4 °C, since
increasing detector temperatures increase the dark current and changing spectrometer temperatures degrade the imaging of the
spectrometers (by broadening the instrument's spectral response function). Temperature stability for some flights lasted up to
9 hours, while when flying for longer periods at higher ambient temperatures (i.e. at low altitudes), the stable measurement
interval lasted only 3 hours in some cases (particularly during the EMeRGe mission). Spectra recorded during sharp turns of
the aircraft are also discarded from analysis. Communication problems between the BAHAMAS and mini-DOAS instruments
during four flights of the EMeRGe mission prevented the live alignment of the telescopes with the horizon, rendering the
correct attribution of observed absorption to a particular layer in the atmosphere practically impossible. Therefore, the affected
flights on 26.07.2017, 28.07.2017, 22.03.2018, and 03.04.2018 are excluded from the analysis.

Unfortunately, not only failure or malfunctions of the mini-DOAS instrument restrict our analysis, but also the availability of
the necessary data measured by the complementary instruments operated on board the HALO aircraft. For example, during the
EMeRGe mission, measurements of VOCs made by the HKMS instrument (and consequently the air mass characterizing plume
tags) are not available on 17.07.2017, while RO_2^* measured with the PERCEAS instrument is not available on 17.03.2018.
During the CAFE-Africa mission, measurements of NO, OH, and HO_2 are unavailable on 10.08.2018, while measurements
of HNO_3 with the CIMS instrument are not available for the first four flights of the mission on 10.08.2018, 12.08.2018,
15.08.2018, and 17.08.2018.

4 Results and Discussion

This section presents the retrieved trace gas VMRs from the EMeRGe and CAFE-Africa missions. While the NO_2 and HCHO
measured by the mini-DOAS instrument compare well with model simulations (see Fig. A1 and Fig. A2 in the Appendix),
the measured HONO is often in excess of model predictions, which requires further discussion and explanation (see Sect.
4.1). Potential heterogeneous and homogeneous sources of the excess HONO are investigated and analyzed in three separate



regimes of the troposphere, the MBL, lower and upper troposphere in sections 4.2, 4.3, and 4.4, respectively. Before discussing the different reasons for inferred excess HONO, we first compare our measured HONO with atmospheric observations of HONO previously published (see Fig. 5).

4.1 (Excess) HONO in the troposphere

305 The HONO VMRs retrieved from the mini-DOAS observations made on board HALO are high in the PBL and free troposphere (FT) (up to 150 ppt) for every flight of the EMeRGe mission (see Fig. 5) compared to our expectations from known homogeneous sources (reactions R1 to R3). In addition, in the upper troposphere (UT), mixing ratios of up to 75 ppt were observed during the two flights of the EMeRGe-Asia mission which probed those altitudes. Comparatively little HONO is observed in the free troposphere (FT) (less than 50 ppt) in all missions. In comparison to the EMeRGe mission, where the flight tracks passed through highly polluted air masses, during the CAFE-Africa mission, which took place over the Atlantic Ocean, lower HONO VMRs are retrieved in the FT. Nevertheless, some tens of ppt are still observed within the MBL. In the UT, the HONO VMRs are elevated: more than 100 ppt during all flights of the CAFE-Africa mission. In summary, the HONO VMR measurements in EMeRGe-EU, EMeRGe-Asia and CAFE-Africa are consistently found to be in excess relative to the expectations based on the known gas phase formation mechanisms and thus model predictions (see below).

315 Zhang et al. (2009); Li et al. (2014); Heue et al. (2014); Ye et al. (2016b, 2018); Andersen et al. (2023) measured HONO from aircraft in disparate regions: over a forested region in North Michigan, over the Po Valley of Northern Italy, in a convective cloud over the Caribbean Sea, over the North Atlantic Ocean, over the southeastern US, and in the remote Atlantic troposphere, respectively. Given the individuality of each set of HONO observations, our measurements compare reasonably well, except for some peculiarities addressed below.

320 Figure 6 compares the HONO measured by the mini-DOAS instrument with the predictions of the EMAC and MECO(n) models. So far the EMAC and MECO(n) simulations only include the known gas phase formation mechanisms of HONO (reaction R1 to R3).

For EMeRGe-EU, the EMAC model predicts at most 35 ppt of HONO along the flight track of the HALO aircraft in the boundary layer. The MECO(n) model, by comparison, predicts up to 60 ppt of HONO along the HALO flight track. Neither model predicts appreciable VMRs of HONO in the FT. During EMeRGe-Asia, the EMAC model predicts at most 16 ppt HONO in the PBL along the flight track. The MECO(n) model, by comparison, predicts up to 127 ppt of HONO there. While the MECO(n) model predicts only 2 ppt of HONO in the UT, the EMAC model predicts up to 10 ppt of HONO at 12 km altitude for the HALO flights from Taiwan towards Japan.

330 During both phases of EMeRGe (over Europe and Eastern Asia), the observed HONO VMRs exceed both models' predictions throughout the probed altitude ranges (see Fig. 6). During the European phase, the observations are in excess of model predictions by at least a factor of two, and up to a factor of five. During the Asian phase, the excess relative to predictions is model and altitude dependent and may exceed one order of magnitude. For the CAFE-Africa mission, only the EMAC model simulations are available for comparison. The retrieved HONO VMRs are here, again, much larger than the model predictions.

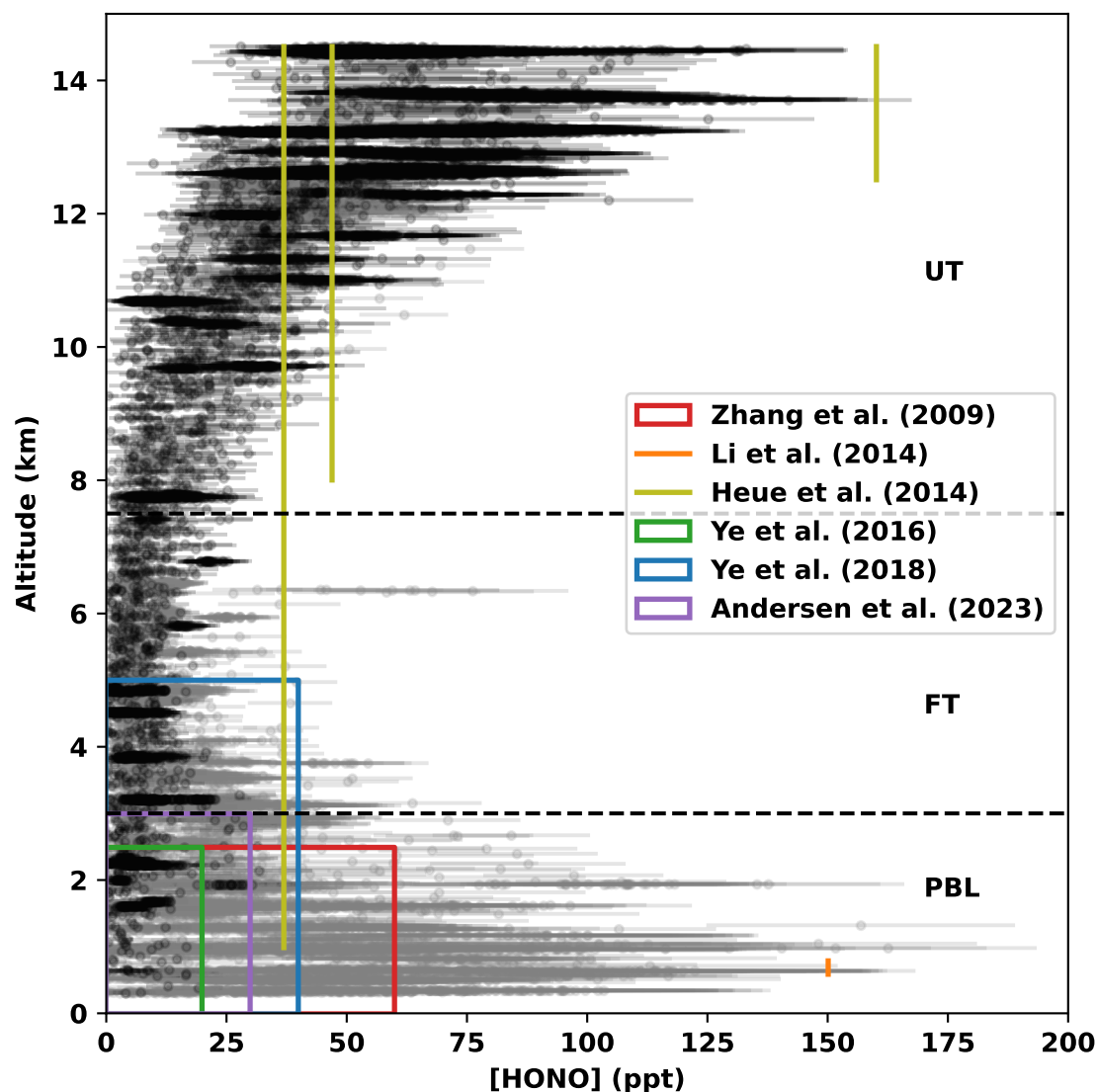


Figure 5. Comparison of airborne HONO altitude profiles reported here, as well as regions representing the range of airborne HONO observations reported previously (Zhang et al., 2009; Li et al., 2014; Heue et al., 2014; Ye et al., 2016a, 2018; Andersen et al., 2023). Data from the EMeRGe mission is drawn in gray, data from the CAFE-Africa mission is drawn in black. Previously reported HONO observations from aircraft are limited to the LT with only one exception (Heue et al., 2014), the altitude of which is not precisely defined. The HONO VMRs reported by Heue et al. (2014) are converted from DOAS retrievals within a thunderstorm cloud and are sensitive to the assumed cloud height. The horizontal dashed-lines visually distinguish the PBL (Sect. 4.2), as well as the free (Sect. 4.3) and upper (Sect. 4.4) troposphere.

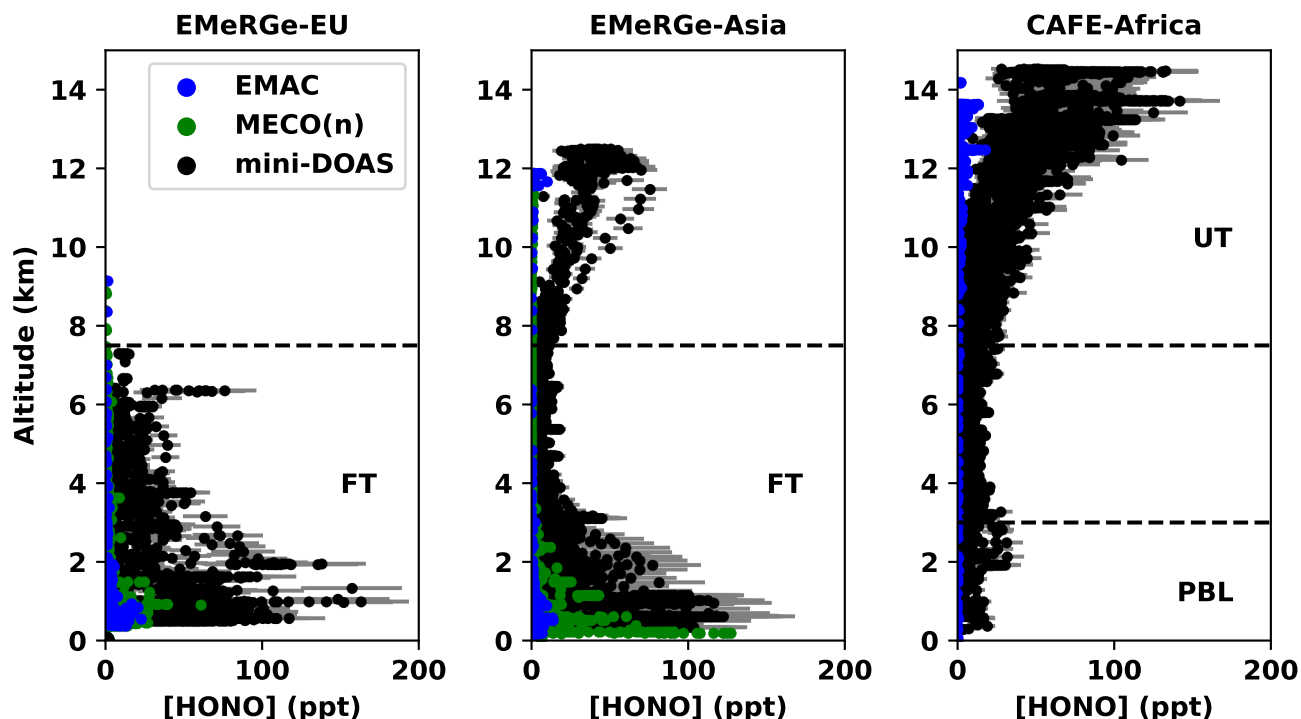


Figure 6. Altitude profiles of HONO as observed by the mini-DOAS instrument (black – with uncertainty in gray), as predicted by the EMAC model (blue), and as predicted by the MECO(n) model (green), for the three research missions: EMeRGe-EU (left), EMeRGe-Asia (center), and CAFE-Africa (right). MECO(n) data is not available for the CAFE-Africa mission. The horizontal dashed-lines visually distinguish the PBL (Sect. 4.2), the FT (Sect. 4.3) and UT (Sect. 4.4).

The EMAC model correctly predicts the general shape of the retrieved HONO profiles, but on average predicts VMRs in the
 335 single digits (ppt), and never more than 18 ppt along the flight track of the HALO aircraft (at 12.5 km altitude).

Since there is general agreement between model predictions and observations of the mini-DOAS instrument for HCHO
 and NO₂ (see Fig. A1 and Fig. A2 in the appendix), the discrepancies between model predicted HONO and the observations
 of the mini-DOAS instrument are unlikely to be due to the model resolution, instrumental or methodological issues. Rather,
 HONO formation in the troposphere (especially the UT) may act via a mechanism (or mechanisms) which are altogether not
 340 represented in the models.

While during the CAFE-Africa campaign, in situ measurements of OH, NO, and J_{HONO} are available to quantify [HONO]_{PSS},
 the measured HONO is still in excess of what would be expected based on those measurements (see below).

The excess HONO VMRs observed with the mini-DOAS instrument require explanation. In the low-NO_x marine boundary
 layer (MBL), our observations largely corroborate previous HONO measurements performed with another technique (see
 345 Andersen et al. (2023)), and thus also serve to validate both sets of measurements (see Sect. 4.2). The latter provides consistent



evidence on the importance of particulate nitrate photolysis as the cause for observed HONO in the MBL (see sect. 4.2). In the polluted PBL and FT more broadly, we investigate heterogeneous formation of HONO (Sect. 4.3). In the cold upper troposphere (UT), we suggest that a heretofore unknown gas-phase mechanism may produce HONO (Sect. 4.4).

4.2 (Excess) HONO in the MBL during CAFE-Africa: Further evidence of particulate nitrate photolysis

350 Within the low- NO_x regime of the marine MBL, a growing body of research attempts to account for observed HONO VMRs by invoking the photolysis of particulate nitrate (Ye et al., 2016a; Reed et al., 2017; Andersen et al., 2023). While the photolysis frequency of particulate nitrate is not measured directly, it has been argued that it is possibly up to two orders of magnitude larger than the photolysis frequency of gaseous nitric acid (Ye et al., 2016a, 2017). The enhancement factors (EF) for nitrate photolysis, defined as

$$355 \quad \text{EF} = \frac{J_{\text{NO}_3^-}}{J_{\text{HNO}_3}} \quad (2)$$

which are derived from field measurements have been significantly different from those determined in laboratories (Romer et al., 2018; Shi et al., 2021). Recently, Andersen et al. (2023) speculated that this discrepancy may arise from a saturation effect, whereby the EF decreases with increasing particulate nitrate concentration in the aerosols, although details of the underlying processes are unclear. Here, we follow the approach of Andersen et al. (2023) and construct the photolysis EF necessary
360 to explain our HONO observations using measured quantities from around the Cape Verde Islands during the CAFE-Africa mission. In the unpolluted MBL, HONO production may be assumed to be largely driven by particulate nitrate photolysis. Under this assumption, as well as the assumption of a photo-stationary state, the EFs can be derived from the following:

$$\text{EF} = \frac{J_{\text{HONO}} \cdot [\text{HONO}]}{J_{\text{HNO}_3} \cdot [\text{pNO}_3^-]} \quad (3)$$

During CAFE-Africa, the C-ToF-AMS instrument measured NO_3^- in sub-micron aerosol, which is unlikely to constitute the
365 whole aerosol nitrate load, due to an unknown fraction tied in coarse mode aerosols (Hrdina et al., 2021). Unfortunately, even though information on the aerosol mass in the micron range is available from the SKY-OPC instrument, the nitrate fraction across different size regimes cannot assumed to be constant (Lee et al., 2008) and therefore total particulate nitrate cannot be inferred. However, other quantities (NO , NO_2 , HONO, SA_{total} , and J_{HNO_3}) measured from the HALO aircraft during the CAFE-Africa mission are largely in range of and thus corroborate the measurements of Andersen et al. (2023) for the MBL
370 around the Cape Verde islands in summer.

Assuming that either (a) all aerosol nitrate resides in the sub-micron aerosols or that (b) only a fraction of total nitrates are found in the sub-micron aerosol (Hrdina et al., 2021) modulates the resultant EFs (panel a versus panel b in Figure 7).

In both cases a decrease in EFs with the particulate nitrate concentration is observed, in agreement with the findings of Andersen et al. (2023). Further, a more consistent picture arises compared to the findings of Andersen et al. (2023) when
375 coarse mode nitrate is taken into account (panel b in Figure 7). The missing HONO source strength and rate of particulate nitrate photolysis also then match better with those observed by Ye et al. (2016b) and Andersen et al. (2023).

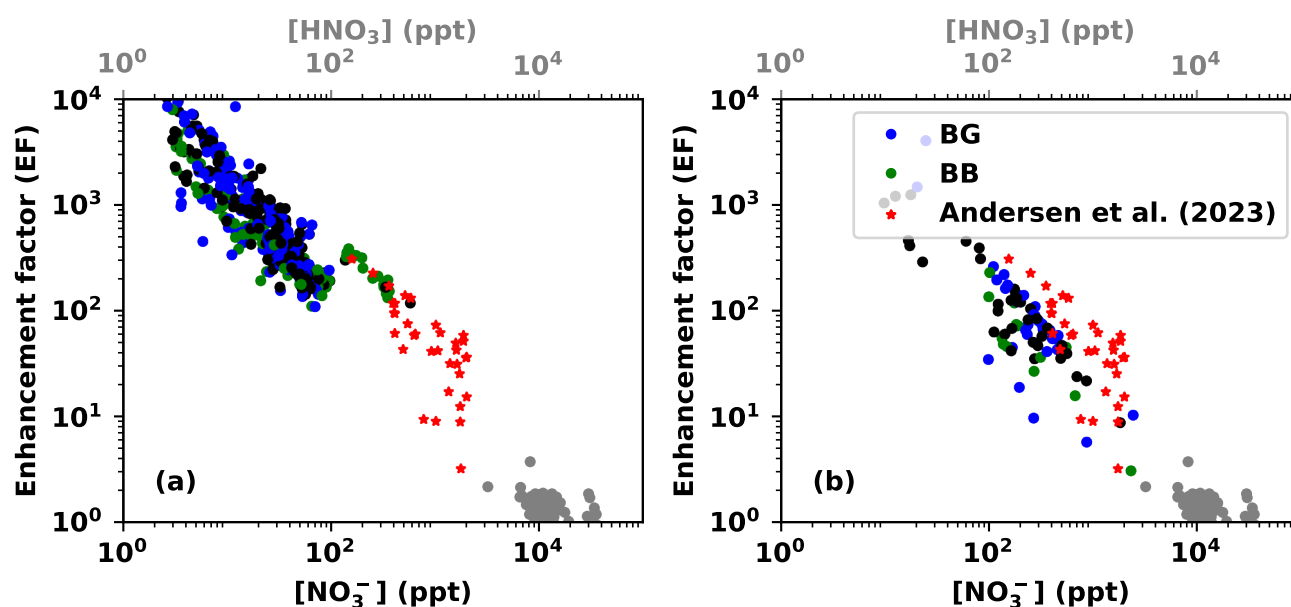


Figure 7. Inferred enhancement factor (EF) in the photolysis frequency of particulate nitrate relative to that of gaseous nitric acid necessary to match the missing HONO source, plotted as a function of the (sub-micron) particulate nitrate VMR (ppt), when the measured sub-micron to total aerosol volume ratio is not taken into account (panel a). The color of the plotted point is indicative of the influence of biomass burning, shown in green, while background air is in blue. Data with missing tags are shown in black. For comparison, the data from Andersen et al. (2023) are shown as red stars. In gray, the EFs are calculated relative to the amount of HNO_3 observed by the CIMS instrument. In panel b, the observed sub-micron particulate nitrate concentration has been scaled by the ratio of coarse mode particle volume to fine mode particle volume, reducing the resulting EFs. Data are from the lowermost 3 km from flights to and from the island of Sal, Cape Verde in August 2018 during the CAFE-Africa mission. Note the logarithmic axes.

Moreover, the degree by which gaseous nitric acid photolysis can contribute to HONO formation can be inferred from HNO_3 as measured by the CIMS instrument and the photolysis frequency measured by the HALO-SR-A instrument. Note that the CIMS instrument was designed to measure PAN rather than nitric acid and (through use of a thermal dissociation inlet) not only measures gaseous nitric acid, but also detects some particulate at the same mass-to-charge ratio (62 and 190) if the nitrate is thermally labile (i.e, ammonium nitrate or HNO_3 weakly bound to black carbon).

If all the HNO_3 measured by the CIMS instrument were actually in particulate form rather than gas phase, the resulting high levels of particulate nitrate would mean that no enhancement in the frequency of particulate nitrate photolysis (relative to the frequency of gaseous nitric acid photolysis) would be necessary to explain our HONO observations. However, this is unlikely, as the HNO_3 detected by the CIMS instrument exceeds the particulate nitrate measured by the C-ToF-AMS instrument by orders of magnitude, and the two are not strictly correlated.



Nevertheless, it can be seen that measured HNO_3 concentrations fit into the overall picture with EFs which reach unity. Since the photolysis frequency of HNO_3 is however prohibitively slow ($J_{\text{HNO}_3} \sim 1 \cdot 10^{-6} \text{ s}^{-1}$), it is unlikely that it contributes to re-noxification (or HONO formation) in the MBL.

390 4.3 HONO in the polluted PBL and FT during EMERGE: Evidence for heterogeneous HONO formation?

The air masses sampled during EMERGE-EU were primarily confined to the PBL and FT, particularly to less than 6 km altitude (Andrés Hernández et al., 2022). Most of the air masses sampled were in high- NO_x environments. EMERGE-EU is characterized by mostly continental background air, with some instances of anthropogenic influence (Förster et al., 2023). The HONO VMRs observed in the PBL and FT during the EMERGE-EU mission exceed predictions of the EMAC and MECO(n) models, which are based on gas phase production. Therefore, we next consider possible heterogeneous sources of HONO. Like the EMERGE-EU mission, the -Asia mission was largely confined to the PBL and FT, with exceptions only during the final two flights leading from Taiwan towards Japan at high altitudes. The air masses sampled were high- NO_x environments, and there was regular detection of benzene from anthropogenic plumes. In addition, the air masses sampled during EMERGE-Asia were often influenced by biomass burning (Lin et al., 2023). Here, as before, HONO VMRs observed with the mini-DOAS instrument exceed model simulations. This excess HONO certainly requires heterogeneous sources beyond the photolysis of particulate nitrate.

In order to investigate if either (a) a specific parameter directly or (b) which of the many proposed HONO formation mechanisms listed in Table A1 correlates well with the observed HONO VMRs, for both options the Spearman correlations are investigated (Figure 8, left column for case (a) and right column of case (b)). For case (b) the reactants from each formation mechanism are multiplied and their product is correlated with the observed HONO (Figure 8, right column). Correlations are determined with the Spearman correlation coefficient rather than the Pearson coefficient, to account for the case that the relationship is non-linear (for example due to saturation effects). While the HONO formation rate necessary to match its loss via photolysis is what should be correlated with the reactants of these mechanisms, many include photolysis frequencies themselves. Therefore, the correlation analysis is performed against the retrieved HONO VMRs to avoid an auto-correlation with the photolysis frequencies measured by the HALO-SR-A instrument. Similarly, the correlations are determined between VMRs instead of concentrations to avoid auto-correlations as a function of atmospheric density. Several of the in situ instruments have time resolutions of only 15, 30, or 60 seconds, so for each spectrum recorded by the mini-DOAS instrument, all data reported by the in situ instruments are averaged over the integration time of the mini-DOAS spectra (30 s). This down-sampling avoids interpolation or repeated values, which may lead to spurious or diluted correlations, respectively.

The observed HONO VMRs may however also be correlated directly with other gases and atmospheric parameters simultaneously observed on board the HALO aircraft. The trace gases retrieved with the mini-DOAS usually share a strong auto-correlation ($\rho > 0.7$). While the correlation between HCHO and HONO is not necessitated by their photochemical relationship, Hendrick et al. (2014) also observed a strong correlation of HONO with NO_2 . Since most of the heterogeneous sources of HONO proposed in Table A1 require NO_2 as a reactant, the correlation between HONO and NO_2 is to be expected. However, any correlation between the observed HONO and some other gas, parameter, or the product of the reactants of some

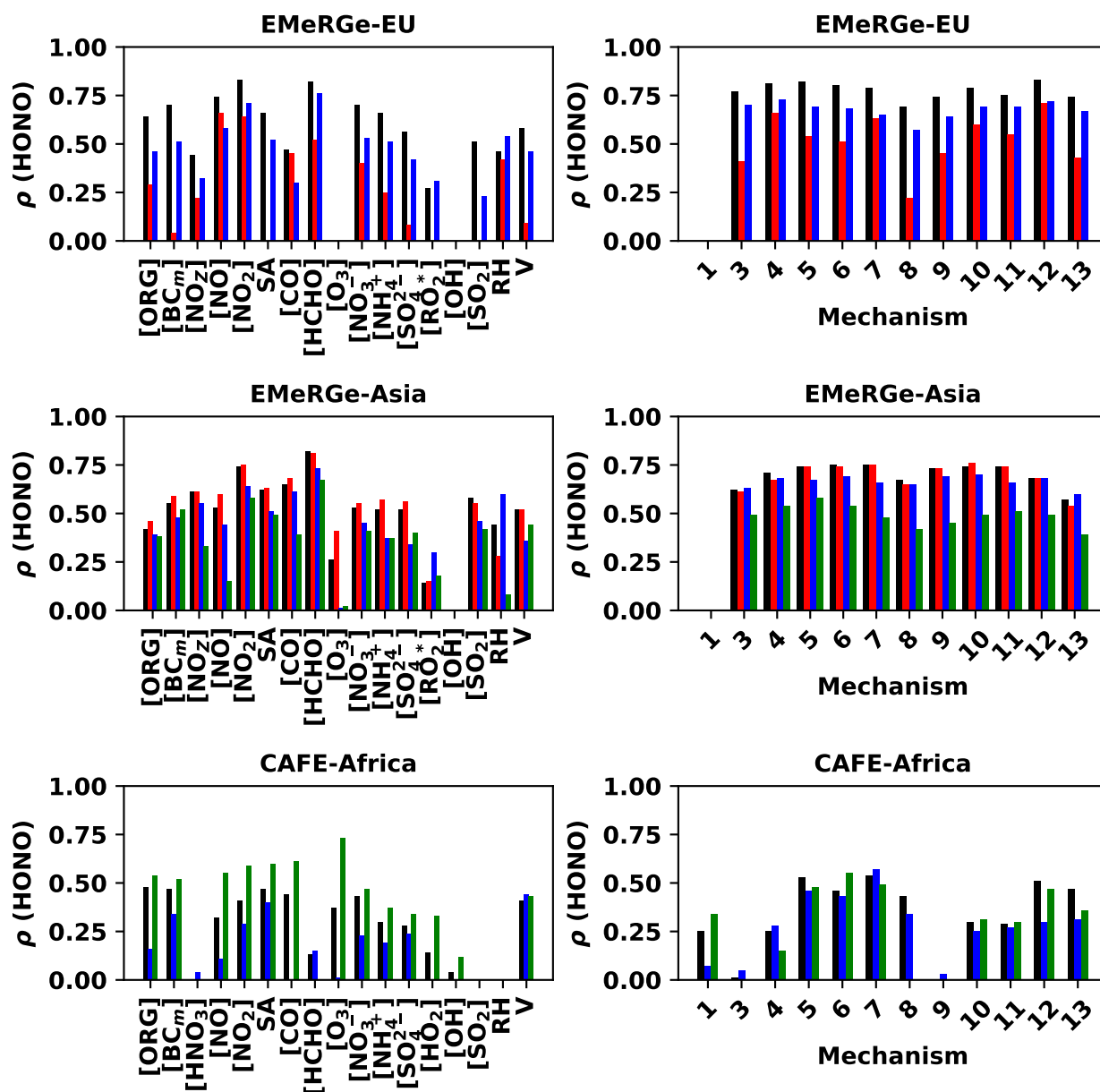


Figure 8. Spearman correlation coefficients ρ between the observed HONO VMRs and other parameters simultaneously measured on board the HALO aircraft (left column) (for the measured parameters see Table 2) and the product of reactants of twelve of the thirteen heterogeneous HONO formation mechanisms listed in Table A1 (right column) for the EMeRGe-EU (upper), EMeRGe-Asia (middle), and CAFE-Africa (lower) missions. The data shown here is from the PBL and FT. The data in red, green, blue and black are those tagged as anthropogenic (AG), biomass burning (BB), background (BG), or all data, respectively. SA, RH, and V refer to aerosol surface area, relative humidity, and aerosol volume, respectively.



hypothetical formation mechanism should ideally correlate more strongly than this threshold, i.e. the correlation with NO_2 (0.7).

Furthermore, not all species listed in Table A1 were measured during the EMeRGe mission (for details see (Andrés Hernández et al., 2022)). Indeed, no instrumentation to detect nitro-phenols was available for any of the three missions, so Mechanism
425 2 is left out of this analysis entirely. Nitric acid data is unavailable during the EMeRGe mission, therefore a proxy (NO_z) is constructed by subtracting NO_x ($\text{NO} + \text{NO}_2$) from the NO_y measured by the AENEAS instrument. OH was measured during the CAFE-Africa mission but not during both EMeRGe missions, precluding analysis of Mechanism 1 for the latter, while measured RO_2^* may only serve as a proxy for HO_2 during the EMeRGe missions.

The observed HONO correlates with several other simultaneously measured species, as well as with the formation mecha-
430 nisms proposed in Table A1 (see Fig. 8). Unsurprisingly, the proposed formation mechanisms are correlated to varying strengths with the observed HONO. The strength of the Spearman correlation coefficient varies with air mass type (anthropogenic, biomass burning, background), so filtering the lower tropospheric EMeRGe data further according to air mass type yields different correlations.

Across the EMeRGe mission, in high- NO_x air masses, nearly every mechanism correlates with the observed HONO. Sepa-
435 rating the observations according to their air mass tags reveals that some correlations are weaker in the biomass burning plumes probed during EMeRGe-Asia and in anthropogenic air during EMeRGe-EU (see Fig. 8). The proposed formation mechanisms all have some humidity dependence, since water vapor is likely a necessary, but not sufficient, component of the formation of HONO in the PBL and FT.

Generally, Mechanisms 5, 7 and 12 are correlated best with the observed HONO in all probed environments, while Mecha-
440 nisms 9, 10 and 11 only correlate with the observed HONO in the polluted high- NO_x air masses during the EMeRGe mission. The lack of correlation between the observed HONO and Mechanisms 8 and 13 may arise from underestimation of measured particulate nitrate and gaseous nitric acid. Otherwise, the use of NO_z as a proxy for HNO_3 for the EMeRGe mission may obscure any correlation. The dependence of the EF for the photolysis of particulate nitrate on the nitrate load (see Sect. 4.2) may also confound a simple monotonic relationship between the observed HONO and the components of Mechanism 13. The
445 observed HONO is correlated with the presence of NO_2 , daylight, and some catalytic surface (i.e. soot, mineral dust, organics) in all air masses, as well as with haze aerosol water reactions in polluted air masses and to a lesser extent with the photolysis of nitrates in pristine air masses.

Previous studies have found similar relationships between NO_2 , aerosol and HONO. Xing et al. (2023) found that the heterogeneous reaction of NO_2 on aerosols produces HONO. The photolytic nature of heterogeneous HONO production has
450 also been reported previously: Lee et al. (2016) found a HONO source from NO_2 requiring sunlight. Zheng et al. (2020b), Jiang et al. (2020) and Yu et al. (2022) describe photo-enhanced heterogeneous conversion of NO_2 to HONO on aerosol surfaces. Singh et al. (2021) found during eclipse conditions that the HONO source must be photochemical. Hu et al. (2022) speculated that the conversion of NO_2 on BC enhanced by light may be a likely heterogeneous source of HONO, along with the photolysis of particulate nitrate.



455 This analysis may be limited by the spatial and temporal resolutions of the mini-DOAS instrument, as well as those of
the in situ instruments: the necessary down-sampling of parameters reported by in situ instruments may obscure correlations.
Chemical interferences of the in situ instruments also obscure a precise attribution of observed HONO formation to a particular
mechanism or even phase (Mechanisms 8 and 13). The suitability of proxies also limits the scope of the analysis, e.g. whether
black carbon mass (or number) is a suitable proxy for the presence of soot, particularly fresh soot (Mechanism 5). NO_x may be
460 also a poor proxy for HNO₃ (Mechanisms 8 and 9), while although HCHO is indicative of active VOC chemistry, it does not
represent total VOCs (Mechanism 9). Moreover, volume, mass, and number of particles with a diameter larger than 500 nm
are the only quantities available to determine the presence of dust (Mechanism 7).

We also lack any measurements of aerosol pH, while the aerosol water content is represented only by relative humidity.
These variables are not directly interchangeable, but instrumentation to observe aerosol water content and pH directly were not
465 present, and attempts to model aerosol water content and pH led to nonphysical results. Moreover, the amount of particulate
ammonium is not synonymous with that of gas phase ammonia (Mechanism 10). Nor does the amount of aerosol sulfate equal
that of gas phase SO₂ (Mechanism 11). Indeed, the C-ToF-AMS instrument measures only non-refractory sub-micron aerosol
and thereby presents an incomplete picture of the aerosol composition; a more complete aerosol chemical composition would
be necessary to investigate Mechanisms 10, 11, 12, and especially 13 in more detail.

470 Moreover, the pH of haze is not well understood (Tao et al., 2020), though sub-micron aerosol is generally acidic (Weber
et al., 2016). Aerosol acidity is lower in China than in Europe (Ding et al., 2019), in large part due to the partitioning of gas
phase ammonia and particulate ammonium (Zheng et al., 2020a). Without measurements of these quantities (aerosol pH, gas
phase ammonia), we can only observe the output of the aerosol chemistry. Further, the products of aerosol nitrate photolysis
seem to also be pH dependent (Scharko et al., 2014; Benedict et al., 2017).

475 Fu et al. (2019) describe modeling of heterogeneous reactions on surfaces producing HONO, and reports improved model
performance for O₃ and PM_{2.5}. In another modeling study, Zhang et al. (2021) found that HONO produced by heterogeneous
reactions increased the concentration of OH by a factor of two, increased aerosol nitrate via the conversion of NO₂, and
increased SOA formation via reactions of OH with VOCs (see also Xing et al. (2019)). Heterogeneous HONO formation
mechanisms have also been implemented in a chemistry-climate model (Ha et al., 2023), where the heterogeneous formation
480 reactions were found to contribute more to HONO formation than direct emissions, particularly those on aerosol surfaces.
Heterogeneous HONO formation mechanisms in the LT then represent a critical subject in the understanding of tropospheric
oxidation capacity.

In summary, because of the lack of data and/or the weak correlations inferred from the relevant parameters, we cannot
firmly conclude on or reject any of the proposed heterogeneous HONO formation mechanisms listed in Table A1. Further, it is
485 also likely that some HONO formation mechanisms act in parallel, though at varying strengths over time, which complicates
deciphering the relevant HONO mechanisms from field data.

However, the field data easily allow inferring the necessary source strength for closing the excess HONO budget. The
necessary source strength reaches up to 0.3 ppb h⁻¹ in the MBL, up to 1 ppb h⁻¹ in the polluted PBL, up to 0.6 ppb h⁻¹ in
the FT and ranges from 0.3 to 1.6 ppb h⁻¹ in the UT. This may represent a significant modification to the oxidation capacity

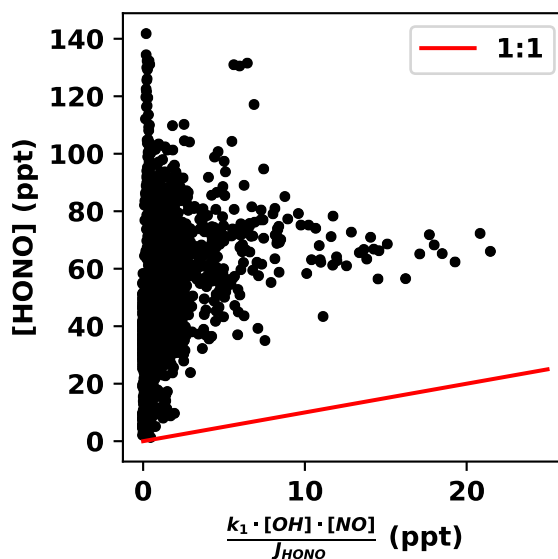


Figure 9. [HONO] as measured by the mini-DOAS instrument plotted as a function of [HONO]_{PSS} determined from in situ measurements of [OH], [NO], and J_{HONO}. Data are from the UT, i.e. above 7.5 km altitude during the CAFE-Africa mission.

of the PBL and the lower part of the FT. Previously reported daytime heterogeneous HONO sources in the NO_x polluted atmosphere include those reported by Li et al. (2012) (0.77 ppb h⁻¹), Ryan et al. (2018) (1 ppb h⁻¹), Jiang et al. (2020) (0.64 ppb h⁻¹), and Yu et al. (2022) (0.65 ppb h⁻¹), albeit at lower altitudes.

4.4 Gas phase formation and oxidation of peroxyxynitrous acid (HOONO): A possible explanation for excess-HONO in the cold UT?

HONO VMRs in the tropical UT inferred from the mini-DOAS measurements during the CAFE-Africa mission are largely more than (about a factor of five) what may be expected according to the known gas phase formation mechanisms and what is predicted by the EMAC model. While the presence of enhanced NO_x and HO_x from lightning are likely at these altitudes (Wennberg et al., 1998; Winterrath et al., 1999; Zhu et al., 2019; Mao et al., 2021; Brune et al., 2021; Tadic et al., 2021), the in situ measurements of NO and OH by the MPIC and of J_{HONO} by the HALO-SR from on board the HALO aircraft allow us to quantify the gas phase formation of HONO and thus excess HONO (see Fig. 9). Meanwhile, heterogeneous formation of HONO by one of the processes listed in Table A1 can largely be excluded based on the low aerosol surface and the necessary HONO formation rates which are in the range of hundreds of ppt h⁻¹.

Unexpectedly high HONO SCDs have also previously been observed using DOAS measurements in the limb direction from a balloon in the vicinity of a cumulonimbus cloud reaching the tropopause over Northeastern Brazil on June 13, 2005, but due to some clouds within the line of sight, [HONO] could not be inferred (Kritten, 2009). Further, Heue et al. (2014) reported



increased amounts of HONO (~ 160 ppt) (and of HCHO and NO_x) in a thunderstorm cloud probed by the CARIBIC flying laboratory (Civil Aircraft for the Regular investigation of the atmosphere based on an Instrument Container) over the Caribbean Sea in August 2011. Recent studies (Brune et al., 2021; Jenkins and Brune, 2025) highlight that oxidants and indeed HONO may be produced by lightning. Such extreme HONO production events in the vicinity of thunderstorm clouds may explain the variable HONO VMRs retrieved by the mini-DOAS at constant altitude, given the averaging volume of the scaling method compared to the in-situ measurements of NO, OH, and J_{HONO} .

In contrast, a preliminary analysis of spectra collected in polar air-masses in the low- NO_x UT indicates only 15ppt of HONO, an order of magnitude less than the VMRs observed during CAFE-Africa. The excess HONO observed in the UT during CAFE-Africa as well as EMeRGe-Asia (see Fig. 6) then indicates the necessity of sufficient NO_x precursors.

Another indication of the present deficit in our understanding of the coupled NO_x and HO_x cycles in the UT comes from two findings. First, it has been known for some time that in the UT, the measured (Leighton) ratio $\frac{\text{NO}_2}{\text{NO}}$ is often much larger than modeled when accounting for all known NO oxidants (Silvern et al., 2018; Shah et al., 2023). Second, also based on measurements of OH and HO_2 (or HO_x in the UT at twilight), Wennberg et al. (1999) speculated on a photolytic pathway for HO_2 production by peroxyxynitric acid (HNO_4) photolysis in the wavelength range $650 \leq \lambda \leq 1250$ nm.

Here, we suggest and investigate in some detail another explanation to reconcile our findings and the findings listed above, i.e. the existence of peroxyxynitrous acid (HOONO) in the cold UT, a potential intermediate candidate to form HONO and a so far overlooked species in the coupling of the NO_x and HO_x cycles.

Based on the suggestion of Amedro et al. (2020) that peroxyxynitrous acid (HOONO) may be present in the UT, we investigated its potential role to explain (a) our observation of excess HONO, (b) help to close the gap between measured and modeled $\frac{\text{NO}_2}{\text{NO}}$ and (c) provide a source for additional HO_2 at twilight in the UT.

Unfortunately, to date there are no reported measurements of HOONO in the atmosphere, but there are a wealth of experimental and theoretical studies on HOONO available, from which some information can be gained for our study (Golden et al., 2003; Zhu and Lin, 2003; Bohn and Zetzsch, 1997; Fry et al., 2004; Zhang and Donahue, 2006; Mollner et al., 2010; Bean et al., 2003; Chebbi et al., 2024; Butkovskaya et al., 2007). Unfortunately, most studies involve warmer (ambient) temperatures than relevant for the upper troposphere $\leq 220\text{K}$, which at present may limit a further quantification of the role HOONO may play in the UT.

Given the body of information already available on HOONO , there are several open questions regarding its potential role in UT photochemistry: (1) which reactions produce and destroy HOONO in the cold UT? (2) what are their temperature and pressure dependencies? (3) how much HOONO can be expected to be found in the cold UT? (4) may photochemical reactions of HOONO with oxidants efficiently produce HONO?

Accordingly, in the following we briefly review several theoretical and experimental studies of HOONO to determine what is known or controversial about the formation of HOONO in the atmosphere (for a possible reaction diagram see Fig. A4 in the appendix).



From theoretical and laboratory studies, it is known that HOONO forms in a side channel (8%) of the well studied reaction
 540 of OH and NO₂ which otherwise forms nitric acid (Mollner et al., 2010):



Moreover, Butkovskaya et al. (2007) suggested that again in a side channel (or as an intermediate) the reaction of HO₂ and NO into OH and NO₂:



545 may not only produce nitric acid,



while ab initio and master equation studies (Zhu and Lin, 2003; Zhang and Donahue, 2006) suggest that reaction R6 may proceed via HOONO as an intermediate.



550 These reactions are summarized in Fig. A4 in the appendix.

While unimolecular thermal decay is rapid at room temperatures, under the temperature and pressure conditions of the UT, the loss coefficient for thermal decomposition recommended by the IUPAC is 10⁻⁶ s⁻¹ (Golden et al., 2003). While such a slow decay could lead to some 80 ppt of HOONO in the UT, this is very much an upper bound and will be reduced by UV photolysis and reaction with OH (Fry et al., 2004).

555 Of note is that since most if not all laboratory studies of HOONO were conducted at room temperature, the short lifetime of HOONO may have obscured details of its unimolecular decay, unlike the information provided by theoretical studies. However, these theoretical studies suggest that in the cold UT, the known thermal decomposition of HOONO into its products OH and NO₂ may take up to 14 days, and therefore sizable amounts of HOONO would build up in this part of the atmosphere.

More recent studies also calculated the photolysis frequency of HOONO in the IR or UV. It was found that the lifetime of
 560 HOONO against photolysis may be limited to 45 hours in the IR (Fry et al., 2004) and 30 minutes in the UV (Chebbi et al., 2024).

Noteworthy is also, that neither unimolecular decay nor photolysis of HOONO would produce HONO, since besides being thermo-chemically unfavorable, it would require a rearrangement of the host molecule.

Further, since all reactive nitrogen may not build up as HOONO, it must be removed from the UT by either photolysis, or
 565 oxidation or both (see below). However, unless the photolysis rate of HOONO proceeds apace of the HONO photolysis rate, it cannot explain our HONO observations.

Instead, we further discuss thermo-chemically favorable loss mechanisms of HOONO, specifically three reactions which on paper lead from HOONO to HONO.



In order to investigate the steady state abundance of the relevant species (HOONO, HO₂, NO, NO₂, HONO,) from
570 which the required reaction rate coefficients for both the formation and destruction of HOONO can be estimated, we use on
board measured photolysis frequencies and VMRs of OH, NO, HO₂, NO₂, HONO, and O₃.

By considering a PSS, we quantify the reaction rate coefficients needed for the formation of relevant amounts of HOONO
and oxidation into HONO at UT temperatures. From the known HONO destruction rate ($J_{\text{HONO}} [\text{HONO}]$) of hundreds of
ppt h⁻¹, we can determine the required production rate of HONO and hence the production rate of HOONO ($k_7 [\text{HO}_2] [\text{NO}]$
575 + $k_4 [\text{HO}] [\text{NO}_2]$) and finally the reaction rate with an unknown oxidant (X) leading to HONO.

In consequence, the necessary production rate of HONO is

$$J_{\text{HONO}} \cdot [\text{HONO}] = k_7 \cdot [\text{HO}_2] \cdot [\text{NO}] + k_4 \cdot [\text{OH}] \cdot [\text{NO}_2] \quad (4)$$

$$= k_X \cdot [\text{X}] \cdot [\text{HOONO}] \quad (5)$$

Since in the UT, [HO₂] is much more abundant than [OH], the reaction of OH with NO₂ can be discarded in this context.

580 In the following, we consider three potential oxidants: O₃, OH, and NO (= X), of which the reactions with HOONO are all
exothermic (see Table A3).



585 In the absence of kinetic data or quantum chemical calculations regarding the reaction of HOONO with X and by rearrange-
ment of equation 5, we estimate the necessary reaction rate coefficients as a function of HOONO, for each $\frac{J_{\text{HONO}} \cdot [\text{HONO}]}{[\text{X}]}$ (see
Figure 10).

It is unlikely that the reaction of HOONO with OH may explain our HONO observations (see Fig. 10), since the necessary
reaction rate coefficient exceeds the maximum possible gas phase reaction rate coefficient for most measurements of OH,
590 unless more than 1 ppb HOONO is assumed (which would (often) exceed the NO_y budget in the UT (Wei et al., 2025)).

O₃ is abundant enough to explain a potential HONO source term, provided that HOONO exists only in the parts per trillion.

Meanwhile, the necessary reaction of HOONO with NO could explain a HONO source term if HOONO is found in the
tens of ppt, as is predicted by Amedro et al. (2020). However, both reactions would have a significant effect on the nitrogen
and ozone budgets of the UT, which for ozone is unlikely based on field observations. Here, the necessary reaction of HOONO
595 with O₃ would create an unlikely several ppb per day loss term for O₃ in the UT ($0.2 \text{ ppt s}^{-1} \cdot 43200 \text{ s} \approx 9 \text{ ppb day}^{-1}$),

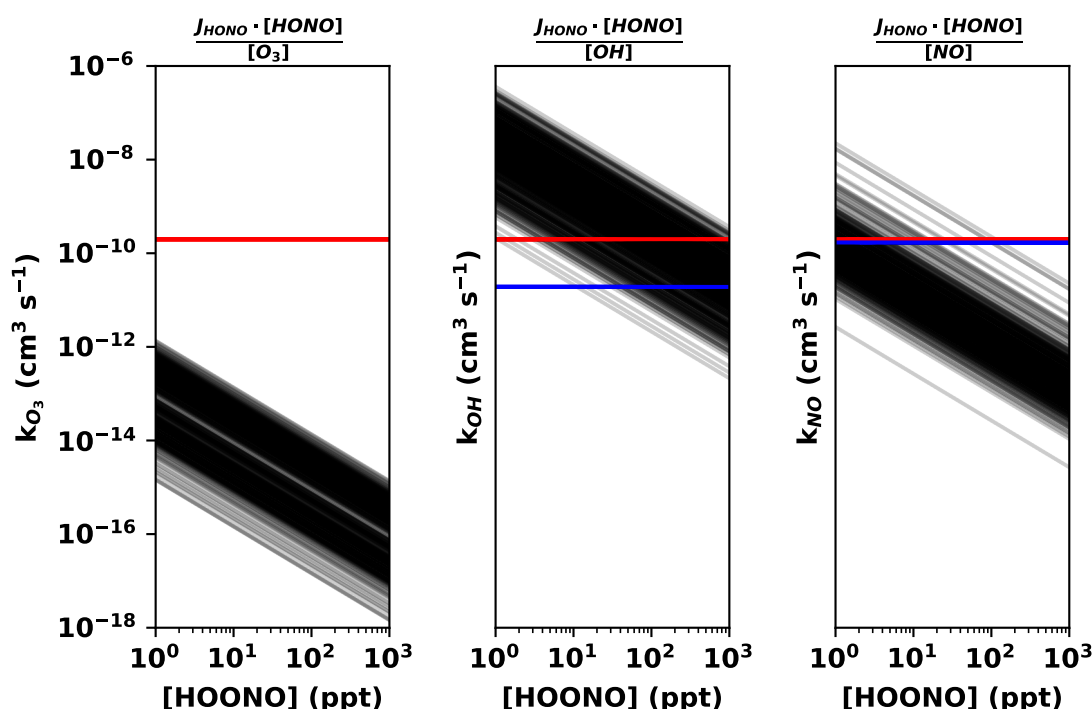


Figure 10. Required (two body) reaction rate coefficient k_X to solve equation 5 for measured concentrations of O_3 , OH , and NO ($= X$) as a function of assumed $HOONO$ VMRs. Each straight black line represent a single measurement of the involved species from the CAFE-Africa mission, i.e. data from eleven CAFE-Africa flights visually overlap. The horizontal red line in each panel represents the maximum reaction rate coefficient possible if each collision of the reactants would be successful. Accounting for activation energies reduces the upper bound further (blue lines); the upper bound for O_3 is 14 orders of magnitude below the graph at this scale. The steric effects (due to the relative orientations of the reactants) would further reduce the reaction rate in practice. Note the logarithmic axes.

which is not observed (Nussbaumer et al., 2023). Also, reaction R8 would require a rearrangement of intramolecular (bonded) O atoms through potentially large energy barriers, which is rather unlikely. Both arguments practically exclude reaction R8.

The proposed reaction of $HOONO$ with NO would produce NO_2 , creating a net-zero effect on the nitrogen budget by substituting reactions R7 and R10 for reaction R5, followed by the photolysis of $HONO$ into OH and NO .

600 In this way, $HOONO$ would act as a reservoir of NO_2 (and HO_x), biasing atmospheric measurements of NO_2 at temperatures sufficient to thermally dissociate $HOONO$ (see Silvern et al. (2018); Nussbaumer et al. (2021a); Shah et al. (2023)). Since OH would be recycled in the photolysis of $HONO$, the formation of $HOONO$ and reaction with NO would also not have an impact on HO_x in the UT, but $HOONO$ would simply serve as a temporary reservoir for OH . Potentially, both of these reactions take place, which would modulate the effect of either one in isolation.



605 Figure 10 indicates plausible pathways for the production of HONO from HOONO. However, there remain some open questions:

- Past laboratory studies of the $\text{HO}_2 + \text{NO}$ reaction have been performed at or near room temperature (Bohn and Zetzsch, 1997; Mertens et al., 2022), where HOONO would thermally decompose faster than the time frame given by the experiment, which would preclude HOONO detection. Further, the presence of NO in the reaction chamber would
610 potentially destroy HOONO. On the other hand, Butkovskaya et al. (2005, 2007) only measure some of the relevant species, precluding the detection of intermediates entirely. To what extent could the formation/presence of HOONO have been overlooked in these experiments? To date, only Butkovskaya et al. (2005, 2007) conducted experiments at these cold temperatures of the UT, and their results remain uncorroborated.
- The formation of HOONO via reaction R7 is potentially much more efficient than by reaction R4, and the reactants are
615 also more abundant in the UT during the CAFE-Africa mission ($\text{OH} \approx 1$ ppt, $\text{NO}_2 < 100$ ppt, $\text{NO} \gg 100$ ppt, $\text{HO}_2 \approx 10$ ppt). If reaction R4 produces HOONO at a sufficient rate to accumulate tens of ppt of HOONO in the UT against thermal decomposition or photolysis (Amedro et al., 2020), then even a minor branching ratio between reactions R7 and R5 would significantly increase the production (and therefore concentration) of HOONO (and potentially HONO) expected in the cold UT.

620 Our HONO measurements in the UT during CAFE-Africa offer a new line of evidence regarding necessary modifications of the NO_x and HO_x photochemistry in the cold UT. Peroxynitrous acid may become a precursor for HONO only if it is formed at a sufficient yield by reaction R7, survives thermal decomposition at the cold temperatures of the UT, and reacts with some oxidant at a sufficient rate to sustain HONO formation against its loss via photolysis. Here, we show that the reaction of HOONO with NO or O_3 is possible only on thermochemical grounds, and while the abundances of O_3 and NO
625 are sufficiently large, kinetic data at low temperatures (and pressures) are still missing. Whether the potential formation of HOONO via reaction R7 is fast enough to sustain the reservoir is unclear.

Most necessary to investigate this subject further are measurements of HOONO and its photolysis frequency in the atmosphere. In the absence of HOONO measurements, the mechanism may be inferred by observing HONO formation, or OH- HO_2 cycle chain lengths under certain conditions. The reaction rate coefficient of reaction R7 needs to be quantified in
630 the laboratory, especially at cold temperatures. Experimental and quantum chemical investigations of the potential reactions of HOONO with e.g. NO, O_3 are essential to reduce uncertainty regarding the lifetime and fate of HOONO and the potential for it to be a significant source of HONO in the UT.

Discussions among the co-authors suggested HONO formation mechanisms which share reactants with those listed in Table A1, which this analysis cannot entirely exclude. For example, the reaction of HO_2 with NO_2 , which has been determined to
635 be negligible (Graham et al., 1977), is similar to mechanism 3. The ostensibly heterogeneous reaction of HNO_3 with HCHO suggested by Chatfield (1994) may be investigated with the correlations of mechanism 9. Mechanism 6, the reaction of N_2O_4 – the formation of which is temperature dependent – on water surfaces (Horváth et al., 1988), should be more relevant in the UT. Unfortunately, aerosol surface area is limited within the air masses observed during the CAFE-Africa mission and



correlation analysis does not validate any particular formation mechanism (see Fig. A3 in the appendix). These and other gas
 640 phase reactions and heterogeneous routes to HONO should be investigated in a study on the global atmospheric budget of
 HONO.

5 Conclusions and Outlook

The present study reports on novel airborne remote sensing observations of nitrous acid in the troposphere from the HALO
 aircraft during 25 scientific flights of the EMERGE-EU, -Asia, and CAFE-Africa missions in summer 2017, spring 2018, and
 645 fall 2018, respectively. This work encompasses 200 DOAS retrievals of SCDs of O₃, O₄, NO₂, HCHO and HONO, in the
 UV-A and visible wavelength ranges, which are converted to VMRs using the O₃/O₄ scaling method. The observations of
 nitrous acid are complemented by coincident measurements of HCHO and NO₂, as well as simultaneous measurements of
 other trace gases and atmospheric parameters from a suite of in situ instruments on board the HALO aircraft. The atmospheric
 chemistry models EMAC and MECO(n) provide simulations for a priori information and post analysis comparison.

650 Since no other in situ instrument on board the HALO aircraft measures HONO, our mini-DOAS HONO measurements can
 only be compared with HONO measurements in climatologically similar conditions (a) made by a different technique within
 in the MBL around the Cape Verde Islands, (b) those made within the PBL, FT and UT made elsewhere in the world, and (c)
 model predictions (see Figure 5 and related references). For the latter it is in general found that, both the EMAC and MECO(n)
 models predict less HONO than is observed during all missions. This excess HONO has been observed in previous studies in
 655 the boundary layer and free troposphere (e.g. Li et al. (2014); Lee et al. (2016); Jiang et al. (2020)), but rarely from aircraft,
 especially in the UT. Elevated HONO is often observed in the PBL and FT, and has only previously been reported in the UT
 from air-borne DOAS measurements.

While the HCHO and NO₂ measurements compare well to model predictions, the observed HONO VMRs exceed model
 predictions by more than a factor of five and often up to an order of magnitude. Given the lifetime of HONO against photolysis
 660 (approximately 10 minutes — 8–12 minutes according to the measurements of the HALO-SR-A instrument) and the time scales
 for vertical transport, the HONO measured outside the lower boundary layer cannot be explained by surface fluxes, especially
 the elevated HONO observed in the FT and UT. This work therefore presents further compelling evidence for unidentified
 HONO sources in the troposphere, though the dominant HONO production mechanism may change with altitude and ambient
 conditions. Also, since these HONO production mechanisms may operate in parallel at varying strength, it is difficult or even
 665 impossible to decipher their relative strengths at any time and location without additional information, i.e. measurements of
 the relevant parameters (as evidenced in Table A1).

The HONO measured in the MBL at low-NO_x concentrations during the CAFE-Africa mission over the tropical Atlantic
 largely corroborates the findings, i.e. the production of HONO by nitrate photolysis, of Andersen et al. (2023) in the same
 region. This agreement of HONO measured with two different techniques in similar ambient conditions provides further
 670 evidence that the excess HONO observed with the mini-DOAS instrument is not due to methodological issues related to
 the employed limb spectroscopy. Moreover, the observed HONO in the 10 to 20 ppt range may be explained primarily by



the photolysis of nitrates, in agreement with previous studies (Ye et al., 2016b; Reed et al., 2017; Andersen et al., 2023). In particular, the EF in the frequency of particulate nitrate photolysis (relative to the photolysis frequency of gaseous nitric acid) is found to depend on the nitrate load. Unfortunately, our inferred EF cannot be precisely determined with the instruments on board the HALO aircraft, since only a minor fraction of total particulate nitrate was measured.

Within more polluted air masses, observed HONO may not be explained by the photolysis of nitrates alone. Excess HONO observed during the EMeRGe missions is largely confined to the PBL and FT, where most species implicated in the literature as potential HONO sources also have elevated VMRs, especially in the high-NO_x polluted boundary layer probed during those missions. Determining a single dominant HONO source in this context proves confounding. Several mechanisms may work in concert, depending on the chemical composition of the specific air mass being probed. In general, the reaction of NO₂ on humid aerosol surfaces are photo-sensitized or -catalyzed and are likely to be relevant in the context of our measurements. This study joins several others which find that HONO is related to production from photo-sensitized reactions of NO₂ (Lee et al., 2016; Zheng et al., 2020b; Jiang et al., 2020; Singh et al., 2021; Yu et al., 2022; Hu et al., 2022; Xing et al., 2023). More precisely determining a specific heterogeneous HONO formation mechanism would require additional instrumentation to quantify the pH of the aerosol, total nitrate load, mineral dust concentrations, etc.

While much of the excess HONO observed during the EMeRGe and CAFE-Africa missions in the PBL and FT can be attributed to formation mechanisms described as heterogeneous, excess HONO in the UT requires an alternative explanation given the timescale for uptake of HONO precursors on aerosols and the required rate of HONO formation. Gas phase explanations in the UT also require a quantification of the HO_x and NO_x budgets. During the EMeRGe missions, coincidentally measured species did not include OH (or HO₂, but RO₂^{*}), precluding analysis of the HO_x budget in the UT. Furthermore, measurements of HNO₃ — which enable an analysis of the NO_y budget — are not available.

Excess HONO (relative to the PSS HONO from measured NO, OH, and J_{HONO}) was also observed during the CAFE-Africa mission within the cold UT. Here, measurements of OH, NO₂, NO, and HO₂ enable the analysis of the HO_x and NO_x budgets. An investigation into the possibility of a gas phase HONO source, namely the oxidation of HOONO by OH, NO, or O₃, raises several hypotheses regarding the as yet largely unexplored photochemistry of HOONO at cold temperatures. In the absence of HOONO measurements in the atmosphere, and lacking kinetic data on HOONO formation and destruction at cold temperatures, our hypotheses that HONO is possibly formed by reactions of NO with HOONO is largely speculative.

The ubiquitous presence of HONO in the troposphere suggests that inconsistencies with models are not from a misunderstood emission strength, but rather a lack of representation and quantification of the reactions which produce HONO (Akimoto and Tanimoto, 2021). Attempts to model heterogeneous HONO formation mechanisms (Fu et al., 2019; Zhang et al., 2021; Ha et al., 2023) narrow (but do not close) the gap between measurements and models. Meanwhile, unquantified NO_x reservoirs evidenced by observed Leighton ratios (Silvern et al., 2018), as well as sources of HO_x (Wennberg et al., 1999) in the UT may arise from the presence of HONO and HOONO at those altitudes.

This study joins a limited set of airborne HONO observations in the upper boundary layer, free and UT under different photochemical conditions (Zhang et al., 2009; Heue et al., 2014; Li et al., 2014; Neuman et al., 2016; Ye et al., 2016b, 2018; Andersen et al., 2023). To our knowledge, the observations reported here represent the most extensive measurements of HONO



in the atmosphere to date. The mini-DOAS instrument has been deployed on several other missions of the HALO aircraft around the globe, the analysis of which may complement the present study, to illuminate the presence and formation mechanism(s) of HONO in the troposphere.

710 The results of our study clearly indicate that further investigation of the presence and formation mechanism(s) of HONO in the troposphere. These airborne observations of excess HONO in the UT urgently require corroborating studies in the laboratory and field. For an improved understanding of excess HONO in the polluted BL and FT, instruments which provide a more complete picture of the aerosol chemical composition and pH would behoove any further investigation. Indeed, it is rather likely that HONO is formed via multiple mechanisms, depending on the chemical composition of the air masses.

715 Future missions of the HALO aircraft which investigate tropospheric photochemistry should include measurements of HONO, since it is central to understand the HO_x budget and the oxidation capacity of the troposphere. Within the present study, the HONO budget could not be closed, therefore further study would require simultaneous airborne measurements of all species relevant to potential HONO formation mechanisms, in particular OH, NO, NO₂, HO₂, HNO₃, HNO₄ and HOONO, as well as relevant aerosol parameters (e.g. chemical composition, pH, and water content). Additionally, instrumentation to
720 determine the presence of ice-clouds would benefit the investigation of HONO formation.

The observed HONO, upon photolysis, represents an OH source term with a strength of up to 0.25 ppt s⁻¹ or 0.9 ppb h⁻¹, depending on the altitude, location, and photochemical regime. This represents a significant source of OH in the troposphere, thereby affecting the atmospheric lifetime (and consequent radiative forcing) of greenhouse gases, such as methane. The presence and sources of HONO in the troposphere thereby affects our understanding of climate change, the fate of most air
725 pollutants, and consequently, human health.

Appendix A: Additional figures and tables



Table A1. Homogeneous (gas phase) and heterogeneous (mixed phase) HONO formation mechanisms investigated in past studies.

No.	Reactants		Products	Reference	Comment
homogeneous					
1	NO + OH + M	→	HONO + M	Wine et al. (2020)	(i)
2	ortho-nitro-phenols + hν	→	HONO + products	Bejan et al. (2006)	(ii)
3	HO ₂ · H ₂ O + NO ₂	→	HONO + O ₂ + H ₂ O	Li et al. (2014)	(iii)
4	NO ₂ + hν	→	NO ₂ [*]	Crowley and Carl (1997)	(iv)
	NO ₂ [*] + H ₂ O	→	HONO + OH	Li et al. (2008)	
heterogeneous					
5	NO ₂ + HC _{red}	→	HONO + HC _{ox}	Ammann et al. (1998)	(v)
6	2NO _{2(g)}	⇌	N ₂ O _{4(g)}	Goodman et al. (1999)	(vi)
	N ₂ O _{4(g)}	⇌	N ₂ O _{4(surface)}	J. Finlayson-Pitts et al. (2003)	
	N ₂ O _{4(surface)}	→	ONONO _{2(surface)}	Yabushita et al. (2009)	
	ONONO _{2(surface)} + NO _{2(g)}	→	N ₂ O _{4(surface)} + NO _{2(g)}	Martins-Costa et al. (2020)	
	ONONO _{2(surface)} + H ₂ O _(surface)	→	HONO _(g,surface) + HNO _{3(surface)}	Gen et al. (2024)	
7	Dust + hν	→	h ⁺ + e ⁻	Ndour et al. (2008)	(vii)
	e ⁻ + O ₂		O ₂ ⁻	Dupart et al. (2014)	
	NO ₂ + O ₂ ⁻ (or e ⁻)	→	NO ₂ ⁻ + O ₂	Dyson et al. (2021)	
8	HNO _{3(ads)} + hν	→	HONO + O(³ P)	Zhou et al. (2003)	(viii)
9	HNO ₃ + VOC	→	HONO + VOC _{ox}	Rutter et al. (2014)	(ix)
10	NH ₃ + ONONO ₂ + nH ₂ O _(l)	→	HONO + HNO ₃ + NH ₃ + (n-1)H ₂ O _(l)	Li et al. (2018a)	(x)
11	2NO _{2(a)} + HSO _{3(a)} ⁻ + H ₂ O _(l)	→	3H _(a) ⁺ + 2NO _{2(a)} ⁻ + SO _{4(a)} ²⁻	Cheng et al. (2016)	(xi)
12	HA + hν	→	A _{red} + X	George et al. (2005)	(xii)
	A _{red} + NO ₂	→	A'' + HONO	Stemmler et al. (2006)	
13	NO ₃ ⁻ + hν	→	NO ₂ + O ⁻	Warneck and Wurzinger (1988)	(xiii)
			(Φ = 0.1)	Mark et al. (1996)	
	NO ₃ ⁻ + hν	→	NO ₂ ⁻ + O	Scharko et al. (2014)	
			33 (Φ = 0.01)	Benedict et al. (2017)	



- (i) Included in atmospheric chemistry models.
- (ii) Ortho-nitro-phenols are not measured in this work.
- (iii) Refuted by Ye et al. (2015) due to a small HONO yield (<0.03), though Li et al. (2015) maintained that a gas phase
 730 source of HONO consumes nitrogen oxides in the troposphere.
- (iv) In the atmosphere, the rate is too small. See also Crowley and Carl (1997); Li et al. (2008); Amedro et al. (2011); Dillon
 and Crowley (2018).
- (v) A rapid HONO formation (but not of HNO_3) is observed from reactions of NO_2 on fresh soot, but soot becomes
 735 deactivated after a few seconds (Kalberer et al., 1999). UV radiation increases the reactivity of the soot (Monge et al.,
 2010).
- (vi) J. Finlayson-Pitts et al. (2003) found that the reaction is first order with respect to NO_2 due to its chemical equilibrium
 with N_2O_4 . The equilibrium constant of N_2O_4 is too small for atmospheric concentrations of NO_2 , even though it may
 increase with decreasing temperature. See also Yabushita et al. (2009); Martins-Costa et al. (2020); Gen et al. (2024).
- (vii) Under UV-A irradiation, Dupart et al. (2014) found $\gamma = 0.6\text{--}2.4 \cdot 10^{-8}$ and a HONO yield of 30 %. Goodman et al.
 740 (1999) performed their experiment on hydrated silica particles, though the reaction applies to surfaces generally.
- (viii) Laufs and Kleffmann (2016) found $J(\text{HNO}_3 \rightarrow \text{HONO}) = 2.4 \cdot 10^{-7} \text{ s}^{-1}$ and for the secondary produced NO_2 a $J(\text{HNO}_3$
 $\rightarrow \text{NO}_2) = 1.1 \cdot 10^{-6} \text{ s}^{-1}$ both at (SZA = 0° , and 50 % RH). N. Sullivan et al. (2018) noted the strong dependence of
 the absorption cross-section of adsorbed HNO_3 on RH. See also Zhou et al. (2003); Ziemba et al. (2010); Song et al.
 (2023a).
- (ix) This mechanism was studied in the context of diesel exhaust. The phase is disputed (Spataro and Ianniello, 2014).
 745
- (x) NH_3 mediation reduces the energy barrier for the reaction to 0.5 kJ/mol. See also Xu et al. (2019).
- (xi) This reaction may be pH dependent; aerosol pH was not measured in this work. See also Li et al. (2018b).
- (xii) HA: humic acid; A_{red} : reductive centers; X: oxidant. George et al. (2005) found a humidity and irradiation dependence.
- (xiii) Scharko et al. (2014) found that the addition of an organic OH scavenger increased the HONO formation by a factor
 750 of four. Benedict et al. (2017) determined the quantum yield ($\phi(\text{NO}_2^-)$) in the photolysis of NO_3^- to 1.1 % (at 313 nm,
 50 μM nitrate, $\text{pH} \geq 5$). They demonstrated that the larger $\phi(\text{NO}_2^-)$ than previously assumed is primarily due to the
 presence of an OH scavenger.



Table A2. For each target trace gas retrieved with DOAS analysis, the retrieval scenario parameters including wavelength range, included absorbers (see Table 1), I_0 effect, Ring effect (R), DOAS polynomial order, and offset polynomial order are specified.

Target	Wavelength (range) [nm]	Fitted absorbers	Parameters	Polynomial	Offset
O ₃	335–362	1, 2, 3, 4	$I_0, R, R \cdot \lambda^4$	2	1
	435–490	1, 2, 3, 4b	$I_0, R, R \cdot \lambda^4$	2	1
O ₄	338–370	1, 2, 3, 4	$I_0, R, R \cdot \lambda^4$	2	1
	434–486	1, 2, 3, 4b	$I_0, R, R \cdot \lambda^4$	2	1
NO ₂	333–379	1, 2, 3, 4, 5, 6	$I_0, R, R \cdot \lambda^4$	2	1
	445–491	1, 2, 3, 4b	$I_0, R, R \cdot \lambda^4$	2	1
HCHO	323–357	1, 2, 3, 4, 5, 6	$I_0, R, R \cdot \lambda^4$	2	1
HONO	337–373	1, 2, 3, 4, 5, 6,	$I_0, R, R \cdot \lambda^4$	2	1



Table A3. Thermochemistry of reactions R8, R9, and R10 at 220 K. For each reaction, the enthalpy (H), the product of entropy (S) and temperature (T), and the Gibbs free energy (G). Entropy and enthalpy data are from <https://webbook.nist.gov> and <https://atct.anl.gov>, except for HOONO, which is taken from Szakács et al. (2011).

reaction	ΔH [kJ mol ⁻¹]	$T^*\Delta S$ [kJ mol ⁻¹]	ΔG [kJ mol ⁻¹]
HOONO + O ₃ → HONO + 2O ₂	-208	33	-241
HOONO + OH → HONO + HO ₂	-91	5	-96
HOONO + NO → HONO + NO ₂	-123	2	-125

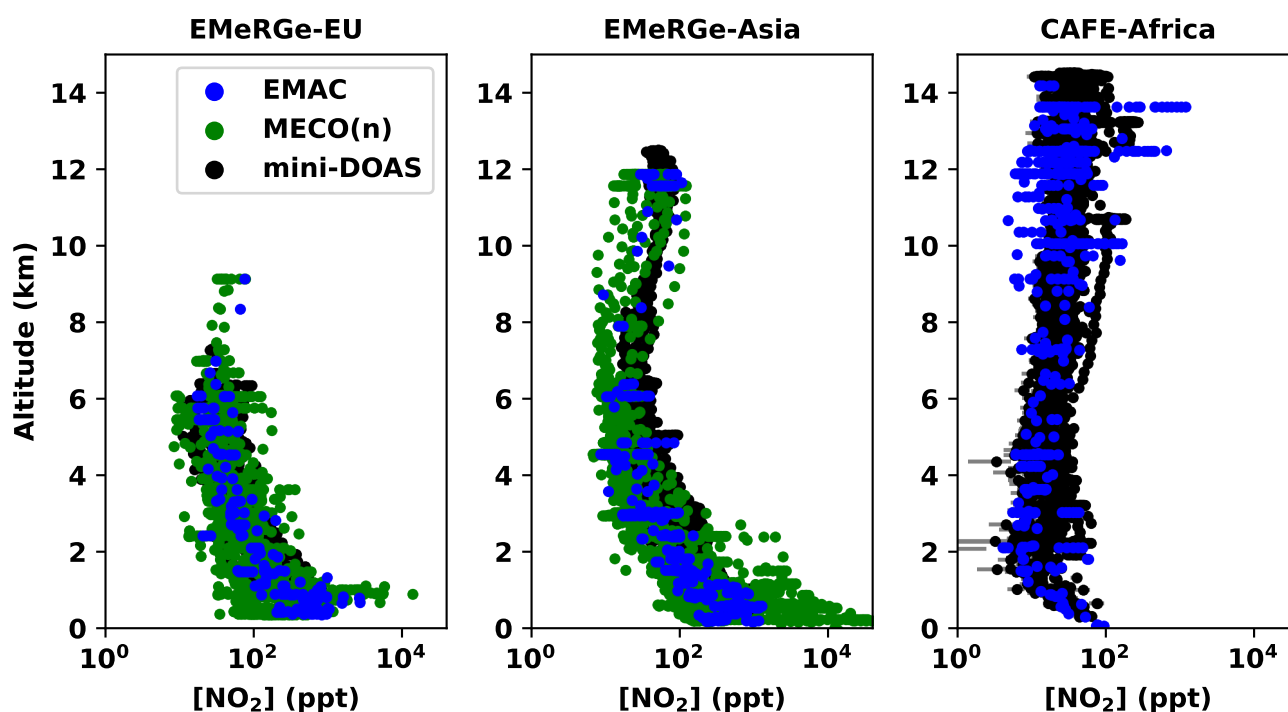


Figure A1. Altitude profiles of NO_2 as observed by the mini-DOAS instrument (black – uncertainties in gray), as predicted by the EMAC model (blue), and as predicted by the MECO(n) model (green), for the three research missions: EMeRGe-EU (left), EMeRGe-Asia (center), and CAFE-Africa (right). MECO(n) data is not available for the CAFE-Africa mission. Note the logarithmic x-axes.

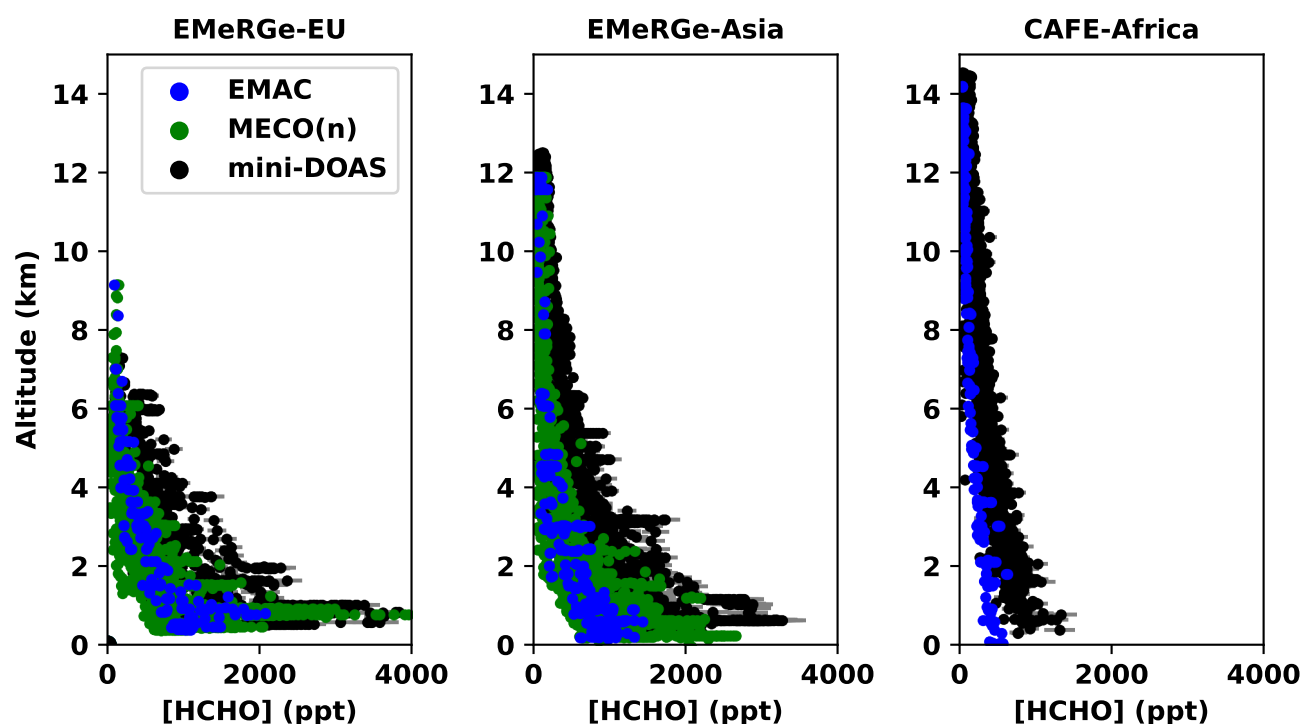


Figure A2. Altitude profiles of HCHO as observed by the mini-DOAS instrument (black – uncertainties in gray), as predicted by the EMAC model (blue), and as predicted by the MECO(n) model (green), for the three research missions: EMeRGe-EU (left), EMeRGe-Asia (center), and CAFE-Africa (right). MECO(n) data is not available for the CAFE-Africa mission.

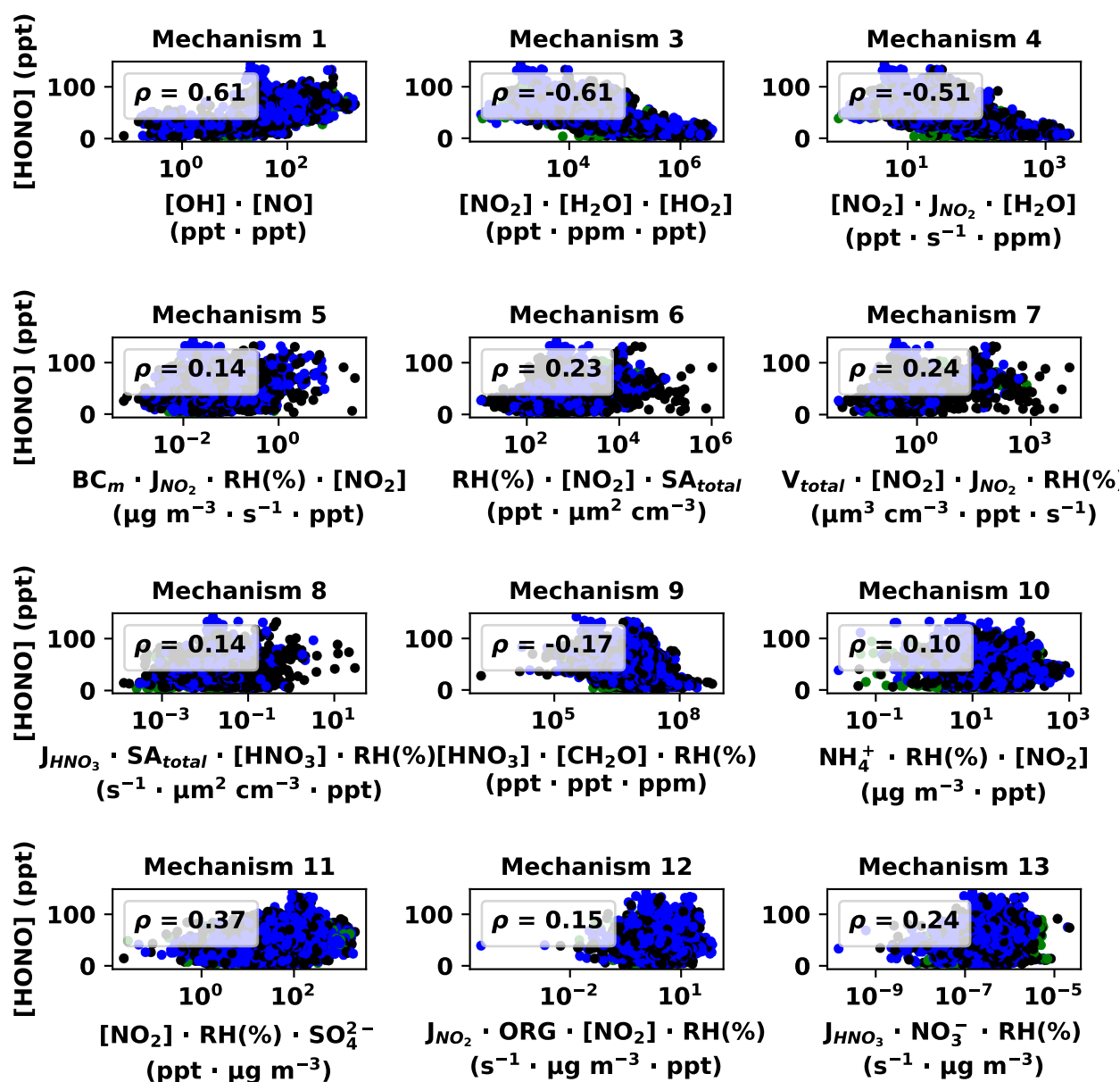


Figure A3. For twelve of the thirteen potential HONO formation mechanisms listed in Table A1, the observed HONO VMRs retrieved from 6929 spectra are plotted against the product of any measured reactants (or proxies thereof), from the CAFE-Africa mission, in the UT. In each panel, the Spearman correlation coefficient ρ is given. Data is colored by the tags described in Sect. 3.3; green represents biomass burning influence, and blue is assumed to be background air. Missing tags are represented in black. Note the logarithmic x axes. Mechanism 2 is excluded entirely because ortho-nitro-phenols were never measured.

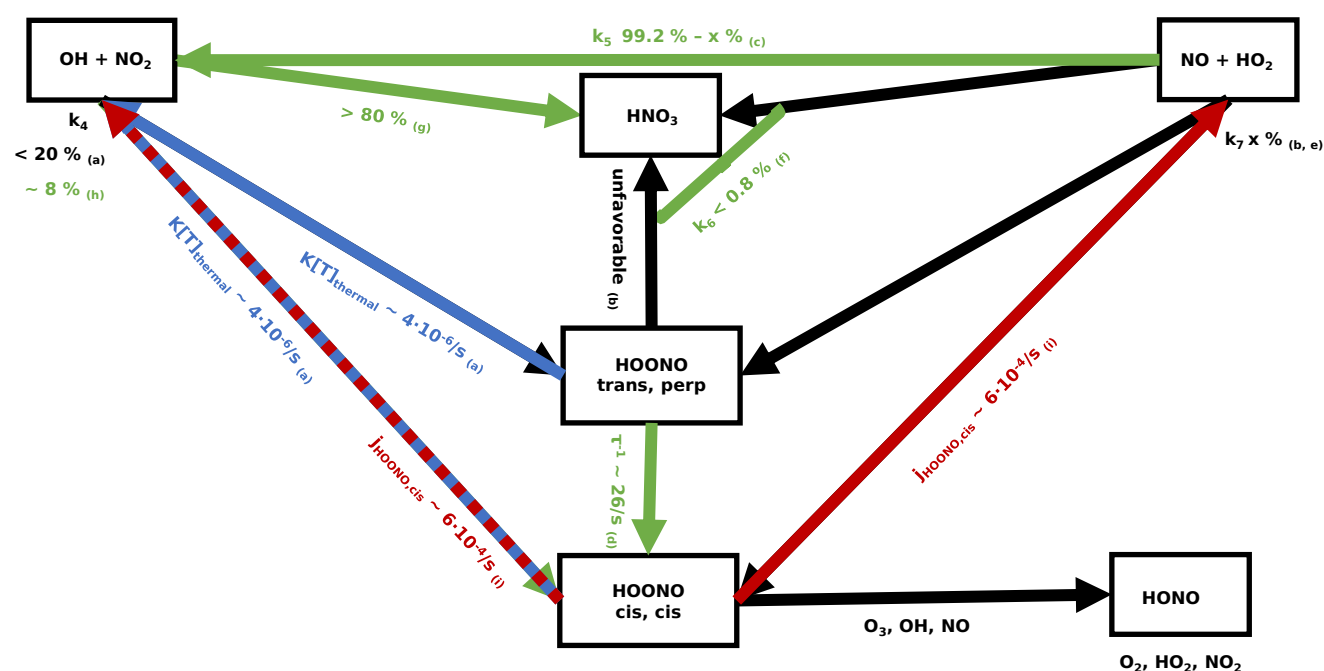


Figure A4. Possible reaction diagram leading to the formation and destruction of HOONO at temperature and pressure conditions of the UT, based on a review of the available literature (studies (a) to (i): Golden et al. (2003); Zhu and Lin (2003); Bohn and Zetzsch (1997); Fry et al. (2004); Zhang and Donahue (2006); Butkovskaya et al. (2007); Mollner et al. (2010); Bean et al. (2003); Chebbi et al. (2024)). Green arrows represent experimental measurements, while black arrows represent master equation or ab initio studies. The blue arrows represent the thermal decomposition of HOONO, $k[T]_{thermal}$ (at 220 K and 267 mbar), while the red arrows represent photolysis.



Data availability. The mini-DOAS data — as well as data from the other instruments on board HALO — are archived in the HALO repository, which can be accessed after signing a data protocol.

755 *Author contributions.* BW and MR operated the mini-DOAS instrument. SR and PJ performed the EMAC simulations. MM performed the MECO(n) simulations. BW performed the data analysis and wrote the manuscript, with contributions from all co-authors.

Competing interests. At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics. The authors also have no other competing interests to declare.

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765 *Acknowledgements.* We are grateful to the HALO community for organizing the research missions. JPB and AMD proposed, coordinated, and provided the scientific leadership for the EMerGe campaigns in Europe and Asia. These initiatives were partly funded through the Priority Program (Schwerpunktprogramm) SPP 1294, Atmospheric and Earth System Research with HALO – High Altitude and Long Range Research Aircraft, of the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), as well as by the University and State of Bremen. In addition, the University and State of Bremen supported the individual research of JPB and AMD. DT and SR gratefully acknowledge the Gauss Centre for Supercomputing e.V. (www.gauss-centre.eu) for funding this project by providing computing time on the GCS Supercomputer JUWELS (Alvarez, 2021) and by the John von Neumann Institute for Computing (NIC) at the Jülich Supercomputing Centre (JSC). The authors gratefully acknowledge the Earth System Modelling Project (ESM) for funding this work by providing computing
770 time on the ESM partition of the supercomputer JUWELS at the Jülich Supercomputing Centre (JSC).

Financial support. This research was supported by the German Research Foundation (DFG; HALO-SPP 1294), specifically the research grants (DFG; grant nos. PF 384/7-1, PF 384/9-1, PF 384/16-1, PF 384/17, PF 384/19, PF 384/24-1, BU 688/27-1, BU 2599/10-1, BO 1829/10-1, SCHN 1138/5-1). HKMS measurements were funded by the DFG under the grant no. NE 2150/1-1 and by the Karlsruhe Institute of Technology.



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