Airborne measurements of nitrous acid (HONO), hydroxyl (OH), nitric oxide (NO), hydroperoxyl (HO2), and nitrogen dioxide (NO2) in the upper troposphere (UT): is peroxynitrous acid (HOONO) a source of HONO?

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Why and how we measure HONO in the troposphere

- OH, the most important oxidant in the atmosphere, is produced from HONO photolysis.
- In the troposphere, measured HONO often exceeds model predictions.
- There may also be an unaccounted NO_x reservoir in the upper troposphere (1).
- Onboard the HALO aircraft, HONO (and other gases) is measured in limb scattered UV/vis skylight using the mini-DOAS instrument. The DOAS inferred absorptions are interpreted by radiative transfer calculations and by applying the O_4 scaling method (2).

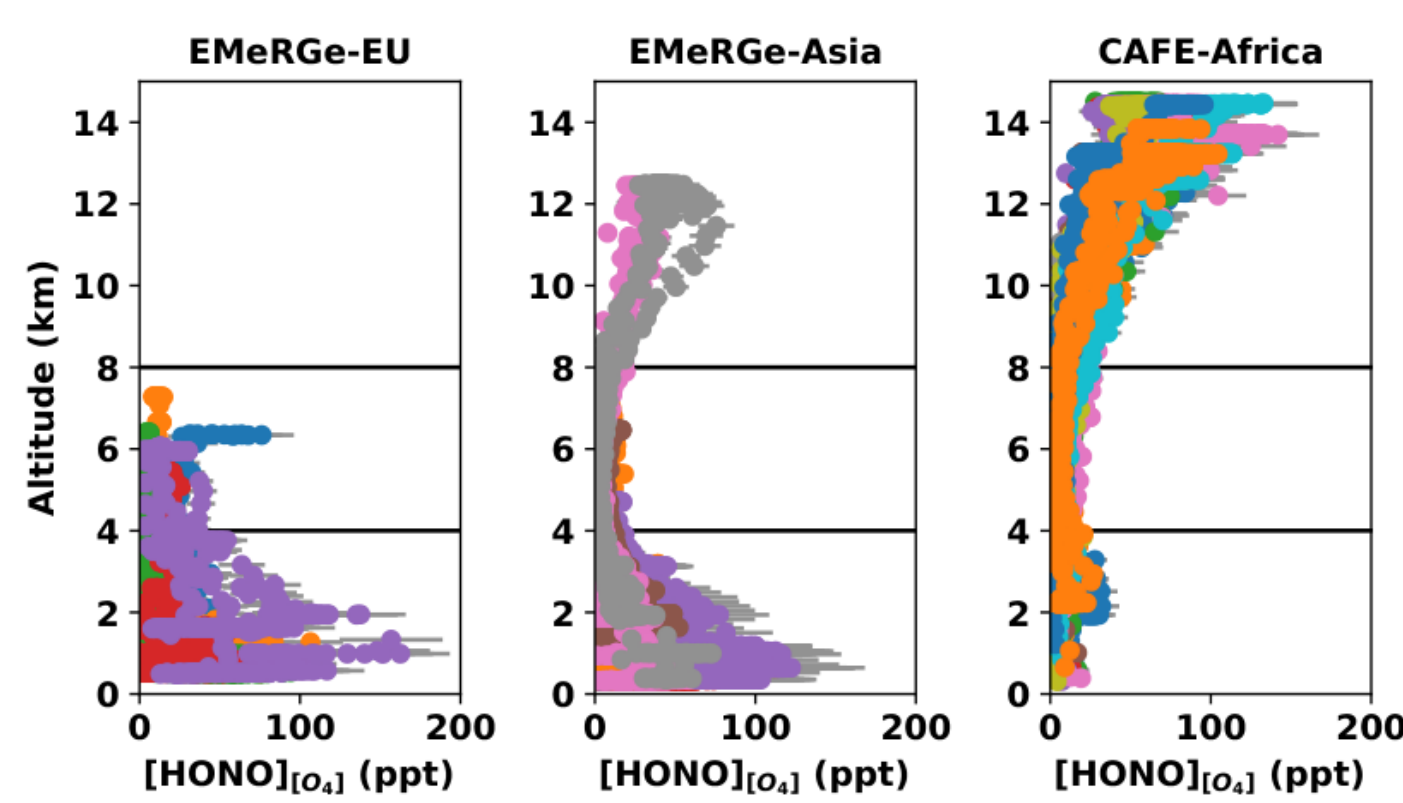## Measurements of excess HONO in the troposphere

Fig. 1: Altitude profiles of HONO volume mixing ratios from the EMeRGe-EU (2017), -Asia (2018), and CAFE-Africa (2018) campaigns. The high VMRs in the lower troposphere during EMeRGe and the upper troposphere during CAFE exceed predictions of the EMAC and MECO(n) models by a factor of 2-10.

- Excess HONO (relative to model predictions) is observed in the polluted air masses of the EMeRGe campaigns, above the boundary layer, and into the free troposphere.
- According to the literature there are several potential heterogeneous sources of HONO; most require NO_2 and aerosol or cloud particles.
- The correlation between reactants (or proxies thereof) and the HONO source depends on the chemical composition of the air masses.

Table 1: Thirteen potential HONO sources according to previous studies. Most are mixed phase reactions. Some gas phase reactions have been discounted (ibid.).

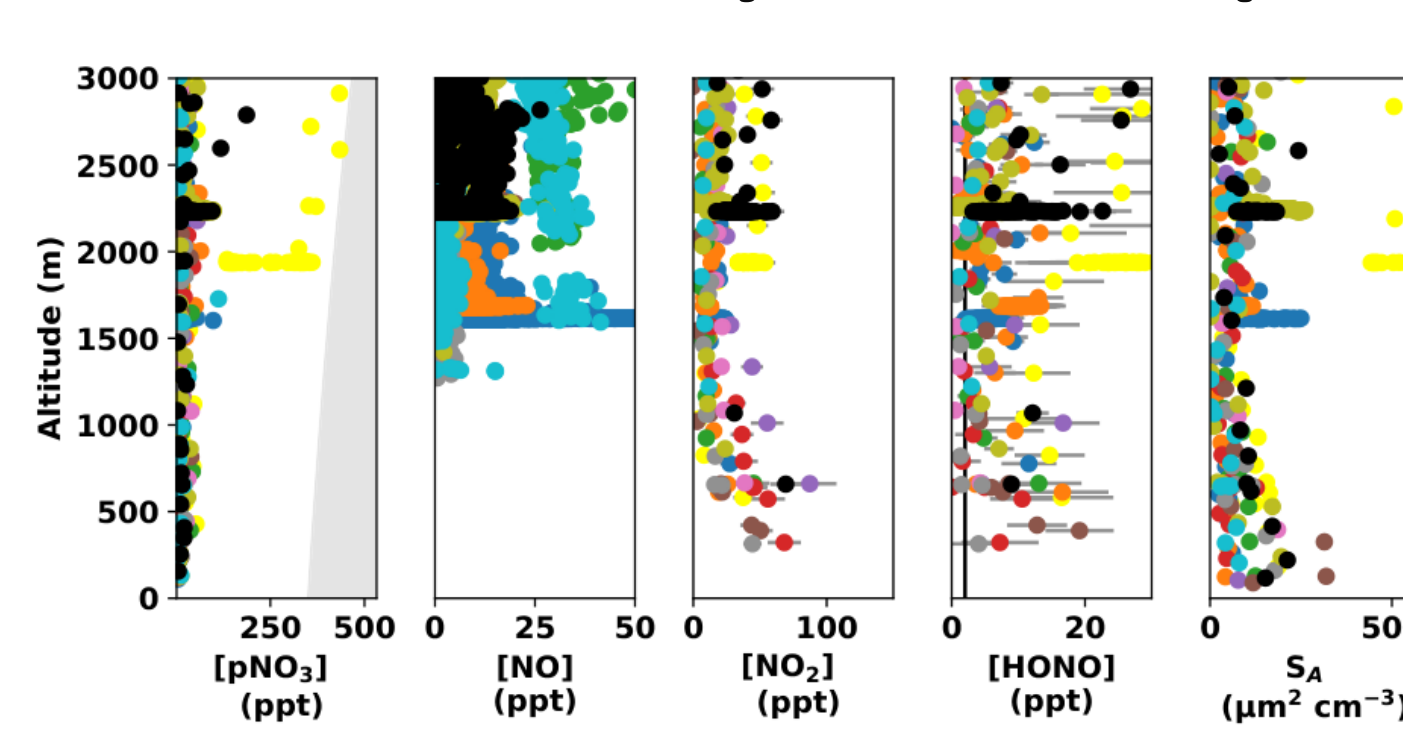## Photolysis of particulate nitrate in the low-NO_x MBL

Fig. 2: Altitude profiles of nitrogen containing species and aerosol surface area in the MBL during CAFE-Africa. The black line in the fourth panel represents HONO formed by the known gas phase reaction OH + NO.

- Our measured HONO in the low-NO_x marine boundary layer (MBL) is corroborated by those of Andersen et al. (2023). Here, measured HONO still exceeds model predictions as well as gas phase formation according to measured OH and NO.
- Under these low-NO_x conditions, photolysis of pNO_3 may explain HONO in the observed tens of ppt range (Ye et al., 2016).
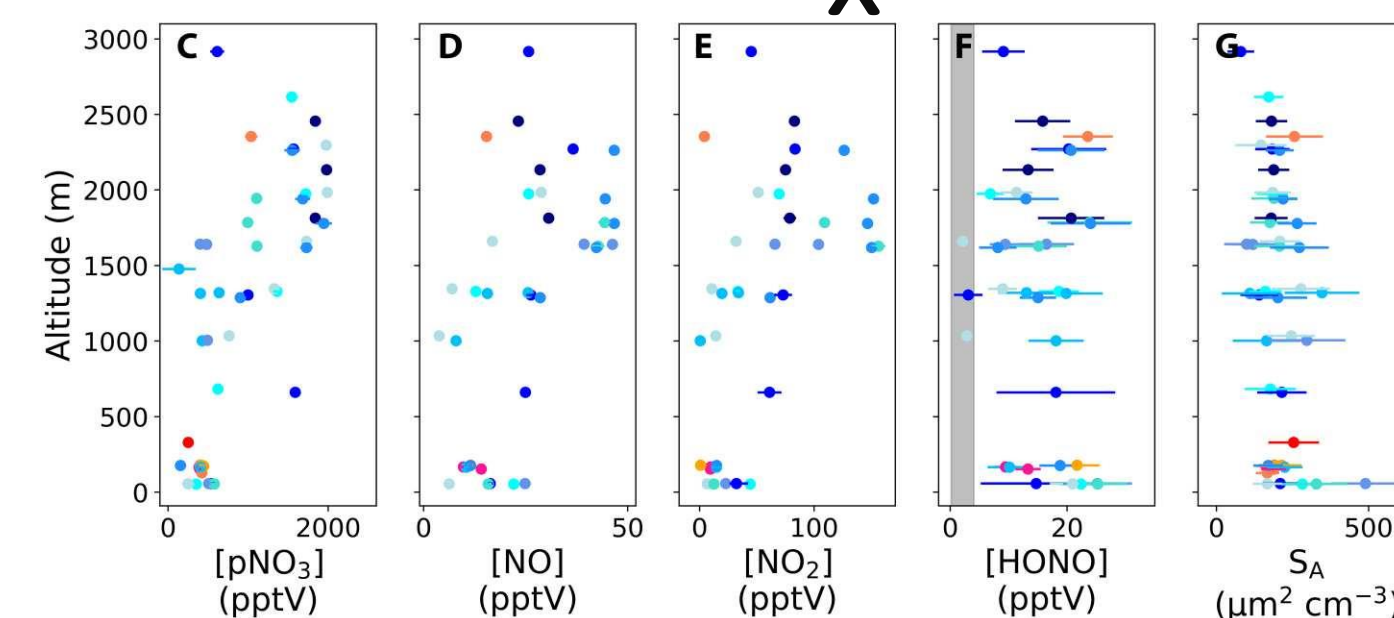

Fig. 3: Altitude profiles of nitrogen containing species and aerosol surface area in the MBL from Andersen et al. (2023). The order of magnitude discrepancy in observed pNO_3 (c.f. Fig. 2) is due to different particle sizes being measured by the instruments.

HOONO as a potential gas phase source of HONO

- In the UT, upwards of 100 ppt HONO is measured during most flights (Fig. 1, right panel). This exceeds model predictions, and gas phase formation from OH + NO.
- Heterogeneous sources can be ruled out by the collision rate of air with measured aerosol surface area. Therefore, one may speculate on other gas-phase HONO formation.
- An explanation may be (exothermal) reactions of peroxynitrous acid (HOONO) with other oxidants (O_3, OH, NO, ...).
- Gas phase formation of HOONO is known from the reaction OH + NO_2 (5), but controversial for HO_2 + NO (6).
- HOONO has not yet been measured in the atmosphere. The time for unimolecular decay at low temperatures (~220 K) due to chemical equilibrium is ~ 14 days. Other losses such as photolysis or oxidation are not quantified.
- The steady state production and destruction rates of HOONO necessary to explain our observations can be determined from the measured quantities OH, NO, NO_2, HO_2, O_3, J_{HONO} and HONO.
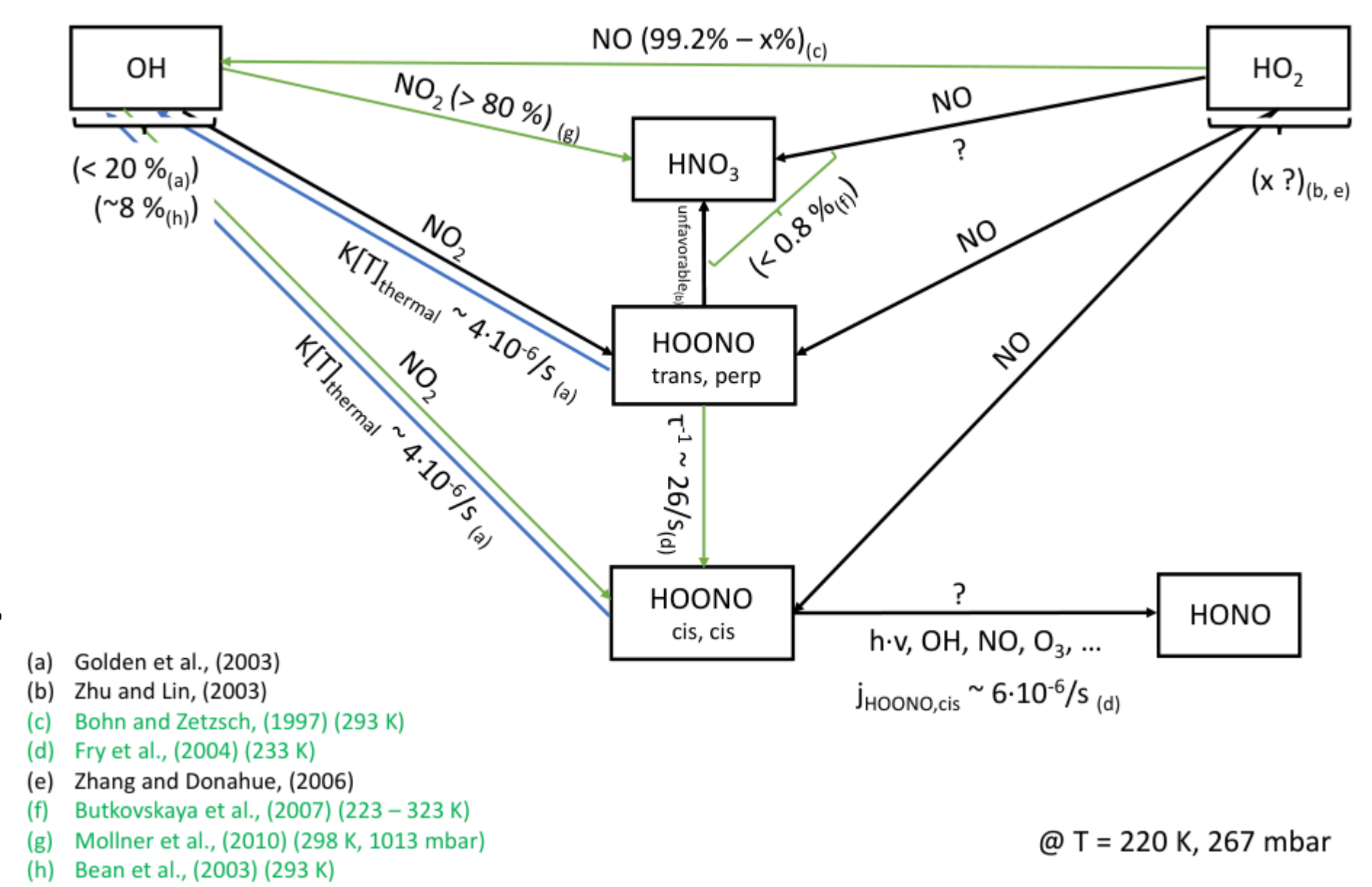

Fig. 4: Reaction diagram of the formation of HOONO according to the recent literature.

Conclusions

I. In the polluted boundary layer and free troposphere, HONO is produced heterogeneously; precise mechanisms remain elusive.

II. In the low-NO_x MBL, HONO is chiefly produced by the photolysis of pNO_3 (Ye et al., 2016; Andersen et al., 2023; and the present study).

III. In the UT, heterogeneous sources of HONO at the required rate can be ruled out. We speculate that HONO is produced from the oxidation of HOONO by OH, NO or O_3, the former being produced by the reaction of HO_2 and NO and surviving thermal decomposition at low temperatures. Reaction kinetics studies are underway to determine the feasibility of these results.

IV. Further study requires measurements of HOONO in the atmosphere, as well as laboratory measurements of its formation and destruction for relevant atmospheric temperatures and pressures.

Acknowledgements

References

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