Response to Comment on “Missing gas-phase source of HONO inferred from Zeppelin measurements in the troposphere”

Ye et al. have determined a maximum nitrous acid (HONO) yield of 3% for the reaction \( \text{HO}_2 \cdot \text{H}_2\text{O} + \text{NO}_2 \), which is much lower than the yield used in our work. This finding, however, does not affect our main result that HONO in the investigated Po Valley region is mainly from a gas-phase source that consumes nitrogen oxides.

The self-cleansing capacity of the atmosphere is largely dependent on the concentration level of hydroxyl radicals (OH) (7). Nitrous acid (HONO) is an important precursor of OH in the troposphere (2–4). Based on observations of HONO and its budget in the Po Valley region in Italy, we concluded that HONO formation in a sunlit layer separated from the ground surface is from a gas-phase source consuming nitrogen oxides (\( \text{NO}_x = \text{NO} + \text{NO}_2 \) and potentially hydrogen oxide (\( \text{HO}_x = \text{OH} + \text{HO}_2 \)) radicals (5). In our work, we proposed that the reaction \( \text{HO}_2 \cdot \text{H}_2\text{O} + \text{NO}_2 \) could be the HONO source if its HONO yield was 100%. Based on airborne observations in the United States, Ye et al. (6) determined an upper limit of 3% for the HONO yield in the reaction \( \text{HO}_2 \cdot \text{H}_2\text{O} + \text{NO}_2 \), much less than necessary to explain our HONO observations. Ye et al. therefore imply that other HONO sources are active. As an example, they suggest photolysis of particulate nitrate and speculate that the corresponding net source of \( \text{NO}_x \) may be lower than predicted in our work because of missing \( \text{NO}_x \) sinks in our model calculations.

The major conclusion of our paper (5) is based on the analysis of the observed \( \text{NO}_x \) and \( \text{HO}_x \) budgets, where we considered sources that either release HONO from stable precursors (external source) or generate HONO by consuming \( \text{NO}_x \) and/or \( \text{HO}_x \) (see Section 1.2 in the supplementary materials of (5)). The important aspect is that if HONO is formed by a mechanism that consumes \( \text{HO}_x \), the net contribution of HONO photolysis to the HONO production can become small. Our sensitivity tests analyzing observed \( \text{NO}_x \) and \( \text{OH} \) concentrations point to a gas-phase source that requires \( \text{NO}_x \) and, at a less confident level, also \( \text{HO}_x \). At this stage, we did not make any assumption regarding the exact mechanism forming HONO, and thus this main finding is independent of the specific reaction in question.

Given the availability of the measured parameters, we only considered reactions that directly consume \( \text{NO}_x \) and \( \text{HO}_x \) to produce HONO. Experiments still ongoing in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric Photochemistry In a large Reaction Chamber) at our institute imply that none of these reactions (including \( \text{HO}_2 \cdot \text{H}_2\text{O} + \text{NO}_2 \)) can substantially contribute to the HONO formation. This is in agreement with the results by Ye et al. If the process producing HONO is not related to the consumption of \( \text{HO}_x \) radicals, we agree with the conclusion by Ye et al. that HONO should remain an important net OH precursor.

Furthermore, Ye et al. suggest particulate nitrate photolysis as a potential HONO source under our measurement conditions. Particulate nitrate photolysis is an external source of HONO and was therefore not considered in our work. During the Pan-European Gas-Aerosols Climate Interaction Study (PEGASOS) field campaign in the Po Valley (see Section 1.1 in the supplementary materials of (5)), the spatial distribution of aerosol composition was measured on a number of flights. The average particulate nitrate concentration in the residual layer was -1 to 2 \( \mu \text{g m}^{-3} \) (7). If we assume that the observed HONO was formed exclusively from photolysis of particulate nitrate, the required photolysis frequency would be \( -3 \times 10^{-1} \text{ s}^{-1} \), which is an order of magnitude greater than that reported in the literature for surface adsorbed HNO_3 under full sun conditions (8). Substantial HONO formation by nitrate photolysis is therefore unlikely.

Regarding potentially missing \( \text{NO}_x \) sinks in our model, we note that the full RACM-MIM-GK mechanism (9) was applied. In addition to the \( \text{OH} + \text{NO}_x \) reaction, the formation of organic nitrates (RONO_2) and peroxyacetyl nitrates (PANs) is included in the mechanism as \( \text{NO}_x \) sinks. Moreover, the model calculations for \( \text{NO}_x \) (i.e., model scenario M2 and M3 in figure 3 of (5)) are constrained by measured OH, trace gases, relative humidity, temperature, pressure, and photolysis frequencies [see section 1.2 in the supplementary materials of (5)]. In general, our model calculations show that the \( \text{NO}_x \) sinks during our observations are dominated by the \( \text{OH} + \text{NO}_x \) reaction. We did not measure alkylperoxy radicals (RO_2), PANs, or bromine monoxide (BrO) during the field campaign. However, based on the model scenario assuming externally formed HONO ([i.e., model scenario M2 in figure 3 of (5)]), we performed additional sensitivity studies on the \( \text{NO}_x \) sinks as suggested by Ye et al. To explain the discrepancy between the measured and modeled \( \text{NO}_x \) concentration via formation of RONO_2, precursor volatile organic compound concentrations would be required to be an order of magnitude higher than the measured values. This results in modeled OH reactivities that are three times higher than measured. Note that for model calculations shown in figure 3 and 4 in (5), given the accuracy of OH reactivity measurement, good agreement is always found between the modeled and measured values. The formation of PANs shows minor influence on the \( \text{NO}_x \) simulation. When we change the initial PANs concentration from 200 parts per trillion (ppt) to 0 in the model, the calculated \( \text{NO}_x \) concentration only decreases by less than 10%. When we include the formation and photolysis of BrONO_2 and set the BrO concentration to a constant value of 3 ppt, the modeled \( \text{NO}_x \) concentration decreases by ~10% and thus still remains significantly higher than the measured values. A match between the modeled and measured \( \text{NO}_x \) concentration can only be reached if the BrO concentration is higher than 30 ppt. High BrO concentrations are usually found under maritime conditions. According to (10), which is cited by Ye et al., a BrO concentration of 3 ppt is a very high value even for a coastal environment. Because our observation area is 100 km away from the Mediterranean coastline, we do not expect high BrO concentrations.

In summary, we do agree with Ye et al. that the specific \( \text{HO}_2 \cdot \text{H}_2\text{O} + \text{NO}_x \) reaction is not an important HONO source, but our main conclusion that HONO is from a gas-phase source that
consumes NOx and is not related to processes at Earth’s surface remains valid for the investigated Po Valley region.

REFERENCES
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Science 348 (6241), 1326.
DOI: 10.1126/science.aaa3777