Replies to reviewers

We thank the reviewers for their comments, which are addressed below. We combine responses from reviewers when they make the same point.

Reviewer 1:

i) *The study adopts a narrow framing of uncertainties surrounding HONO sources, assuming particulate nitrate photolysis as the sole explanation for observed HONO (cf. Eq. 1), without adequate justification. Notably, the role of heterogeneous NO_2 reactions on aerosols is not discussed, although this process is included in GEOS-Chem. What is the uncertainty associated with it? What other mechanisms have been proposed in the literature, and why are they insufficient to explain the observed HONO? Addressing these questions is necessary to substantiate the study's conclusion that the HONO observations point to a fundamental gap in our understanding.*

Reviewer 2:

a) The two assumptions of the parameterization method are critical to the study's conclusions but require rigorous uncertainty propagation analysis. Addressing these through sensitivity analyses, mechanistic refinements, and observational validation would strengthen the parameterization's robustness and provide clearer boundaries for the proposed renoxification impacts. Attributing observed HONO enhancements exclusively to nitrate photolysis lacks comprehensive validation, as alternative NO_x-related HONO sources could not contribute to NO_x regeneration source. A fixed HONO/NO_2 production ratio, based on a median value reported in Ye et al., neglects a large span of it. Such ratio uncertainties directly affect NO_x and O_3 simulations, just like EF and particulate nitrate.

We agree with both reviewers' comments here. We have reframed the question to be a more explicit exploration of what would happen if nitrate photolysis is the sole missing HONO source. We update the title of the paper to reflect this ("A nitrate photolysis source of remote tropospheric HONO is incompatible with current understanding of atmospheric chemistry"). We have included further quantitative discussion of alternative HONO production sources in the text which allows us to provide additional evidence as to why a heterogeneous conversion of NO_2 to HONO appears unlikely to be the source at a site such as Cabo Verde (see lines 69-101 of the updated paper). As the reviewer says heterogenous uptake of NO_2 to form HONO is in the GEOS-Chem model but at the measured values of gamma this is a slow process (see the discussion around line 85) and leads to a diurnal cycle (high at night and low during the day) which is the opposite of what is observed.

Reviewer 1

ii) The key result supporting this conclusion is the large effect of the proposed HONO source on the modeled burdens of $O_3$and OH, which is pushed beyond observational bounds. This occurs even though the model underestimates particulate nitrate concentrations and potentially also the HONO source. The issue again is that the study assumes that the missing HONO source is only from particulate nitrate photolysis. If the missing reaction producing HONO consumes NOx (and HOx),

then the impact on O_3 and OH would be smaller. Li et al. (2014; doi: 10.1126/science.1248999) hypothesized such a mechanism, and recent laboratory work by Song et al. (2023; doi: 10.1038/s41612-023-00357-8) provides empirical evidence for another such reaction. This alternative explanation seems more plausible and should be considered.

We include the two references suggested into the text of the paper as potential gas phase sources. We note that there was a formal reply to the Li et al. paper by Ye et al. (2015) who concluded the reaction $HO_2.HO_2.H_2O + NO_2 \rightarrow HONO + O_2 + H_2O$ is an unlikely source for HONO based on their data. The daylight Song et al., mechanism involves conversion of HNO3 adsorbed onto the surface of the chamber which in many ways is similar to the nitrate photolysis process proposed in previous papers and implemented here where the HNO_3 is absorbed into the aerosol. The observations in remote locations show a day time maximum in HONO and so the night-time source suggested in Song et al., is unlikely to be applicable. Please see lines 95 to 101 of the paper for the additional text.

We have also included words in the paper's discussion section to re-iterate that the nitrate photolysis process converts NOy to NOx and that a HONO source that is a conversion from a NOx would likely have smaller impacts on atmospheric composition. Please see lines 623 to 630 of the paper.

iii) The physical interpretation of the parameterization for HONO production from particulate nitrate photolysis is unclear.

From Eqs. 1–4, the HONO production rate is given by:

$P(HONO) = (2/3) \times J(HNO_3) \times EF \times [pNO_3]$

where $EF = C1 / (1 + C2 \times [pNO_3])$. At atmospherically relevant $[pNO_3]$, $C2 \times [pNO_3] >> 1$, which reduces the EF to:

$EF \approx (C1 / C2) / [pNO_3]$

and thus,

$P(HONO) \approx (2/3) \times J(HNO_3) \times (C1 / C2)$

This implies that the HONO production rate is effectively independent of $[pNO_3]$, which is difficult to interpret physically if particulate nitrate photolysis is the missing HONO source.

We agree with the interpretation of the reviewer here and have included discussion in the text. Both our parameterization and that of Andersen are in this regime which is effectively independent of nitrate for most atmospheric conditions. See lines 317 to 326 of the updated text.

Reviewer 2

This study presents a compelling investigation into the role of nitrate aerosol photolysis as a major source of nitrous acid (HONO) in the troposphere, and the role of HONO source in the distribution of NOx and OH. By integrating multi-platform observational data (aircraft, ship, and ground-based campaigns), the authors validate a novel parameterization for nitrate photolysis enhancement factors (EFs), which is first proposed based on laboratory studies. Taking advantage of this parameterization method, the work highlights a previously underestimated renoxification pathway that contributes significantly to reactive nitrogen recycling (~48 Tg N yr^{-1}), rivaling direct anthropogenic NOx emissions. While the author point out that these HONO measurements represent a key uncertainty in our current understanding of atmospheric chemistry, there are several major issues concerning the model, measurements and their comparsions.

Specific comments:

1. *Although the "new" parameterization adapts the pNO3 dependence and fit the field data with a R^2=0.41, the substantial divergence between fitted and observed EFs (spanning >1 order of magnitude) introduces critical uncertainties in HONO predictions.*

We have included further comments about the quality of the fit in the text of the paper and the need for future laboratory and field work to better constrain the EF function. Please see lines 332 to 341 of the updated text

2. *It is a bit confusing that particulate nitrate is underestimated in Figure 2, but overestimated in Figure 6?*

This reflects a general underestimate in total nitrate in the model, but an overestimate in fine mode nitrate. We have updated the captions in Figure 2 and Figure 6 to make this clearer and included a comment to this effect in the discussion (please see lines 632 to 635).

3. *The accurate representation of particulate nitrate (pNO_3^-) concentrations is paramount for reliable HONO source quantification in the model. A key limitation arises because even with the proposed parameterization, the model cannot reconcile observed HONO levels if pNO_3^- is misrepresented (e.g., the current -95% low bias in total nitrate). This interdependency introduces a fundamental uncertainty: errors in pNO_3^- simulation propagate directly into HONO and NO_x predictions, undermining confidence in the inferred atmospheric chemistry impacts (e.g., O_3 and OH increases). While the study acknowledges this issue, it does not address strategies to improve pNO_3^- modeling (e.g., aerosol-phase thermodynamics)—a gap that weakens the mechanistic credibility of the conclusions.*

We include new comments in the paper that outline the need to improve the representation of aerosol nitrate (both in the fine and coarse modes) in order to further improve our understanding of this process. Please see lines 400 and 401 and lines 632 to 635.

4. Current model uncertainties in simulating particulate nitrate, HONO, and NO_x arise not only from incomplete mechanistic understanding but also from critical observational data gaps. Addressing both mechanism weaknesses and these data gaps is essential to advance model.

We include new comments in the paper discussion outlining the need for improved instrumentation to measure low concentrations of HONO and, given the current model simulation, where these measurements should be best undertaken. See lines 638 to 643 of the updated paper.