Dear Reviewer:

We would like to thank the anonymous referee for his/her comprehensive review and valuable suggestions. We have carefully considered each of the referee's comments and suggestions and have revised the manuscript accordingly. In this response, we respond to all of the comments point to point. The referee's comments are listed below in black, our response is given in blue and the modification to the manuscript is listed in red. The page and line numbers for corrections are referred to the revised manuscript; the page and line numbers of the original review manuscript remain unchanged. References relevant to the response are listed at the end of this document.

Comments:

In this manuscript Mao et al. evaluate the change in nitrogen oxide emissions in Ukraine due to the Russia-Ukraine war in 2022 using inversion methods. Overall, the discussed merit is interesting an deserves investigation. Before I can recommend publication in ACP, the authors need to address some fundamental aspects.

Mayor comments

1. I would suggest to rethink your title. Your methodology relies on inversion techniques and uses TROPOMI data as an input. The phrase "Satellites reveal" is thus misleading. In addition the 28% is associated with uncertainties and I would thus remove it from the title.

Response: We sincerely appreciate the reviewer's suggestion. We have revised the title to "Inversion-based assessment of anthropogenic NO_x emission changes in Ukraine during the 2022–2023 war using TROPOMI satellite data".

2. I would expect a significant contribution of direct and indirect war related NO_x emission (e.g., infrastructure fires). In your study, however, you seem to not include any war related emissions. Keeping in mind the fast changing nature of this war, what uncertainties does this introduce to your methodology and your results? To what degree do you think did war related emissions compensate the reductions reported in your study?

Response: Many thanks for this important and thought-provoking comment. We fully agree that the war itself may emits large amounts of NO_x, especially during periods of intense fighting. We have added a new subsection in the Discussion section to discuss the extent to how the war related emissions offset the reductions in anthropogenic NO_x emissions (Fig. R1). Leveraging the spatiotemporally volatile nature of war-related emissions, we compared daily emission estimates during the war with corresponding 30-day Locally Estimated Scatterplot Smoothing (LOESS) emissions. By identifying grid cells with daily anomalies exceeding three standard deviations from the smoothed trend, we delineated "hotspot" regions directly affected by military operations. We then quantified the relative differences between daily and smoothed emissions for both hotspot and non-hotspot areas.

The identified hotspots correspond well with regions experiencing intense military activity, and exhibit significantly higher daily emissions than the smoothed baseline, suggesting the presence of short-term, conflict-induced emission spikes. In contrast, non-hotspot regions showed minimal differences between daily and smoothed values. This analysis suggests that wartime activities offset approximately 8% and 10% of the socio-economics related NO_x emission reductions in 2022 and 2023, respectively.

When these war-related signals were removed, the inversion of 2022 emission reductions exhibited good agreement with the prior EDGAR inventory and independent macroeconomic indicators. This helps to partially explain the lower total reduction than that estimated by bottom-up inventories or energy statistics.

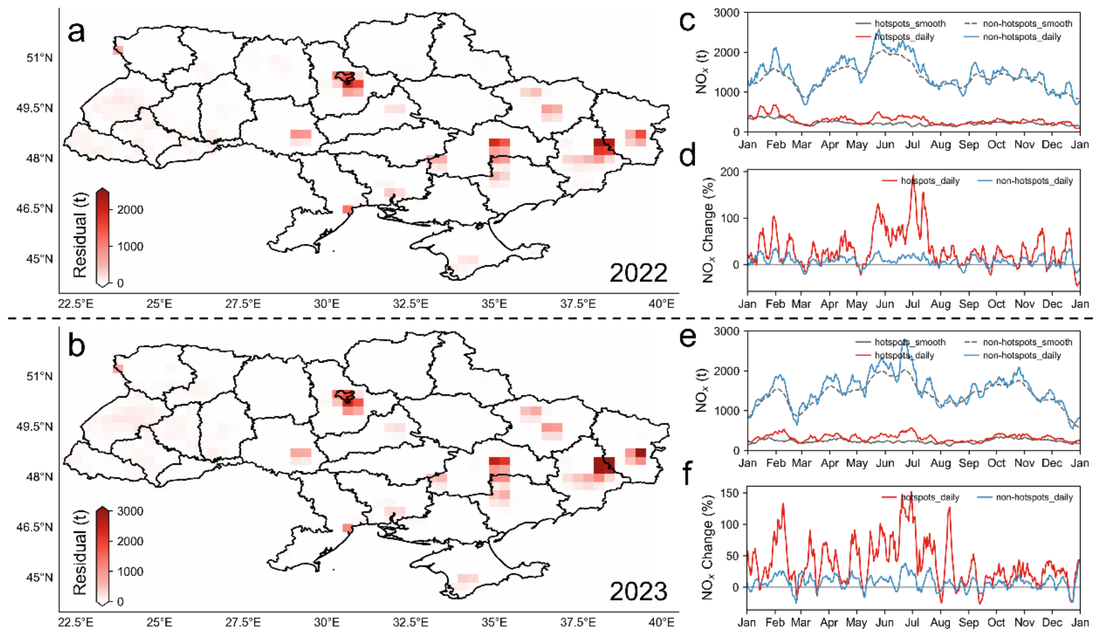

Fig. R1 Spatiotemporal distribution of significant daily anthropogenic NO_x emission anomalies in Ukraine during the 2022 war period (after 24 February) and 2023. (a, b) Spatial distribution of daily cumulative significant emission anomalies relative to the LOESS-smoothed emissions in 2022 (a) and 2023 (b). (c, d) Seasonal variation of daily emissions and LOESS-smoothed emissions (c), and corresponding relative differences (d), for 2022 in war-affected hotspots (grid cells with daily anomalies > 3σ) and non-hotspot regions. (e, f) Same as (c, d), but for 2023. (Fig.4 in the revised manuscript)

We have added this part in section 4.3 in the revised manuscript (see lines 469-507):

As mentioned above, War itself may also lead to large amounts of NO_x emissions, including military vehicles and artillery. Thus, we further assessed the war-related NO_x emissions. We firstly applied Locally Estimated Scatterplot Smoothing (LOESS) and residual analysis to quantify the spatial heterogeneity of significant emission anomalies in the 2022 wartime period and 2023 (Fig. 4a, b). Significant emission anomalies were identified by calculating the cumulative significant residuals (exceeded three times the standard deviation) of daily grid-level emissions relative to the corresponding 30-day LOESS-smoothed values. The results indicate localized positive residual anomalies (red hotspots) were observed along conflict frontlines and logistical hubs, suggesting that military operations and emergency responses significantly elevated emissions in these areas. This is consistent with the severely damaged areas identified by Priyanka Gupta et al. (2024) using NASA MODIS FIRMS active fire detections. We analyzed daily anthropogenic NO_x emissions alongside verified reports of military activity in Ukraine (2022–2023) from BBC and Reuters, and found strong correspondences between emission anomalies and key military events. In Kyiv and Kharkiv, emissions sharply declined following the outbreak of war on 24 February 2022, reaching minima during periods of civilian shutdown. Emissions rebounded during March as military logistics and emergency operations intensified. Kharkiv and Luhansk showed short-term positive anomalies during Ukrainian counteroffensives and Russian reinforcements, while Donetsk experienced sustained negative anomalies due to prolonged conflict and infrastructure damage. Crimea, as a logistical hub, showed persistent emission increases linked to military operations. These findings highlight the potential of high-frequency NO_x emissions as a proxy for monitoring the intensity and evolution of wartime activities.

The emission anomalies observed in the inversion results suggest that wartime activities made a non-negligible contribution to overall NO_x emissions. By comparing daily emissions with their corresponding LOESS-smoothed values, we classified each day's spatial emissions into war-affected hotspots (grid cells with daily anomalies > 3σ) and non-hotspot regions. Results show that during the war periods of 2022 and 2023, the smoothed emissions in hotspot areas were 30.8% and 35.6% lower than the corresponding daily emissions, respectively. In contrast, differences in non-hotspot regions were only 6.7% and 8.2%. This indicates that smoothing effectively filtered out the high-frequency variability associated with military activities in hotspot areas. With this method, we further estimated the relative deviation of the smoothed emissions from the pre-war baseline, finding reductions of 23% in 2022 and 18% in 2023, which closely matching the emission decreases reported by the EDGAR inventory. This suggests that military-related activities offset approximately 8% and 10% of the overall emission reductions in 2022 and 2023, respectively, which partially explains the lower reductions in our inversion than those from bottom-up inventories and independent economic data. However, quantifying the exact compensatory effect of direct war emissions on emission reductions remains methodologically challenging. Because these sources are inherently episodic and spatially concentrated, complicating their separation from background variability in sectoral inventories. These findings highlight warfare as a distinct emission modulator that can temporarily reshape regional source profiles, though its aggregate contribution remains secondary to economy-wide suppression effects in determining net emission trajectories.

3. Please provide further details on the TROPOMI retrievals. The VCDs are obtained from a polar orbit meaning that the same time of day is observed. How does this impact your methodology, especially considering a shift in activities to the night?

Response: Many thanks for this suggestion. Indeed, TROPOMI aboard the Sentinel-5P satellite is in a sun-synchronous orbit and provides NO_2 vertical column densities (VCDs) around local early afternoon (~13:30 LT). As a result, the retrievals reflect only daytime emissions, and can not capture nighttime emission changes. In our inversion framework, we use the TROPOMI NO_2 data to constrain daily anthropogenic NO_x emissions through GEOS-Chem simulations that coincide with the transit times of the corresponding TROPOMI grid. We have added a description in the revised manuscript in Lines 149-151:

TROPOMI is a UV–visible spectrometer aboard the Sentinel-5P satellite in a sun-synchronous polar orbit, crossing the equator at approximately 13:30 local time. We screened GEOS-Chem simulations that overlapped with the transit time of the TROPOMI grid to participate in the inversion.

We acknowledge that in wartime conditions, especially under curfews or infrastructure damage, activity patterns may shift to nighttime (or be suppressed at night for safety). As TROPOMI cannot observe night emissions, this introduces an uncertainty into how representative our estimates are for the true daily total emissions.

We have added a discussion of this limitation and the potential implications for our results in Discussion of the revised manuscript, see Lines 515-524:

Due to the fixed overpass time of TROPOMI at approximately 13:30 local time, the inversion is constrained to reflect emissions around this midday window, limiting its sensitivity to nocturnal emission variations. This temporal sampling introduces a limitation in capturing potential shifts in emission timing, particularly under wartime conditions. During the Russia–Ukraine war, especially in high-risk zones, there may have been a redistribution of human and industrial activities toward nighttime hours due to safety concerns, power rationing, or tactical considerations such as avoiding aerial detection. While such behavioral shifts could potentially increase nocturnal emissions, the current inversion system is unable to capture these changes due to the absence of nighttime satellite data. Thus, while our results provide a robust estimate of daytime anthropogenic NO_x emissions, they may overestimate total emission changes if substantial nocturnal activity occurred. Future work integrating ground-based measurements, high-temporal-resolution modeling, or geostationary satellite data (e.g., TEMPO, Sentinel-4) could help address this temporal limitation.

4. To improve data quality, you perform the inversion of the anthropogenic NO_x emissions on a monthly scale. Since you frequently highlight the fast changing nature of the war, it sounds that using monthly averaged data is not an optimal choice. To what degree does this influence the predicted results?

Response: Many thanks for this comment. We fully agree that using monthly averaged data may limit the ability to capture short-term changes in emissions, especially under rapidly evolving conditions such as wartime disruptions. In light of your suggestion, we have revised the inversion process and the prior inventory. In brief, in the updated inversion method, we adopt the EDGAR inventory updated to 2022 as the prior, and estimate daily anthropogenic NO_x emissions at a spatial resolution of 0.25°×0.3125° using a 7-day moving average of daily TROPOMI observations. A more accurate prior inventory increases the reliability of the inversion results, and the higher spatiotemporal resolution of the emissions provides strong support for evaluating the impact of rapidly changing war events on anthropogenic emissions.

We have added the following descriptions in the revised manuscript (see lines 164–175):

Furthermore, when using TROPOMI NO_2 VCD as observational constraints for inversion, the quality of satellite observations directly impacts the inversion accuracy. In Ukraine, the lack of sufficient valid pixels severely hampers the reliability of daily inversions. We applied a multi-day moving average window to constrain the daily simulated concentrations to address this limitation. The effectiveness of this approach has been demonstrated in previous studies (e.g., Zheng et al., 2020). We evaluated the number of valid TROPOMI observation pixels over Ukraine using different moving average window lengths during the study period (Fig. S1a). When the window size reached 7 days, the data loss significantly decreased, and the proportion of valid grid cells exceeded 90%. However, applying a multi-day average may suppress short-term fluctuations in NO_2 concentrations, potentially limiting the ability to capture rapid changes associated with wartime dynamics. We compared the NO_2 VCDs over Ukraine using 7-day and 11-day moving averages (Fig. S1b). The results showed no substantial difference between the two, but the 11-day average tended to smooth out peak concentrations more strongly. Based on this assessment, we adopted the 7-day moving average of TROPOMI NO_2 VCDs to constrain the model simulations in this study.

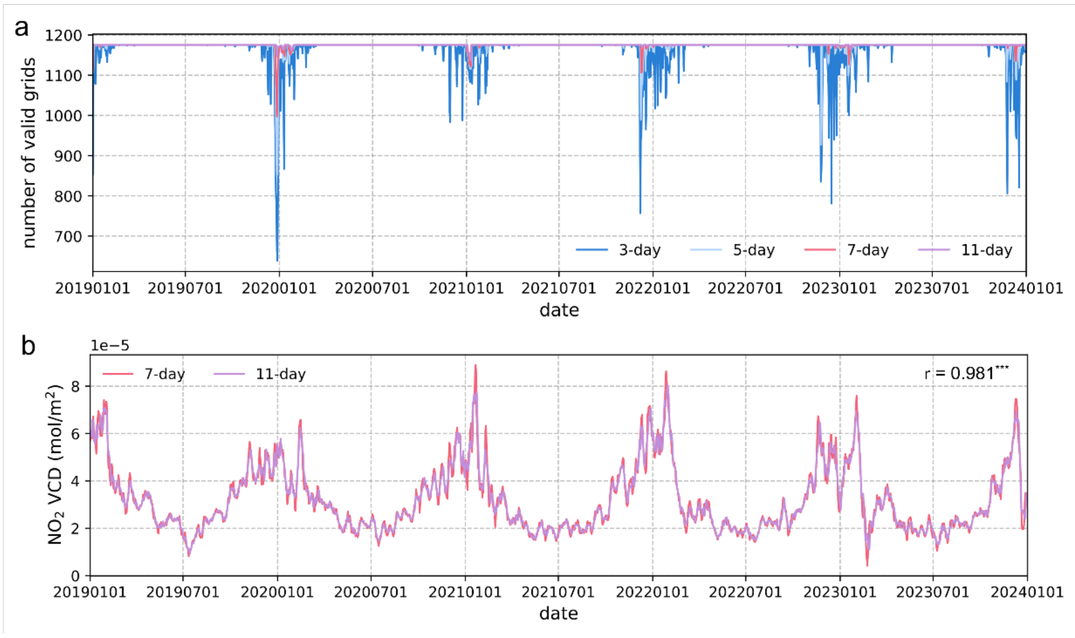

Fig. R2. (a) Number of valid TROPOMI observation grids over Ukraine from 2019 to 2023 under different moving average window lengths. (b) Comparison of daily TROPOMI NO_2 VCDs over Ukraine using 7-day and 11-day moving averages. (Fig.S1 in the revised manuscript)

Based on the determination that a 7-day moving window sufficiently meets the requirements for the inversion, we have updated the inversion methodology section accordingly in the revised manuscript (see Lines 203–206):

Due to the reduced TROPOMI observation coverage on specific days, as discussed in Sect. 2.3, we employed 7-day moving averages of satellite NO_2 observations for comparison with daily simulated VCDs in this study. Specifically, for each day during the study period, the simulated NO_2 VCDs were constrained using the quality-filtered TROPOMI NO_2 VCD observations. This approach has been demonstrated to be effective by Zheng et al (2020).

5. I was surprised to see such a coarse model resolution being used when focusing on such a small region. At the same time, TROPOMI provides data at a km scale. How can you justify such a coarse resolution knowing that other inverse modelling infrastructures provide resolutions at the km scale? How does this affect your results?

Response: Thank you for this thoughtful comment. We agree that the spatial resolution of the inversion is an important aspect, especially when working with high-resolution satellite data like TROPOMI. In our initial submission, we used monthly averaged data and a relatively coarse model resolution. However, in response to your above comments, we have revised our inversion strategy, and now use daily TROPOMI data to perform the inversions at 0.25° × 0.3125° resolution. These revisions have already been detailed in our above responses (see the response to comment on data averaging and method changes). Although the resolution of 0.25° × 0.3125° is still relatively low, it represents the highest regional resolution supported by GEOS-Chem Classic, which we used in this study.

We also explicitly discuss this limitation and its implications in the revised manuscript in Lines 536-538:

In addition, the inversion was conducted at a spatial resolution of 0.25°×0.3125°, which may smooth or omit localized emission signals, leading to potential biases in the estimated NO_x emissions.

Minor comments

1. Line 13: Replace "economic production" with e.g. "society".

Response: Thanks! In the revised manuscript, we have replaced "economic production" with "society" in Line 13 as recommended. The revised text now reads: "The outbreak of the Russia–Ukraine war in 2022 brought a huge impact on the Ukrainian society." (Line 13)

2. Line 18: Your abstract only mentions decreases in NO_x emissions, even though you document increased emissions in urban areas in West Ukraine. This can be misleading and should be mentioned in the abstract.

Response: Many thanks for this suggestion. We have revised the abstract to explicitly mention both the overall decreasing trend and the localized increases in urban areas of West Ukraine. The updated text now reads (see Lines 18-21):

Regionally, Eastern Ukraine experienced larger reductions in NO_x emissions in both 2022 and 2023 by 29% and 17%, respectively, due to direct damage from frontline military operations. In contrast, Western Ukraine experienced a relatively modest emission reductions of only 8% in 2022 with emissions increasing in some regions. In 2023, the emissions increased in most western regions.

3. The introduction would greatly benefit from a figure which shows yearly average NO_x VCD from TROPOPMI for the base year as well as 2022.

Response: Many thanks for this suggestion. We have added the spatial distribution of the relative changes in TROPOMI NO_2 vertical column densities (VCDs) during the wartime period in 2022 and throughout the year 2023, compared to the corresponding baseline periods in the Satellite NO_2 VCD Observations subsection in the revised manuscript. This figure provides a visual overview of spatial changes in NO_2 concentrations over Ukraine and helps set the stage for the inversion-based emission analysis. The corresponding description has been included in the revised manuscript to enhance clarity and context (Line 156-160):

In this study, we quantified relative changes in TROPOMI NO_2 VCDs between the wartime period in 2022 and full year of 2023 and the corresponding periods in pre-war baseline (mean of 2019 and 2021; excluding 2020 due to COVID-19 anomalies, same thereafter) (Fig. 1). Results demonstrate that satellite NO_2 VCDs effectively capture spatiotemporal variability of air pollution during the war, though their representation of ground-level emissions remains limited given their tropospheric column nature.

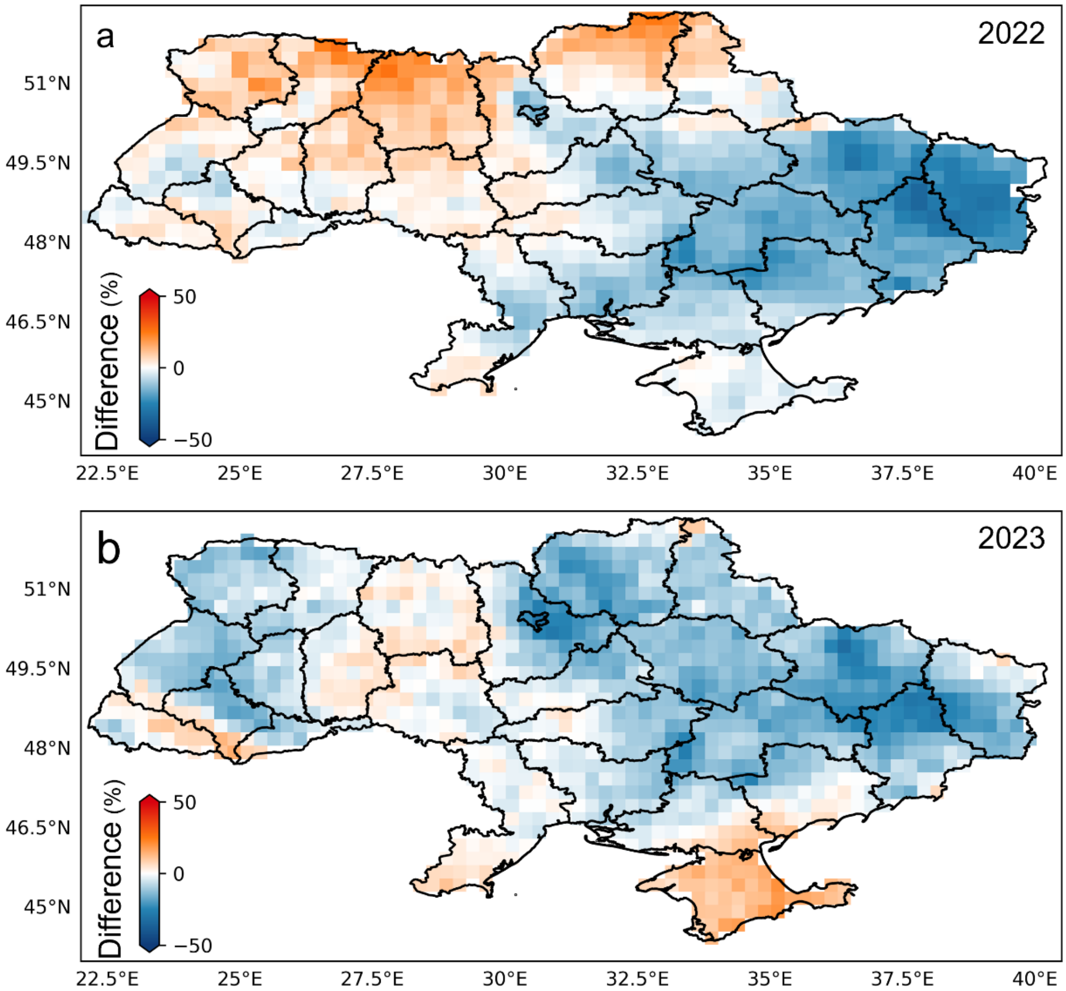

Fig. R3 The Spatial changes in satellite-observed NO_2 VCDs are illustrated (a) during the war (March to December) in 2022 and (b) in 2023 relative to the corresponding periods of baseline (average of 2019 and 2021). (Fig.1 in the revised manuscript)

4. Line 196: Please elaborate on the factors 1.2 and 0.7.

Response: Thank you for your comment. We agree that the originally used perturbation factors (1.2 and 0.7) in the OSSE lacked a clear justification and could be misleading. In the revised manuscript, we have updated this section to provide a more scientifically grounded basis for the assumed emission perturbations. Specifically, we now assume that the true emissions in 2022 are 0.5 times the EDGAR prior, based on the reported average uncertainty of NO_x emissions over the European Union (~51.7%) in the EDGAR inventory (Crippa et al., 2018). For 2023, we assume the true emissions are 1.25 times those of 2022, guided by the observed interannual variability in TROPOMI NO_2 VCDs, which exceeded 25% in some months.

These changes are now reflected in the revised manuscript (Line 232-237), and we believe they provide a more realistic and traceable basis for evaluating the OSSE performance:

In the OSSE, we used the EDGAR emissions in 2022 as the prior, assuming that the true emissions in

2022 were 0.5 times the prior, and the true emissions in 2023 were 1.25 times the true values in 2022. The assumed true emissions for 2022 were informed by the average uncertainty of NO_x emissions over the European Union as reported by the EDGAR inventory, which is approximately 51.7% (Crippa et al., 2018). The assumed true emissions for 2023 were guided by the interannual variability of TROPOMI NO_2 VCDs, which showed that monthly NO_2 concentrations in 2023 differed from those in 2022 by more than 25% in certain months.

5. Line 244: How do you account for the population migration in your emission datasets?

Response: Thank you! We fully agree that population migration could influence anthropogenic NO_x emissions, especially in the context of large-scale displacement during the war. However, we were unable to obtain spatially and temporally resolved population migration data with sufficient accuracy to be integrated into our emission estimates or inversion framework.

As per your suggestion, we have revised the manuscript to emphasize the lack of quantitative data on population displacement. The updated sentence reads (Lines 281-286):

After September, the NO_x emissions showed a new round of decline of 23.8% (±4.3%), reaching a peak decline of 30.5% (±5.5%) in December. This was primarily due to the increased energy demand in the baseline years and intensified energy shortages in 2022 during the cold season. Notably, although we cannot precisely quantify the contribution of population displacement to emission reductions, the continued outflow of residents due to the ongoing impacts of the war likely contributed to the enhanced decrease in wintertime NO_x emissions.

6. Line 271: What "drivers" are you referring to? How does military activity related to transport compensate these changes?

Response: Thank you for your helpful question. We realize that the term "drivers" in the original sentence was ambiguous. To improve clarity, we have revised this part of the manuscript to explicitly discuss the sector-specific seasonal patterns during the war, based on a detailed comparison of anthropogenic NO_x emissions from each sector between the war years and the baseline period. In the revised manuscript, we removed the vague reference to "drivers" and instead provided a quantitative analysis showing that during the early months of the war (March–May 2022), the transport sector initially experienced a sharp decline in emissions due to conflict-related disruption, including damaged infrastructure and reduced civilian mobility. However, the reduction was less pronounced than in other sectors, and even partially rebounded in subsequent months, possibly due to military transport activities, humanitarian logistics, and evacuation-related movement. For example, transport-related emissions declined by 24% (±4.3%) in March 2022 and only slightly further in April. These updates help clarify that while infrastructure damage led to a persistent reduction in transport emissions, increased demand from military-related mobility may have partially compensated for what would otherwise have been a deeper decline.

Please see the Lines 325-328 in the revised manuscript:

The transportation sector demonstrated notable responsiveness to increased transportation demand during the war, with a 24% (±4.3%) decline in emissions observed in March, followed by a slight rebound. Owing to military transport activities, humanitarian logistics, and evacuation-related movement, the transport emissions was smaller than others in 8% (±1.4%).

7. Line 417: Please elaborate on what policies you are referring to.

Response: Thank you for the suggestion. We have revised the sentence in the conclusion to clarify the types of policies our findings may inform. Specifically, we now refer to post-war reconstruction planning, energy security strategies, and emission mitigation policies, which are all areas where understanding wartime emission dynamics and infrastructure impacts can provide valuable insights (see the Lines 558-560):

While our analysis is only a snapshot of the impacts of war, the findings have far-reaching implications for further research and for informing post-war reconstruction planning, energy security strategies, and emission mitigation policies.

8. Fig. 1 and 2: Please fix the inconsistencies in the x-axis labels.

Response: Thank you for pointing this out. We have carefully reviewed and corrected the inconsistencies in the x-axis labels of all Figures in the revised manuscript to ensure uniform formatting and clarity. The updated figures now use consistent date formats and labeling intervals across both panels. We believe this improves the visual coherence and readability of the figures.