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Reply to: NO_2 satellite retrievals biased by absorption in water

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Hao Kong[1], Jintai Lin[1,2] ✉, Guiqian Tang[3], Yuhang Zhang[1], Chunjin Li[1], Chenghao Xu[1], Lu Shen[1], Xuejun Liu[4], Kun Yang[5,6], Hang Su[7], Wanyun Xu[8] & Wanshan Tan[1]

REPLYING TO: L. D. Labzovskii et al. *Nature Geoscience* https://doi.org/10.1038/s41561-024-01545-8 (2024)

Our recent research[1] found high emissions of nitrogen oxides ($NO_x = NO + NO_2$), mainly in the form of NO, from microbial sources in 135 large lakes on the Tibetan Plateau (TP), away from direct human influences. This discovery was based on emission inversion from the POMINO-TROPOMI tropospheric NO_2 vertical column density (VCD) satellite product[2], which was derived on top of the satellite slant column density (SCD) data from KNMI[3]. Labzovskii et al.[4] proposed that the high NO_2 VCDs over the TP lakes could be alternatively explained as spectral contributions by absorption in lake water (chlorophyll) that were not accounted for in SCD fitting. This hypothesis lacks supporting evidence. In contrast, recent independent in situ measurements inspired by our finding supported the existence of high NO_2 VCDs and NO_x emissions from the TP lakes.

In situ measurements support high NO_2 VCDs over TP lakes

To the best of our knowledge, before our study, there were no ground-based flux measurements of NO_x over the TP lakes or other inland waters away from human activities[1]. There were also no measurements of NO_2 concentrations at these TP lakes available for a meaningful comparison with satellite NO_2 data. Abundant ground-based measurements in the polluted regions have suggested an overall slight underestimate of our satellite NO_2 data[2,5], which was corrected in our emission inversion[6].

Recent independent in situ measurements of near-surface NO_2 mixing ratios at the Nam Co Lake (Fig. 1a) support the existence of high NO_2 VCDs over the TP lakes. Nam Co was the second-highest emitting lake in our study. The in situ measurements were inspired by our study and were conducted from 10 September to 17 October 2023, employing Thermo Scientific 42CTL[7]. The NO_2 VCDs in these two months are lower than in summer by ~10%.

The in situ NO_2 measurements at Nam Co exhibit a clear nighttime minimum and an afternoon peak (Fig. 1b), suggesting natural sources. The NO_2 mixing ratios reach ~2.6 ppbv around the TROPOMI overpass time. To estimate the tropospheric VCDs from near-surface measurements at Nam Co, we made use of near-surface NO_2 measurements by the Ministry of Ecology and Environment (MEE) in Lhasa, ~120 km to the southeast of Nam Co. At the TROPOMI overpass time from 10 September to 17 October 2023, the near-surface NO_2 in Lhasa was ~4.2 ppbv (averaged over six MEE sites), with a TROPOMI NO_2 VCD of ~1.2×10^{15} molecules cm^{-2}. Thus, the average NO_2 VCD at the bank of Nam Co is estimated to be ~0.74×10^{15} molecules cm^{-2}, by applying the ratio of VCD to near-surface concentration at Lhasa. This VCD value is consistent with the TROPOMI NO_2 VCD at the respective location (0.92×10^{15} molecules cm^{-2}; Fig. 1a). In addition, there is evident short-distance transport of NO_2 from the lake to the measurement site (Fig. 1a), in support of the lake NO_x sources.

The alternative explanation is compromised by data inadequacy

Satellite data tend to contain random errors from SCD fitting and other aspects of the retrieval process. This was also the reason why we examined the summer mean rather than measurements on any single day. Yet, only pixels from one single orbit on 5 June 2019 were examined by Labzovskii et al.[4] to argue for the absorption spectra of natural water components (chlorophyll) and against the high NO_2 signal. They argued

[1]Laboratory for Climate and Ocean-Atmosphere Studies, Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing, China. [2]Institute of Carbon Neutrality, Peking University, Beijing, China. [3]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China. [4]State Key Laboratory of Nutrient Use and Management, College of Resources and Environmental Sciences, National Academy of Agriculture Green Development, China Agricultural University, Beijing, China. [5]Ministry of Education Key Laboratory for Earth System Modeling, Department of Earth System Science, Tsinghua University, Beijing, China. [6]National Tibetan Plateau Data Center, State Key Laboratory of Tibetan Plateau Earth System and Resource Environment, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, China. [7]Key Laboratory of Atmospheric Environment and Extreme Meteorology, Institute of Atmospheric Physics, Chinese Academy of Science, Beijing, China. [8]State Key Laboratory of Severe Weather & Key Laboratory for Atmospheric Chemistry of CMA, Institute of Atmospheric Composition, Chinese Academy of Meteorological Sciences, Beijing, China. ✉e-mail: linjt@pku.edu.cn

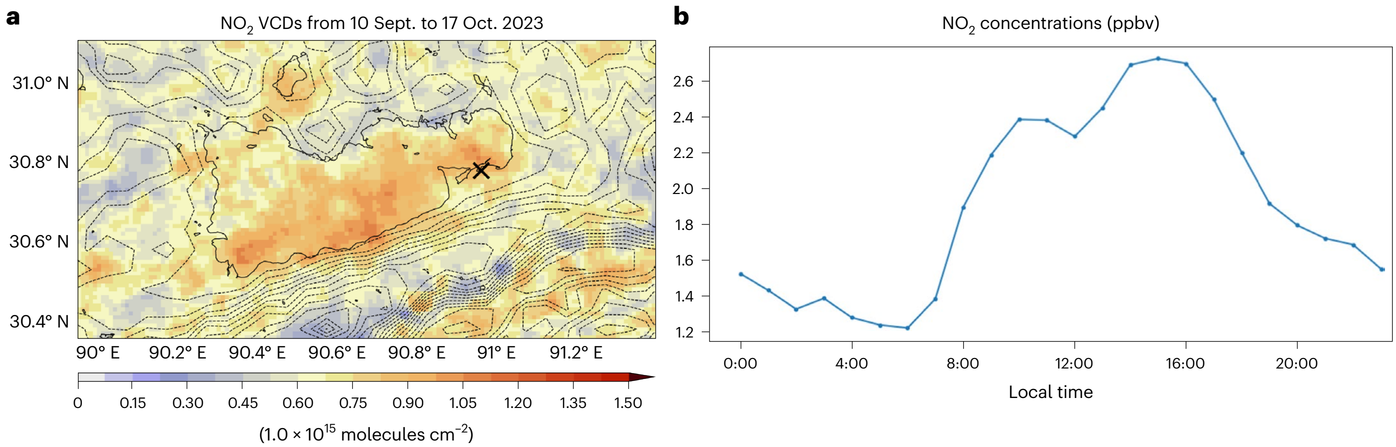

Fig. 1 | In situ measurements of NO_2 over the Nam Co Lake in consistency with satellite data. a, Average NO_2 VCDs from 10 September to 17 October 2023 over the Nam Co Lake. **b**, Hourly variation of near-surface NO_2 mixing ratios averaged from 10 September to 17 October 2023 measured at the Nam Co Lake site. The black cross in **a** denotes the location of the in situ measurement site. Elevation isolines[10] at intervals of 0.1 km are denoted by black dotted lines in **a**.

that 'multiple pixels' (that is, with no specific numbers) in some of their selected 20 lakes (compared to the 135 lakes we studied) exhibit negative water-vapour coefficients from the spectral fitting. However, their fig. 2a showed that few pixels exhibit such phenomena over many major lakes. They also did not establish convincingly that the fitting residuals for these lakes have the same low-frequency feature, which is essential to support their chlorophyll-based explanation. For instance, among the only three lake pixels with detailed fitting residuals (their figs. 1d and 2b), the peak around 445 nm in the residual for the Nam Co Lake pixel is absent in the other two lake pixels.

Note that the detailed residual spectral data for SCD fitting are not publicly available to allow an independent analysis.

Evidence for chlorophyll absorption is lacking

Very weak, if any, evidence exists to support their hypothesis that chlorophyll could have caused the residual feature and, more importantly, invalidated the NO_2 retrieval. The chlorophyll concentrations are typically low in the TP lakes[8], as noted in our paper. Labzovskii et al.[4] relied on a reference9 providing absorption spectra of 305 chlorophyll species, but they showed neither high-frequency spectra of chlorophyll similar to (and thus interfering) NO_2, nor chlorophyll spectra similar to the residual feature for the lakes. We examined all of these chlorophyll spectra and found that none exhibits NO_2-like high-frequency features, and none resembles the residual feature shown in their paper[4]. The chlorophyll spectra are generally low-frequency and could be affected by NO_2 absorption, but their lack of high-frequency features make it hard to affect the high-frequency fitting for NO_2 SCDs.

Besides, the fitting window of NO_2 was 405–465 nm (ref. 3), rather than 430–460 nm as claimed by Labzovskii et al.[4], and no low-frequency fitting residuals occur below 430 nm (their figs. 1d and 2b).

Spectral fitting residuals do not necessarily invalidate NO_2 SCDs

Our emission inversion based on POMINO-TROPOMI NO_2 VCDs only used the satellite pixels with qa_value > 0.5 and a cloud radiance fraction of <50%. This criterion is equivalent to the qa_value > 0.75 commonly recommended for the official NO_2 VCD dataset. The impacts of spectral-fitting errors for SCDs were minimized by applying this criterion. In fact, the root-mean-square errors for the fitting residuals over most TP lakes are comparable with the pixels over the surrounding land.

Labzovskii et al.[4] claimed the NO_2 difference between a lake pixel and a surrounding land pixel (7% for geometry-accounted SCD) to be purely caused by the potential chlorophyll-associated non-white-noise spectral-fitting residual issue. However, they did not really calculate to what extent such a spectral residual is translated into an overestimation (if any) in SCDs and then tropospheric VCDs. Thus, the 7% difference could just (mainly) reflect the actual lake–land difference due to lake NO_x emissions. Moreover, there is also a lack of statistical significance in establishing their claims about SCD errors (they show quantitative results for only two pixels in one lake). Furthermore, their consideration of surface reflectance has already been accounted for in our emission inversion.

In conclusion, we agree that the fitting issue revealed by Labzovskii et al.[4] suggests a source of uncertainty that has not been explicitly characterized. However, the current evidence does not suggest substantial errors in the NO_2 SCD data, nor does it support the alternative chlorophyll hypothesis that could possibly invalidate our emission inversion results.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41561-024-01546-7.

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Data availability
Data obtained from publicly available sources are available from the references. In situ measurements of near-surface NO_2 mixing ratios are available on a collaboration basis.

Code availability
Codes for NO_2 VCD retrieval and NO emission inversion are available on a collaboration basis.

Author contributions
J.L. conceived the response. H.K. and J.L. assessed the impacts of chlorophyll absorption and spectral fitting residuals. Y.Z. helped interpret satellite NO_2 data. G.T. provided and helped interpret the in situ measurements. C.X. helped interpret the TP environment. W.T. helped assess the impacts of spectral fitting residuals. H.K. and J.L. analysed the results and wrote the response with comments from C.L., L.S., X.L., K.Y., H.S. and W.X.

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to Jintai Lin.

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