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NO_2 satellite retrievals biased by absorption in water

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Localized tropospheric nitrogen oxides ($NO_x = NO + NO_2$) are mostly formed from emission sources, such as large cities[1], mineral mining sites[2], busy transportation routes[3], fuel delivery infrastructure[4] and wildfires[5]. Kong et al.[6] recently reported anomalous tropospheric NO_2 columns from spaceborne remote sensing observations of the TROPOspheric Monitoring Instrument (TROPOMI) over Tibetan Plateau lakes and attributed them to megacity-scale emissions from these lakes. Here we report serious anomalies in the NO_2 retrievals over most of these lakes, possibly due to absorption in the water, which may have biased the NO_2 retrieval results. Without addressing this potential absorption, it is premature to attribute any anomalies in tropospheric NO_2 to emissions from Tibetan lakes, let alone estimate their magnitude.

We note that Kong et al.[6], in their investigation, relied on observing strong tropospheric NO_2 column increases compared to background levels, using official TROPOMI operational (v2.4)[7] and TROPOMI POMINO (v1.1) data[8,9] for the three summer months of 2019. Although their findings may seem groundbreaking, strong aquatic nitrogen emissions have never been reported, despite a plethora of satellite NO_2-monitoring studies. In fact, Kong et al.[6] were unable to confirm the presence of such emissions using reference observations and to constrain them. They solely relied on vertical NO_2 columnar information from spaceborne differential optical absorption spectroscopy (DOAS). Moreover, NO_2 is retrieved at wavelengths of 430–460 nm, precisely where the absorption of components in natural waters, such as chlorophyll, occurs—the phenomenon extensively exploited by the ocean colour research community[10,11]. Such absorption, if unaccounted for, can bias NO_2 atmospheric retrievals, as the reverse—NO_2 biasing ocean colour retrievals—is well established by the ocean colour research community. With these considerations in mind, we examined the spectral characteristics of vertical column density (VCD) TROPOMI retrieval over the Tibetan lakes and the data Kong et al.[6] used to report their extraordinary claim about previously undetected nitrogenic aquatic emissions of megacity scale from the Tibetan lakes.

The TROPOMI tropospheric NO_2 VCD retrieval consists of three steps: (1) the total NO_2 total slant column density (SCD) is determined using the DOAS approach on TROPOMI spectra; (2) the tropospheric SCD (SCD_{trop}) is then obtained by subtracting the stratospheric SCD from the total SCD, which is (3) ultimately converted to a VCD using air mass factors (AMFs) that depend on several parameters, including surface albedo[7,12,13]. Kong et al.[6] used two different TROPOMI products that have the same SCD_{trop}, and tested the sensitivity of albedos for their AMF calculation during POMINO retrieval (July 2019), thereby evaluating the sensitivity of the VCD to retrieval algorithm input variables. However, if the SCD contained in either product from the operational retrieval had any direct issues, the resultant biases would propagate into the final tropospheric NO_2 signal over the lakes, regardless of the choice of TROPOMI VCD product or the albedo dataset.

We analysed pixels inside and outside the large Tibetan lake (Siling Co), representing 'water' and 'land' retrievals, respectively. We selected two 'land' and 'water' pixels, outside and at the centre of the lake, from 5 June 2019 (Fig. 1a,b). The water pixel has a higher geometric NO_2 column density (GCD) than the land pixel (where GCD is the total SCD divided by the geometric AMF, which accounts only for the viewing geometry): 75.67 $\mu mol\ m^{-2}$, compared with 70.55 $\mu mol\ m^{-2}$ (difference of ~7%; Fig. 1a). This is the same magnitude as the estimate of the GCD precision. As the albedo of the lake (0.078) is lower than the bordering land (0.118), the AMF will be smaller. Therefore, after subtraction of the stratospheric background the difference is amplified in the vertical tropospheric NO_2 column (19.04 ± 8.47 $\mu mol\ m^{-2}$ versus 10.37 ± 5.94 $\mu mol\ m^{-2}$; ~84% difference). The DOAS NO_2 SCD fit includes other relevant absorbers[11] in the 405–465-nm fit window: O_3, water vapour, liquid water and O_2–O_2. The fit is optimized for NO_2, so the other fit coefficients are much less accurate, although reasonable values should be expected. Although the water vapour amount over land ($2.41 \pm 1.81 \times 10^2\ mol\ m^{-2}$) is plausible and positive (Fig. 1b), the water vapour amount over the lake is strongly negative, exceeding its precision ($-17.83 \pm 3.01 \times 10^2\ mol\ m^{-2}$). Such a substantial and unphysical negative water vapour amount clearly indicates a problematic DOAS fit over the lake.

The DOAS fit residual over land (Fig. 1c) shows no clear spectrally correlated variations. However, the fit residual over the Tibetan

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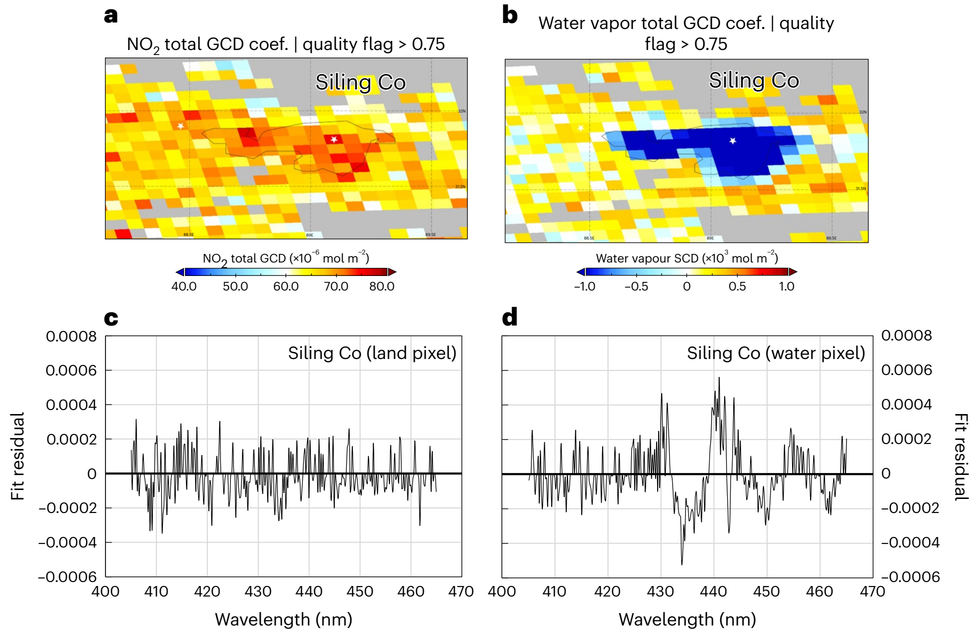

Fig. 1 | a–d, TROPOMI NO_2 total GCD (a) and water vapour (b) fit coefficients (b) over the lake Siling Co with quality flag >0.75 (high quality, cloud-free data), and fit residuals of the two pixels marked in a and b over land (c) and water (d). Pixel centre longitude and latitude are 88.458° E, 31.904° N (land) and 89.095° E, 31.811° N (water). Data are taken from TROPOMI orbit 08511 of 5 June 2019. Standard S5P/TROPOMI level-2 NO_2 (L2_NO2__) data are freely available via the Copernicus Data Space Ecosystem (CDSE, https://dataspace.copernicus.eu/). Detailed analysis data, such as fit residuals, are not available in the regular TROPOMI NO_2 data files but are available upon request (see Data availability statement).

Table 1 | Analysis of fit residuals of ground pixels from orbit 08511 of 5 June 2019 over Tibetan lakes and lakes outside Tibet where residuals and negative water-vapour coefficients were identified

Name	Longitude (E)	Latitude (N)	Residuals	Remark
Qinghai	100.2	36.88	–	No pixels available in orbit 08511
Nam	90.6	30.74	Multiple pixels	
Siling	88.99	31.79	Multiple pixels	
Tangra	86.61	31.07	Multiple pixels	
Ngangla Ringco	83.08	31.54	Multiple pixels	
Zhari Namco	85.62	30.93	Multiple pixels	
Ngoring	97.7	34.9	–	No pixels available in orbit 08511
Ayakkum	89.39	37.55	–	Scene covered by snow/ice
Lumajangdong	81.62	34.02	Multiple pixels	
Migriggyangzham	90.27	33.45	–	Scene covered by snow/ice
Gyeze Caka	80.9	33.95	Multiple pixels	
Cha-pu-yeh cha-ka	84.06	31.41	Multiple pixels	
Pei-ku tso	85.59	28.89	Multiple pixels	
Lagkor	84.13	32.03	Multiple pixels	
Issyk Kul	77.36	42.41	Multiple pixels	
Pangong Tso	78.78	33.72	Multiple pixels	Scene partly covered by snow/ice
Balkhash	78.77	46.45	Multiple pixels	Scene partly covered by snow/ice
Unvs Nuur	92.76	50.2	No pixels	
Khyargas Nuur	93.39	49.05	No pixels	
Khar-Us	92.26	47.9	No pixels	

Tibetan lakes are shown in regular font and lakes outside Tibet in bold font. The top ten lakes of Kong et al.[6] are the first ten listed.

lakes (Fig. 1d) exhibits a relatively low-frequency variability in the 430–460-nm radiance range not accounted for in the DOAS fit. Consequently, the fit coefficients are unphysically altered, affecting the water-vapour and, most crucially, potentially impacting the NO_2 SCD. The NO_2 atmospheric anomalies, which Kong et al.[6] attributed to nitrogenic aquatic emissions, would be affected both seasonally and in magnitude by this effect, which would be exacerbated by the albedo difference aspect mentioned above.

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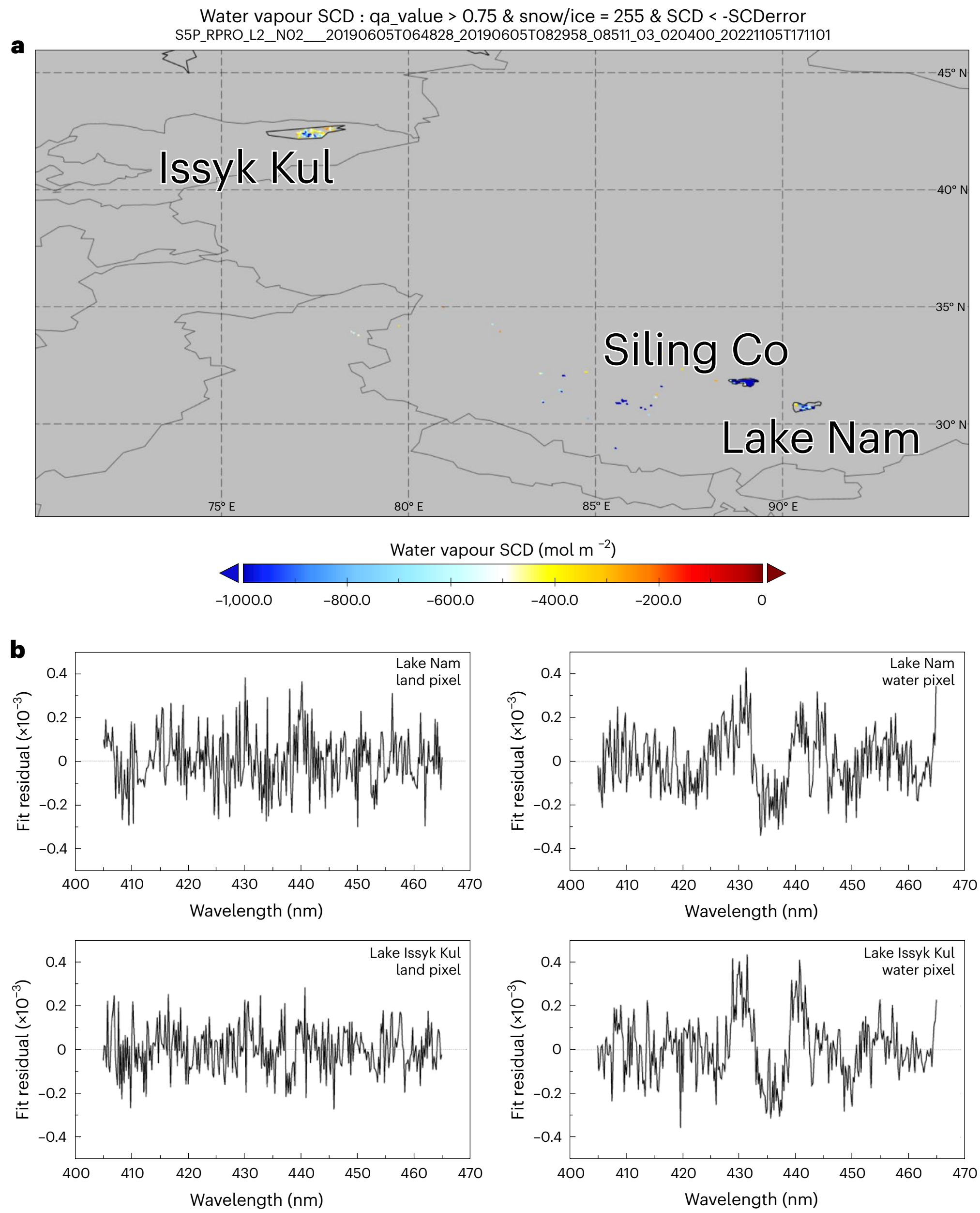

Fig. 2 | a, Map of the water-vapour fit coefficient from the TROPOMI NO_2 retrieval for several lakes in Asia. b, Fit residuals for land pixels (left column) near and water pixels (right column) over Lake Nam in Tibet (top row) and Lake Issyk Kul in Kyrgyzstan (bottom row), which can be compared to Fig. 1c,d for Lake Siling. Data are taken from TROPOMI orbit 08511 of 5 June 2019. Standard S5P/TROPOMI level-2 NO_2 (L2_NO2__) data are freely available via the CDSE (https://dataspace.copernicus.eu/). Detailed analysis data, such as fit residuals, are not available in the regular TROPOMI NO_2 data files but are available upon request (see Data availability statement).

Besides the Siling Co detailed example, we briefly analysed 20 other large lakes, including the top ten from Kong et al.[6] and several other lakes in Asia outside Tibet, for 5 June 2019 (Table 1). Interestingly, similar low-frequency features, not accounted for in the DOAS fit, were found over 13 lakes in Tibet and other major Asian lakes, such as Issyk Kul (Kyrgyzstan). Three Mongolian lakes (Unys Nuur, Khyargas Nuur and Khar-Us) we analysed did not exhibit these spectral artefacts. For the other lakes in Table 1, either no pixels were available (Qinghai, Ngoring) or the scenes were plagued by snow/ice presence (Lumajangdong, Migriggyangzham). As with Siling Co, many pixels over the lakes from Kong et al.[6] included in Table 1 exhibited unphysically negative water-vapour coefficients. These unphysical negative water-vapour coefficients over the lakes of interest are illustrated on the map in Fig. 2a and are quantified for Lake Nam (Tibet) and Issyk Kul (Fig. 2b) water pixels. Obviously, this unaccounted for low-frequency variability in the 430–460-nm range is the same as for Siling Co. The widespread occurrence of such spectral artefacts in TROPOMI data over different lakes in Asia indicates that the unresolved spectral features over water might be a systematic problem that had remained unaccounted for in previous TROPOMI-based works over Tibetan lakes, as in the Kong et al.[6] study.

We demonstrate clear evidence of unresolved spectral features in the TROPOMI VCD NO_2 retrieval in the 430–460-nm range over water bodies of Tibetan lakes that explain ~7% of the observed increase in the retrieved NO_2 SCD for one of the largest Tibetan lakes—Siling Co. Spectral features were found over most lakes (more than ten cases), from Kong et al.[6] in Tibet and in some other large lakes in Asia (like Issyk Kul) for a single orbit in June 2019. The apparent enhancement in tropospheric NO_2 is limited to the pixels over water, without signatures of NO_2 plumes, suggesting that major emissions into the atmosphere are unlikely. The bias-driving spectral feature was observed precisely at the interval of water-component absorption, where correcting for NO_2 spectral absorption has become standard practice in retrievals of ocean colour[14]. Without considering this absorption interplay, it is not possible to attribute any anomalies in NO_2 to emission processes occurring over Tibetan lakes, let alone estimate their magnitude. The existing TROPOMI quality flag should be updated by incorporating the information from water-vapour fit coefficients and by including an additional statistical test on fit residuals to label potential retrieval issues.

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/s41561-024-01545-8.

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Data availability
Standard S5P/TROPOMI level-2 NO2 (L2__NO2___) data are freely available via the Copernicus Data Space Ecosystem (https://dataspace.copernicus.eu/). Detailed analysis data, such as fit residuals, are not available in the regular TROPOMI NO_2 data files but are available upon request. Data used for the analysis are available upon request at this stage of the submission. No restriction on data availability applies to the data we used.

Code availability
Codes used for conducting our study are available upon request.

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Author contributions
L.D.L. developed the conceptual framework and carried out implementation, data analysis, plotting and writing. R.v.d.A. devised the original idea for the manuscript, and contributed to writing, editing and supervising. J.v.G. performed data analysis, writing, editing and plotting. J.d.L. carried out conceptual framework development, writing and editing. M.L. provided methodological support and editing. H.E., X.L. and J.D. carried out editing. B.L. performed sensitivity experimentation. A.R. carried out editing and plotting.

Competing interests
The authors declare no competing interests.

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