

## Authors' response to comments from Anonymous Referee #1

### General comments:

This paper presents NO<sub>2</sub> results from the GEMS instrument for June-August 2021 using the POMINO algorithm involves detailed improvements to cloud retrieval, surface reflectance and profiles and has previously been applied to measurements over Asia from TROPOMI and OMI. This is the first NO<sub>2</sub> retrieval I have seen from GEMS in the refereed literature, and it is exciting to see this first attempt at NO<sub>2</sub> retrievals.

Unfortunately, the early operational version of GEMS NO<sub>2</sub> slant columns retrieval have shown significant bias, and so the authors apply a scaling to the slant columns using TROPOMI and GEOS-Chem. This is not ideal, but at least allows the authors to proceed with a comprehensive NO<sub>2</sub> retrieval while the NO<sub>2</sub> slant columns retrievals are being improved.

The comparisons with MAX-DOAS and an extensive set of surface monitors show some biases but are actually pretty promising for a first attempt of NO<sub>2</sub> retrievals from geostationary orbit. It would be nice to see a more detailed discussion of possible uncertainties in the product, but on the other hand, this is a first attempt and there will likely be campaigns and retrieval improvements to come that will help to isolate error sources, and perhaps those discussions can be saved for future work.

Overall, I think this is a well-written and clear paper, and a careful first analysis of GEMS data. I recommend it be published after addressing a few minor comments.

We sincerely thank the Referee #1 for reviewing our paper and providing constructive comments for improvement. We updated our POMINO-GEMS algorithm by replacing nested GEOS-Chem v9-02 derived stratospheric NO<sub>2</sub> VCDs with NASA GEOS-CF v1 derived stratospheric NO<sub>2</sub> VCDs, and reprocessed all retrievals. Updated validation results show great improvement in NO<sub>2</sub> diurnal patterns between POMINO-GEMS and ground-based MAX-DOAS measurements. We also use mobile-car MAX-DOAS measurements in the Three Rivers' Source region on the Tibetan Plateau to validate POMINO-GEMS retrievals, and good agreement is also shown in terms of NO<sub>2</sub> diurnal variation. Responses to these general and specific comments are provided below.

As this is the first geostationary mission able to measure NO<sub>2</sub>, it would be nice to see more discussion about sources of diurnal uncertainties (even qualitative discussion). The MAX-DOAS and GEMS NO<sub>2</sub> seem to have different trends in the afternoon measurements at many sites. What could cause this?

Validation results of updated POMINO-GEMS tropospheric NO<sub>2</sub> VCDs using ground-based MAX-DOAS measurements show much improved and great correlation of NO<sub>2</sub> diurnal variations at Xuzhou ( $R = 0.82$ ), Hefei ( $R = 0.96$ ), Fudan University ( $R = 0.84$ ), Nanhui ( $R = 0.79$ ), Xianghe ( $R = 0.94$ ) and Dianshan Lake ( $R = 0.60$ ) sites, even though the correlations are modest at Chongming (rural) and Fukue (remote) sites. We have added more discussion in the revised manuscript.

Currently, we are not able to quantitatively attribute the sources of POMINO-GEMS tropospheric NO<sub>2</sub> diurnal uncertainties for each hour and pixel. However, in a qualitative perspective, the retrieval

uncertainties for remote regions might vary little during the daytime, which are likely caused by choices on the reference spectra used in spectral fitting processes. Over polluted regions, the diurnal uncertainties of aerosol extinction profiles and a priori NO<sub>2</sub> profiles are likely to be the dominant sources for the diurnal NO<sub>2</sub> retrieval uncertainties. We will quantify the sources of diurnal retrieval uncertainties in future studies.

In Line 543-559, we added:

“Figure 9 compares the diurnal variation of tropospheric NO<sub>2</sub> VCDs between POMINO-GEMS and MAX-DOAS at eight stations. At each site, NO<sub>2</sub> values are averaged in JJA 2021 at each hour for comparison, and the number of valid days for each hour is also shown. The Cape Hedo site is not included because there are few valid MAX-DOAS data points at each hour. Figure 10a-f show that at the urban and suburban sites, MAX-DOAS NO<sub>2</sub> (black lines) peaks in the mid-to-late morning, declines towards the minimum values at noon around 13:00 LST, and then gradually increases in the afternoon. Strong correlation of NO<sub>2</sub> diurnal variation between POMINO-GEMS (red solid lines) and MAX-DOAS is found at Xuzhou ( $R = 0.82$ ), Hefei ( $R = 0.96$ ), Fudan University ( $R = 0.84$ ), Nanhui ( $R = 0.79$ ) and Xianghe ( $R = 0.94$ ). At the Dianshan Lake site, POMINO-GEMS NO<sub>2</sub> columns increase but MAX-DOAS data decrease from 08:00 to 09:00 LST, resulting in a lower correlation coefficient ( $R = 0.60$ ). At Chongming and Fukue sites, MAX-DOAS NO<sub>2</sub> shows a peak in the morning without evident increase in the early afternoon, but this diurnal pattern is not fully captured by POMINO-GEMS. At Fukue, POMINO-GEMS NO<sub>2</sub> exhibit abrupt changes at 12:00 and 13:00 LST due to few valid data.

In addition, comparison of POMINO-GEMS diurnal variation with NO<sub>2</sub> data from GOME-2 in the morning and OMI and TROPOMI in the early afternoon shows good agreement at Hefei, Nanhui, Dianshan Lake, Chongming and Fukue sites. The differences between POMINO-GEMS to MAX-DOAS NO<sub>2</sub> VCDs are comparable or smaller than those between LEO satellite and MAX-DOAS NO<sub>2</sub> VCDs.”

How accurate are the GEOS-Chem profiles over a day? Do they look like the MAX-DOAS profiles?

We agree that it is important to know the performance of GEOS-Chem on simulating NO<sub>2</sub> vertical profiles. Although we didn't evaluate the accuracy and diurnal variations of nested GEOS-Chem v9-02 simulated NO<sub>2</sub> profiles, they have been used in our POMINO-OMI and POMINO-TROPOMI research products. Validation results show higher accuracy of previous POMINO products compared with independent ground-based measurements (Liu et al., 2019; Liu et al., 2020). Besides, Yang et al. (2023) have tested the performance of GEOS-Chem CTM to simulate hourly NO<sub>2</sub> vertical profiles for GEMS AMF calculation. Therefore, we quoted the discussion of Yang et al. (2023) in Section 3.5 to briefly discuss the AMF uncertainties from NO<sub>2</sub> profiles. In addition, we do not have ground-based MAX-DOAS NO<sub>2</sub> profiles at any station, so we cannot compare and discuss the NO<sub>2</sub> profiles between GEOS-Chem simulations and MAX-DOAS measurements.

In Line 697-703, we added:

“The uncertainty in a priori NO<sub>2</sub> vertical profiles is estimated to cause an AMF error by 10% (Liu et al., 2020). Yang et al. (2023) suggested that the NO<sub>2</sub> profiles from GEOS-Chem (version 13.3.4) might contain incorrect timing of PBL mixing growth in the morning and thus introduce a relative root-mean-square error of 7.6% and NMB of 2.7% in AMF; however, this error could be greatly dampened by averaging over a long time period. The free tropospheric NO<sub>2</sub> bias in GEOS-Chem NO<sub>2</sub> profiles might

also contribute to the retrieval errors especially over remote regions.”

Are any errors expected from the application of a LEO BRDF to an AMF calculation?

It is true that systematic errors might arise by using LEO BRDF to calculate AMFs for GEMS. However, we think these errors are much less than those from aerosol corrections and priori NO<sub>2</sub> profiles. Since GEMS BRDF L2 product has been available, we will test the differences caused by this issue in the future, and replace current MODIS BRDF data with GEMS product if necessary.

Also, there is no discussion of MAX-DOAS uncertainties themselves.

We have added discussion of MAX-DOAS uncertainties themselves in the revised manuscript.

In Line 347-349, we added:

“Kanaya et al. (2014) and Hendrick et al. (2014) have discussed the error in MAX-DOAS NO<sub>2</sub> retrieval: uncertainties from a priori aerosol and NO<sub>2</sub> profiles are the largest source by 10% – 14%, and the total retrieval uncertainty is typically 12% – 17%.”

### **Specific comments:**

Line 75: This is a specific technique that is used for many missions and trace gases, but not all (for instance, direct fitting of radiances can also be used). Suggest change to more general “using spectral fitting” or similar.

Thank you for your suggestion. We have changed the expression to “The first step is to retrieve total NO<sub>2</sub> slant column densities (SCDs) with spectral fitting techniques, such as the Differential Optical Absorption Spectroscopy (DOAS)”.

Line 88: Are they using an online calculation or look up tables based on VLIDORT?

They use a precomputed look-up table of box AMFs based on VLIDORT version 2.6. We have updated the description in the revised manuscript (Line 97-99).

Line 154: “daily NO<sub>2</sub>, pressure, temperature and aerosol vertical profiles”. These haven’t been introduced yet. Are they coming from the GEOS-Chem model or TROPOMI?

They come from nested GEOS-Chem v9-02 simulations. We have updated the description in the revised manuscript (Line 167-169).

Figure 2 caption: Is GEMS product only at TROPOMI overpass time or all hours? Described in text but should also be mentioned in caption.

Thank you for your suggestion. We have updated Figure 2 in the revised manuscript.

Section 2.1.3: there must be several assumptions made to use this method of scaling GEMS to TROPOMI. Can you mention them? For instance, geometric AMFs won't account for GEO vs LEO issues like relative azimuth angle. Do these make any difference?

Thank you for your suggestion. We have added a paragraph to discuss the assumption we make in this correction.

In Line 237-241, we added:

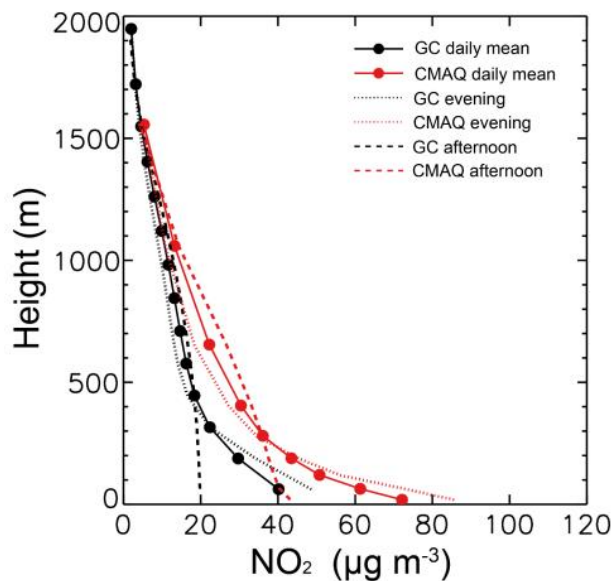
“In Eq. (2), we implement a simple geometric correction (concerning SZAs and VZAs) for AMFs instead of using the actual AMFs; the latter could account for the differences in relative azimuth angles and other factors. Specific derivation of this assumption is given in Section 1 of the Supplement Information (SI). The correction is assumed to be acceptable with an extra uncertainty introduced to the total NO<sub>2</sub> SCDs, as will be further discussed in Section 3.5.”

Line 232: What do you use over water where BRDF is not available (open ocean) or is inaccurate (for example in coastal regions)?

We use MODIS BRDF coefficients over land and coastal ocean regions, and OMLER v3 albedo over open ocean. We have updated the sentences in the revised manuscript (Line 306-309).

Line 262: Since these data are being used for validation, it would be good to further justify “multiplied by a factor of 2 to roughly account”. Does NO<sub>2</sub> necessarily change linearly in those bottom 130 m?

We use the constant correction factor of 2 based on Liu et al. (2018). Figure 12 in this paper (shown below) compares mean NO<sub>2</sub> vertical profiles over Eastern China from nested GEOS-Chem v9-02 and WRF/CMAQ v5.0.1. CMAQ simulations show much stronger vertical gradient of NO<sub>2</sub> from its first layer (about 40 m) to its second layer (about 80 m), but GEOS-Chem cannot fully capture the vertical gradient of NO<sub>2</sub> concentrations. Therefore, we decided to roughly account for this issue by implementing a simple correction with a factor of 2. We admit that NO<sub>2</sub> concentrations don't necessarily change linearly below 130 m, so the correction factor of 2 must introduces systematic bias of satellite derived surface NO<sub>2</sub> concentrations. However, the diurnal variations of satellite derived surface NO<sub>2</sub> concentrations are still consistent with those of MEE data, with correlation coefficients great than 0.96. We have added more sentences on this issue in the revised manuscript.



**Figure 12.** Eastern China mean NO<sub>2</sub> vertical profiles simulated by GEOS-Chem and CMAQ averaged over 25 October–25 December 2013. The black and red dots denote the center of each vertical layer in the two models. The evening is from 20:00 to 23:00 LT, while the afternoon is from 12:00 to 15:00 LT.

In Line 339-341, we added:

“However, the constant correction factor of 2 neglects the diurnal variation of NO<sub>2</sub> vertical gradient, which is related to the diurnal variation of planetary boundary layer (PBL) heights. This issue is discussed in detail in Section 3.4”

In Line 631-639, we added:

“The discrepancies between POMINO-GEMS and MEE surface NO<sub>2</sub> concentrations at different hours are likely caused by the assumed constant correction factor of 2 to account for the vertical gradient of NO<sub>2</sub> from the height of ground instrument to the center of the first model layer (Section 2.2). In the morning when the PBL is low, most NO<sub>2</sub> molecules are near the ground and the vertical gradient of NO<sub>2</sub> over polluted regions is the largest in the daytime, so the factor of 2 may lead to underestimation of derived surface NO<sub>2</sub> concentrations. In contrast, in the afternoon, the PBL mixing is much stronger and the vertical gradient of NO<sub>2</sub> is much smaller, thus the factor of 2 may lead to overestimated surface NO<sub>2</sub> concentrations.”

Section 2.4: What are uncertainties in MEE measurements and what are the details of the observations? Are they chemiluminescence measurements that suffer from bias in NO<sub>2</sub>? This is mentioned later but I think is appropriate to include in this section.

Thank you for your suggestion. We have updated the description of the details of MEE measurements in Section 2.5.

In Line 396-402, we added:

“At MEE sites, molybdenum catalyzed conversion from NO<sub>2</sub> to NO and subsequent chemiluminescence measurement of NO is done to estimate NO<sub>2</sub> concentrations. The heated molybdenum catalyst has low

chemical selectivity, leading to strong interference from other oxidized nitrogen species such as nitric acid (HNO<sub>3</sub>) and peroxyacetyl nitrate (PAN). Therefore, MEE data tend to overestimate the actual NO<sub>2</sub> concentrations, with the extent of overestimation about 10% – 50% (Boersma et al., 2009; Liu et al., 2018). The overestimation is dependent on the oxidation level of NO<sub>x</sub>, but is currently unclear for each site and hour.”

Figure 7 and Line 342-354: The bias between GEMS and TROPOMI is different between ocean and land. Several reasons are given but I don't understand why these would produce different bias over land and water – is it just that the bias are actually following locations of no aerosols vs. high aerosols and not necessarily associated with water/land? Is there any way that the surface itself can influence this bias?

The writing here is indeed misleading. We have added a section (Section 3) in the Supplement Information (SI) to discuss the reasons for the differences between POMINO-GEMS and POMINO-TROPOMI v1.2.2 tropospheric NO<sub>2</sub> VCDs. Besides, previous studies have shown the effects of surface reflectance on NO<sub>2</sub> retrieval, but there is no apparent relationship between bias and surface conditions (Zhou et al., 2010; Lin et al., 2015; Vasilkov et al., 2016).

Line 455: “assume no error contributions from the GEOS-Chem-based scaling”: Wondering here on what this assumption is based? Are there any references describing accuracy of diurnal variation of NO<sub>2</sub> from GEOS-Chem?

Since we have decided to replace GEOS-Chem stratospheric NO<sub>2</sub> VCDs with those from GEOS-CF, we have updated the sentences in Section 3.5. As far as we know, there is no study validating the diurnal variations of stratospheric NO<sub>2</sub> from GEOS-CF v1 product, but our comparison between GEOS-CF and TROPOMI shows great consistency. Therefore, the GEOS-CF v1 dataset is in general reliable in our algorithm.

In Line 684-690, we added:

“In constructing the stratospheric NO<sub>2</sub> SCDs, the stratospheric VCDs are taken from TROPOMI PAL v2.3.1, scaled based on GEOS-CF v1 stratospheric NO<sub>2</sub> to account for diurnal variation, and then applied with geometric AMFs. We assign a constant error of  $0.2 \times 10^{15}$  molec. cm<sup>-2</sup> (5% – 10%) to our hourly stratospheric SCDs, the same as the value for TROPOMI (Van Geffen et al., 2022). Few studies have assessed the accuracy of stratospheric NO<sub>2</sub> and its diurnal variation from GEOS-CF data (Knowland et al., 2022), but our comparison between GEOS-CF and TROPOMI shows great consistency (Section 2.1.5).”

Line 460: Related to previous comment, how good are NO<sub>2</sub> a priori profiles from the model at various times of day? Does uncertainty vary over the days? Also, there is a free troposphere NO<sub>2</sub> bias in GEOS-Chem which can give large errors in NO<sub>2</sub> measurements over remote regions – maybe mention this as a source of uncertainty.

We have quoted the discussion of Yang et al. (2023) which tested the ability of GEOS-Chem CTM to simulate hourly NO<sub>2</sub> vertical profiles for GEMS AMF calculation. The uncertainty of NO<sub>2</sub> a priori profiles is largest in the morning due to incorrect model timing of PBL mixing growth, but becomes

much smaller in the afternoon.

Thank you for your suggestion about the free troposphere NO<sub>2</sub> bias in GEOS-Chem. We have added it in our error analysis.

In Line 698-703, we added:

“The uncertainty in a priori NO<sub>2</sub> vertical profiles is estimated to cause an AMF error by 10% (Liu et al., 2020). Yang et al. (2023) suggested that the NO<sub>2</sub> profiles from GEOS-Chem (version 13.3.4) might contain incorrect timing of PBL mixing growth in the morning and thus introduce a relative root-mean-square error of 7.6% and NMB of 2.7% in AMF; however, this error could be greatly dampened by averaging over a long time period. The free tropospheric NO<sub>2</sub> bias in GEOS-Chem NO<sub>2</sub> profiles might also contribute to the retrieval errors especially over remote regions.”

### **Technical comments:**

Please define POMINO acronym early on. I'm not sure what it stands for.

Done.

Figure 6: Consider adding another set of lat/lon values on the axes. For someone not very familiar with the shape of Chinese provinces, it's hard to figure out the region being examined.

Done.

Figure S5: I find this figure very hard to read, even when zooming. Perhaps increasing the resolution would help (or maybe color palette and/or symbol size?). The sub-figures are even harder to decipher. What are these – they are lacking circles and it's not clear if they are a measurement like the others?

Updated.

Line 258: write out “molecules” instead of using “molec”.

Done.

### **References:**

Boersma, K. F., Jacob, D. J., Trainic, M., Rudich, Y., Desmedt, I., Dirksen, R., and Eskes, H. J.: Validation of urban NO<sub>2</sub> concentrations and their diurnal and seasonal variations observed from the SCIAMACHY and OMI sensors using in situ surface measurements in Israeli cities, *Atmospheric Chemistry and Physics*, 9, 3867-3879, 10.5194/acp-9-3867-2009, 2009.

Hendrick, F., Müller, J.-F., Clémer, K., Wang, P., De Mazière, M., Fayt, C., Gielen, C., Hermans, C., Ma, J. Z., Pinardi, G., Stavrakou, T., Vlemmix, T., and Van Roozendaal, M.: Four years of ground-based MAX-DOAS observations of HONO and NO<sub>2</sub> in the Beijing area, *Atmospheric Chemistry and Physics*, 14, 765-781, 10.5194/acp-14-765-2014, 2014.

Kanaya, Y., Irie, H., Takashima, H., Iwabuchi, H., Akimoto, H., Sudo, K., Gu, M., Chong, J., Kim, Y. J., Lee, H., Li, A., Si, F., Xu, J., Xie, P.-H., Liu, W.-Q., Dzhola, A., Postylyakov, O., Ivanov, V., Grechko,

E., Terpugova, S., and Panchenko, M.: Long-term MAX-DOAS network observations of NO<sub>2</sub> in Russia and Asia (MADRAS) during the period 2007–2012: instrumentation, elucidation of climatology, and comparisons with OMI satellite observations and global model simulations, *Atmospheric Chemistry and Physics*, 14, 7909–7927, 10.5194/acp-14-7909-2014, 2014.

Knowland, K. E., Keller, C. A., Wales, P. A., Wargan, K., Coy, L., Johnson, M. S., Liu, J., Lucchesi, R. A., Eastham, S. D., Fleming, E., Liang, Q., Leblanc, T., Livesey, N. J., Walker, K. A., Ott, L. E., and Pawson, S.: NASA GEOS Composition Forecast Modeling System GEOS-CF v1.0: Stratospheric Composition, *Journal of Advances in Modeling Earth Systems*, 14, e2021MS002852, <https://doi.org/10.1029/2021MS002852>, 2022.

Lin, J. T., Liu, M. Y., Xin, J. Y., Boersma, K. F., Spurr, R., Martin, R., and Zhang, Q.: Influence of aerosols and surface reflectance on satellite NO<sub>2</sub> retrieval: seasonal and spatial characteristics and implications for NO<sub>x</sub> emission constraints, *Atmospheric Chemistry and Physics*, 15, 11217–11241, 10.5194/acp-15-11217-2015, 2015.

Liu, M., Lin, J., Wang, Y., Sun, Y., Zheng, B., Shao, J., Chen, L., Zheng, Y., Chen, J., Fu, T. M., Yan, Y., Zhang, Q., and Wu, Z.: Spatiotemporal variability of NO<sub>2</sub> and PM<sub>2.5</sub> over Eastern China: observational and model analyses with a novel statistical method, *Atmos. Chem. Phys.*, 18, 12933–12952, 10.5194/acp-18-12933-2018, 2018.

Liu, M., Lin, J., Kong, H., Boersma, K. F., Eskes, H., Kanaya, Y., He, Q., Tian, X., Qin, K., Xie, P., Spurr, R., Ni, R., Yan, Y., Weng, H., and Wang, J.: A new TROPOMI product for tropospheric NO<sub>2</sub> columns over East Asia with explicit aerosol corrections, *Atmos. Meas. Tech.*, 13, 4247–4259, 10.5194/amt-13-4247-2020, 2020.

Liu, M., Lin, J., Boersma, K. F., Pinardi, G., Wang, Y., Chimot, J., Wagner, T., Xie, P., Eskes, H., Van Roozendael, M., Hendrick, F., Wang, P., Wang, T., Yan, Y., Chen, L., and Ni, R.: Improved aerosol correction for OMI tropospheric NO<sub>2</sub> retrieval over East Asia: constraint from CALIOP aerosol vertical profile, *Atmospheric Measurement Techniques*, 12, 1–21, 10.5194/amt-12-1-2019, 2019.

Van Geffen, J., Eskes, H., Boersma, K. F., and Veefkind, P.: TROPOMI ATBD of the total and tropospheric NO<sub>2</sub> data products, 2022.

Vasilkov, A. P., Qin, W., Krotkov, N. A., Lamsal, L. N., Spurr, R., Haffner, D. P., Joiner, J., Yang, E., and Marchenko, S.: Accounting for the Effects of Surface BRDF on Satellite Cloud and Trace-Gas Retrievals: A New Approach Based on Geometry-Dependent Lambertian-Equivalent Reflectivity Applied to OMI Algorithms, *Atmospheric Measurement Techniques*, 10, 333–349, 2016.

Yang, L. H., Jacob, D. J., Colombi, N. K., Zhai, S., Bates, K. H., Shah, V., Beaudry, E., Yantosca, R. M., Lin, H., Brewer, J. F., Chong, H., Travis, K. R., Crawford, J. H., Lamsal, L. N., Koo, J. H., and Kim, J.: Tropospheric NO<sub>2</sub> vertical profiles over South Korea and their relation to oxidant chemistry: implications for geostationary satellite retrievals and the observation of NO<sub>2</sub> diurnal variation from space, *Atmos. Chem. Phys.*, 23, 2465–2481, 10.5194/acp-23-2465-2023, 2023.

Zhou, Y., Brunner, D., Spurr, R. J. D., Boersma, K. F., Sneep, M., Popp, C., and Buchmann, B.: Accounting for surface reflectance anisotropy in satellite retrievals of tropospheric NO<sub>2</sub>, *Atmospheric Measurement Techniques*, 3, 1185–1203, 2010.