Supplementary Material

Herein we provide further details regarding:

1. Statistics of the DOAS fits
2. Retrieval of the vertical profiles after the MAX-DOAS observations
3. Tests to investigate the vertical sensitivity of the MAX-DOAS observations

1. <u>DOAS fit statistics</u>

The statistic of the retrieval of the BrO differential Slant Column Density (dSCD) and its errors given to the inversion scheme are shown in Fig. S1. Overall, at both sites the median BrO dSCD decreased with the elevation angle of the scan (median relative error between 21 - 39 %).

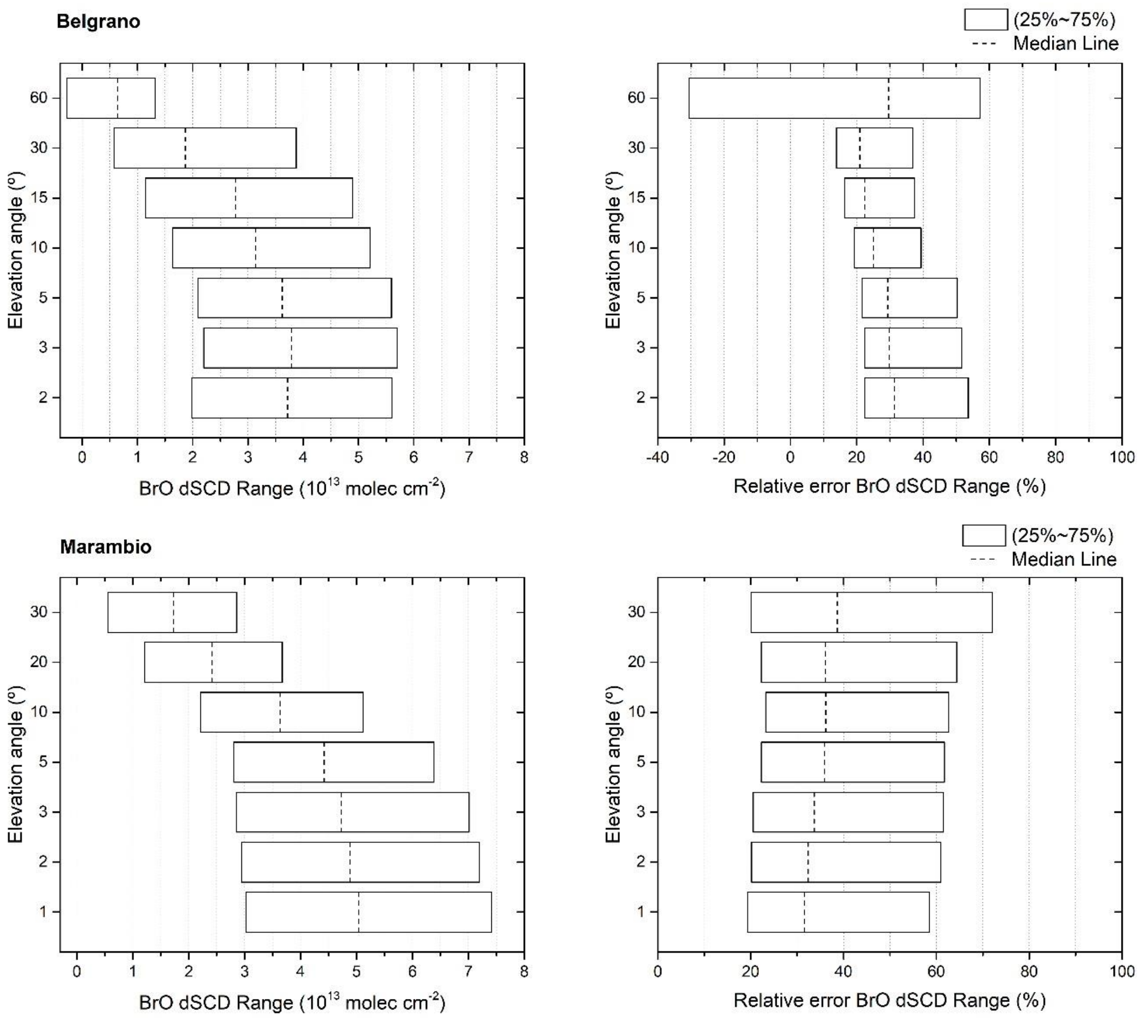

Figure S1: Box chart of the BrO dSCD (left figure) and percentage relative error of the BrO dSCD (right figures) retrieved from Belgrano and from Marambio data (upper and lower figures, respectively). The vertical scale indicates the elevation angle of the retrieved dSCD (depending on the station), while the horizontal scale indicates the range. In all the figures, the boxes provide the 25th to 75th percentile while the median values of the data set are indicated with dashed lines.

In the case of O4, the statistics of the DOAS fit are shown in Fig. S2. Overall, at both sites the median O_4 dSCD decreased with the elevation angle of the scan (median relative error 1.5 - 6 %).

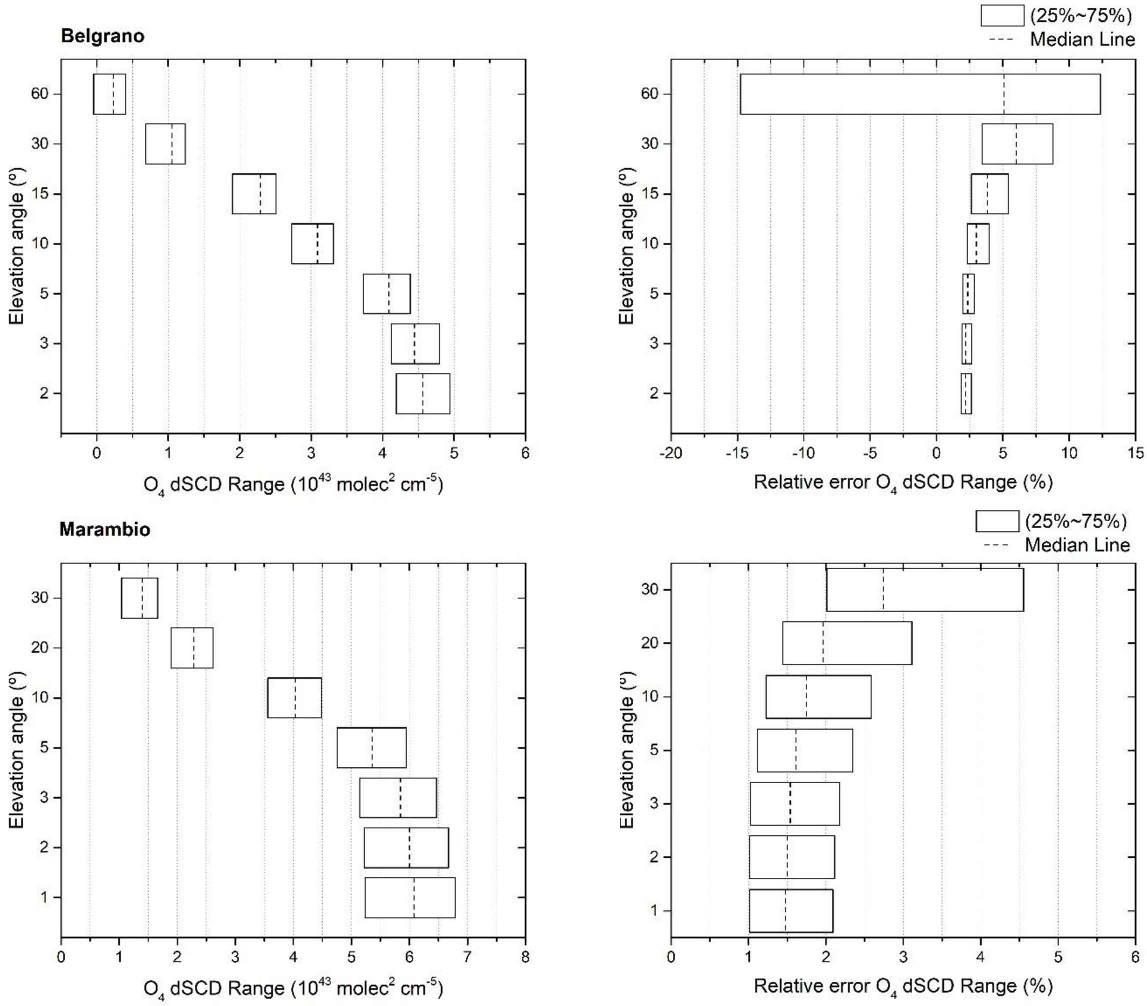

Figure S2: Box chart of the O_4 dSCD (left figure) and percentage relative error of the O_4 dSCD (right figures) retrieved from Belgrano and from Marambio data (upper and lower figures, respectively). The vertical scale indicates the elevation angle of the retrieved dSCD (depending on the station), while the horizontal scale indicates the range. In all the figures, the boxes provide the 25th to 75th percentile while the median values of the data set are indicated with dashed lines.

2. Retrieval of vertical profiles after the MAX-DOAS observations

Degrees of freedom:

In Table S1 below, the reader can find a summary of the degrees of freedom (DOF) of our retrievals. Overall, 93 % and 97 % of the aerosol retrieval at Belgrano and Marambio (respectively) presented DOF > 1. Regarding the retrievals of BrO profiles, 65% and 71% of the retrievals at Belgrano and Marambio (respectively) had DOF > 1.

Table S1: Summary of the degrees of freedom of the profile retrievals performed throughout this study. Mean and standard deviation of the degrees of freedom for the inversion of aerosol extinction and BrO vmr at both sites.

Research site	Inversion	Mean	Standard Deviation
Belgrano	Aerosol	2.21	0.99
	BrO	1.16	0.13
Marambio	Aerosol	1.58	0.74
	BrO	1.21	0.12

<u>Examples of retrieved Averaging Kernels and profiles</u>

Figures S2 and S4 show examples of the averaging kernels (AK) of the aerosol and BrO profile retrievals, respectively. Figures S3 and S5 show the inverted profiles of the aerosols and BrO (respectively) corresponding to those AK.

Overall, most of the information content of our DOAS measurements was higher below an altitude of 1.5-2 km. However, there were days where the particular extinction conditions of the atmosphere (i.e., scattering and/or absorption) rendered information content not negligible up to 4 km (e.g., Fig S2, right). Please, refer to Sect. 3 of this Supplementary Material, for investigations on the vertical sensitivity of the MAX-DOAS method given (realistic) extinction conditions different than those occurred during our measurement period of 2015.

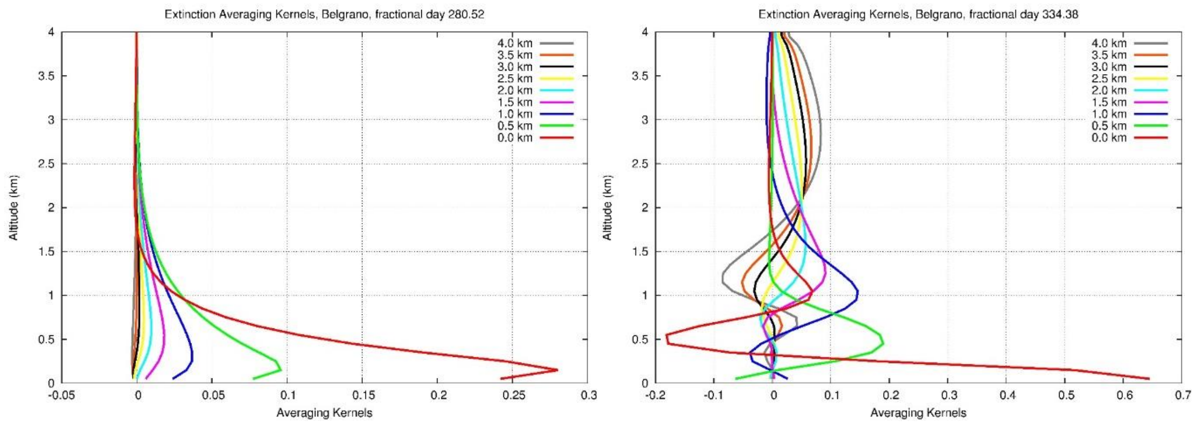

Figure S2: Example of averaging kernels corresponding to extinction profile retrievals at Belgrano. The averaging kernels correspond to the observations performed at Belgrano on (left) 7th October 2015 (12:28 UTC) and (right) 30th November 2015 (09:07 UTC). Note how in the right figure, the sensitivity towards elevated layers is not negligible compared to the left figure.

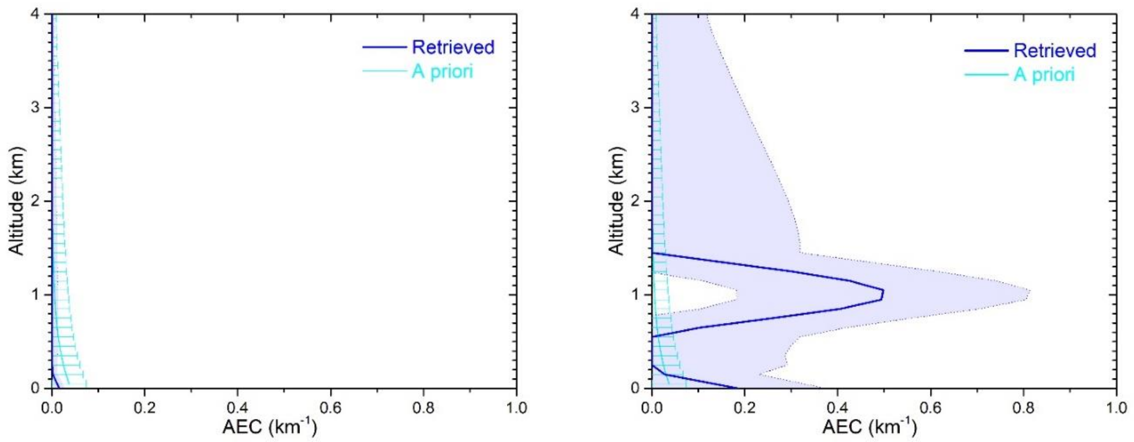

Figure S3: Example of aerosol extinction profiles retrieved at Belgrano. The retrieved profiles correspond to the averaging kernels shown in Fig. S8 (left: 7th October 2015 at 12:28 UTC, right: 30th November 2015 at 09:07 UTC). The blue lines indicate the retrieved BrO vmr profiles (blue shaded areas indicate its error) and the a priori AEC profile is shown in cyan in both figures.

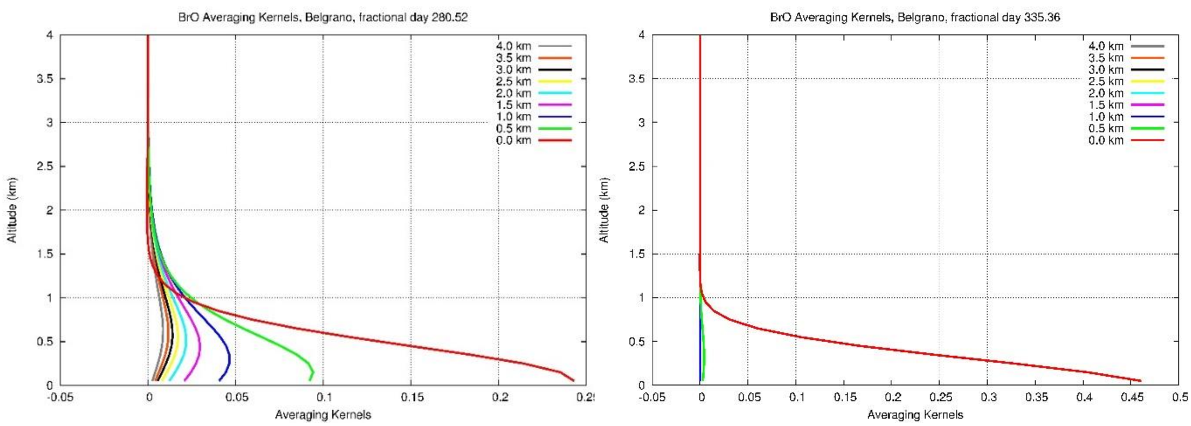

Figure S4: Example of averaging kernels corresponding to BrO profile retrievals at Belgrano. The averaging kernels correspond to the observations performed at Belgrano on (left) 7th October 2015 (12:28 UTC) and (right) 1st December 2015 (08:42 UTC). Note that, on the right figure, the contribution of layers above 1km to the retrieval of BrO at the surface is negligible (while this is not the case on the left figure).

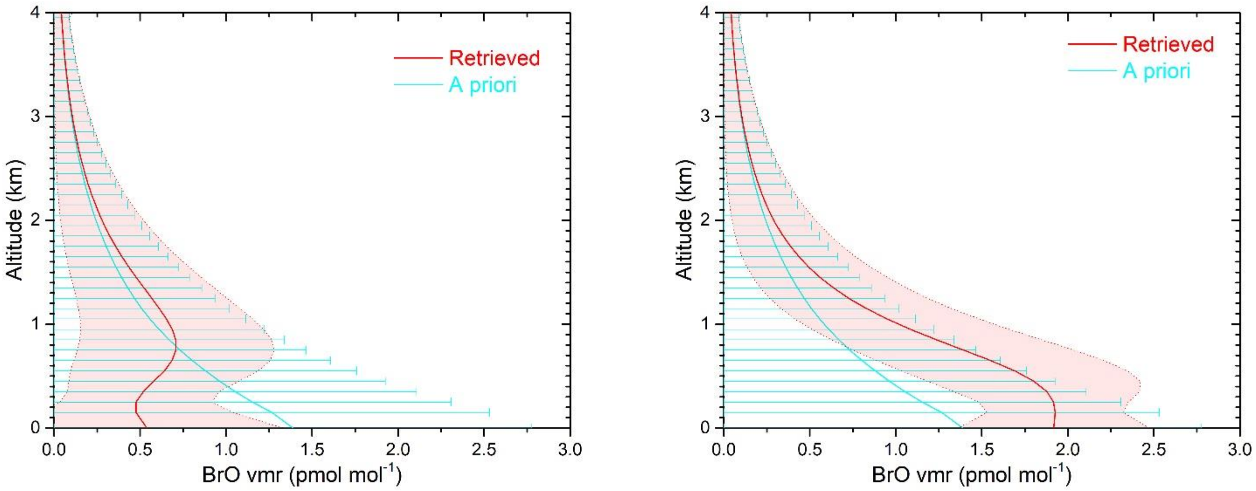

Figure S5: Example of BrO mixing ratio profiles retrieved at Belgrano. The retrieved profiles correspond to the averaging kernels shown in Fig. S10 (left: 7th October 2015 at 12:28 UTC, right: 1st December 2015 at 08:42. UTC). The red lines indicate the retrieved BrO vmr profiles (red shaded areas indicate its error) and the a priori BrO profile is shown in cyan in both figures.

3. <u>Tests to investigate the vertical sensitivity of the MAX-DOAS observations</u>

As mentioned above, the vertical sensitivity of the MAX-DOAS observations depends on the extinction conditions of the atmosphere and the most probable altitude of scattering which also depends on the viewing geometry. Thus, we have performed sensitivity tests with our raditative transfer model (RTM) and inversion scheme to simulate extinction conditions that, although realistic, did not happen in the time frame of our measurements. With these tests, we will investigate the vertical sensitivity that our MAX-DOAS observations are able to achieve. In this sense, we have simulated different aerosol scenarios with layers of AEC = 0.15 km^{-1} located at different altitudes (peaking at 2, 3, 4 and 5 km, see Fig. S6) and include them in our RTM taken the parameterization of the atmosphere at Belgrano as the test bench (i.e., the elevation angles of the MAX-DOAS observations at Belgrano and the same vertical grid, ground albedo, P, T, geometry, ect. used for Belgrano on 11th November).

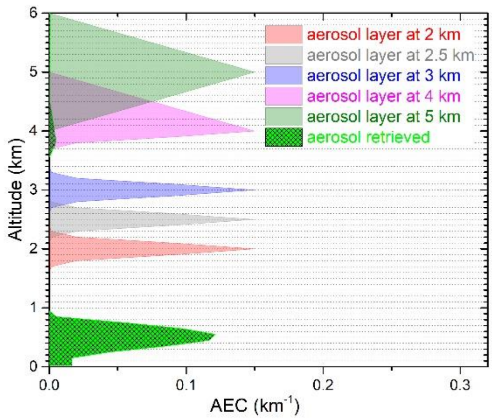

Figure S6: Different aerosol extinction vertical profiles used for investigating the vertical sensitivity of the MAX-DOAS observations. The different plain shaded areas indicate the aerosol layer centered at different altitudes in the parameterization of the atmosphere for the different tests. As an example, the inverted profile for the 10:40 UTC scan (Belgrano, 11th November) is provided in dashed green (i.e., smoothed true profile).

The forward modelling of the O_4 dSCDs with different aerosol scenarios (from no aerosols to the aerosol scenarios shown in Fig. S6) is provided in Fig. S7. In this figure, one can see that, given the elevation angle of the observations at Belgrano, our observations wouldn't be able to distinguish between the aerosol layer centered at 2 km (red line) and one centered at 3 km (in blue), at least not beyond the measurement error. However, observations should be able to distinguish between an aerosol layer at 4 km and an aerosol layer at 5 km. Moreover, observations should be able to capture the difference between an aerosol layer located at 2 km and one located at 4 or 5 km (see for instance the modelled O4 dSCDs at the elevation angle of 30º, blue and green).

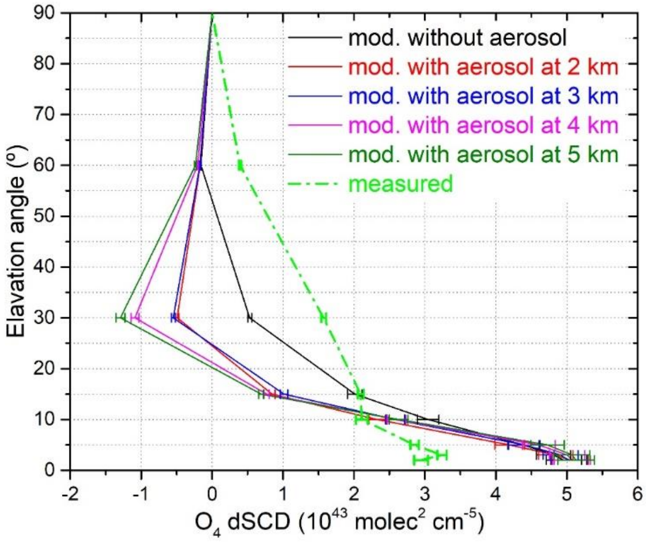

Figure S7: O_4 dSCD under the aerosol scenarios shown in Fig. S4. The different colors refer to the forward modelled dSCD under the different aerosol scenarios shown in Fig. S6 (Belgrano, 11^{th} November, 10:14 UTC). Additionally, the measured dSCD at that moment are also sown in bright green.

Also, in order to investigate the differences between a true uplifted aerosol profile and the retrieved one (i.e., the smooth version of the true profile), using the same a priori aerosol extinction (AEC) profile and covariance as the one used throughout our work, we can retrieve the aerosol profiles from the modelled O4 dSCDs with an aerosol layer peaking at 2 km and also from the modelled O4 dSCDs with an aerosol layer peaking at 4 km. The resulting retrieved AEC profiles are provided in Fig. S8. Note that, although the retrieved aerosol profiles peak at slightly lower latitude than the true profile, there is a clear difference between the altitudes of the maximum AEC retrieved at both instances. In fact, when investigating the averaging kernels corresponding to the aerosol inversion from the modelled O4 dSCDs with an aerosol layer peaking at 4 km (Fig. S9), the retrievals at 3.5 and 4 km are sensible mainly to layers above 2 km. This indicates that our MAX-DOAS observations and profile inversion scheme is able to sense the difference between a layer below 2 km and one at 4 km. Although these simulations indicate that the method is limited to quantitatively retrieved layers aloft, it also shows that, in case of uplifted layers, the retrieved profiles would show the enhancements of AEC at higher altitudes than the ones that we observed when aerosols are close to the surface.

Similarly, sensitivity tests performed with a BrO layer uplifted at different altitudes indicate that our procedure would, for instance, be able to sense a BrO layer centered at 2.5 km. As shown in Fig. S10, in that case and despite the BrO a priori profile peaking at the surface, the retrieval would show a smoothed version of an uplifted BrO layer (at ~1 km) and also negative BrO vmr at the surface (with nonphysical meaning). Note that none of the profiles presented in this work showed this sort of behavior (i.e., no BrO layer above 2 km). Unlike the work of Roscoe et al. (2014), the vertical information content and sensitivity of our MAX-DOAS observations and inversion scheme would not be able to distinguish an uplifted layer of BrO if BrO is also present on the lowest layers of the atmosphere (i.e., in case of a double peak profile). In that "double peak" case, the sensitivity tests indicate that the BrO layer aloft would increase in 20 % the BrO column inferred below that altitude (i.e., VCD2km) and ~10 % the mixing ratios retrieved just above the surface. Note, that the effect of such double peak on the retrieved BrO VCD2km and surface values would also depend on the scattering conditions of the atmosphere.

The sensitivity test performed support the definition of the vertical sensitivity of our MAX-DOAS observations throughout our work (up 4 km for aerosols and up to 2.5-3 km for BrO).

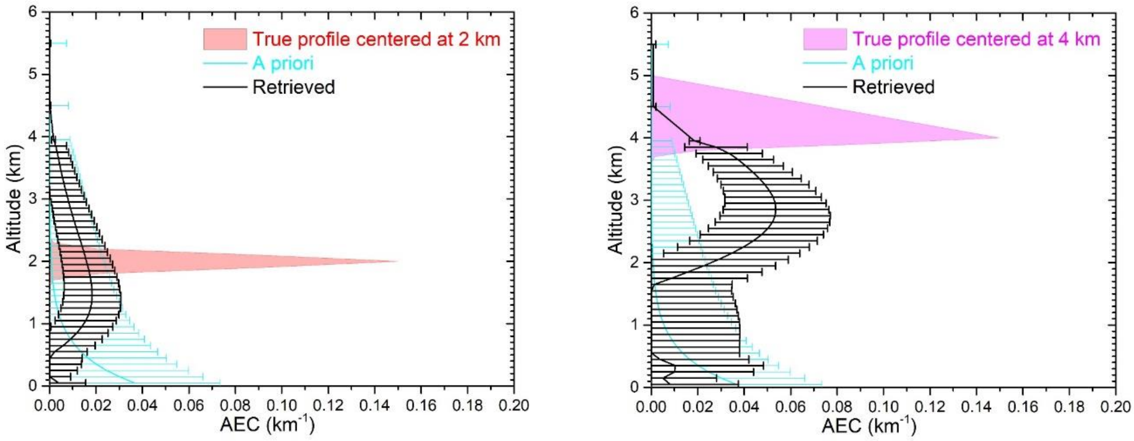

Figure S8: Example of true aerosol extinction profiles vs. the retrieved one (i.e., smoothed true profile). The left figure compares a true profile of an aerosol layer centered at 2 km (shaded in red) with the retrieved profile which peaks at ~1.5 km altitude (in black). The right figure compares a true profile of an aerosol layer centered at 4 km (shaded in pink) with the retrieved profile that peaks at ~3 km (in black). The a priori profile is provided also in both figures (cyan). Belgrano, 11th November, 10:14 UTC.

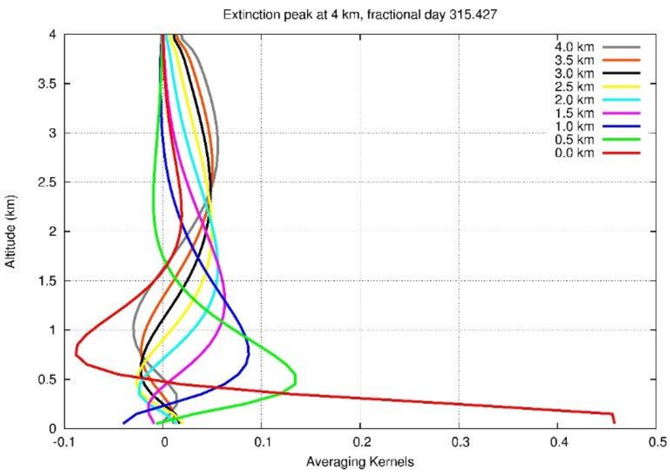

Figure S9: Averaging kernels corresponding to the sensitivity test of inverting an aerosol layer at 4 km (Fig. S5, right figure). Note how the retrieval at 3.5 and 4 km (orange, and grey, respectively) are sensible mainly to layers above 2 km.

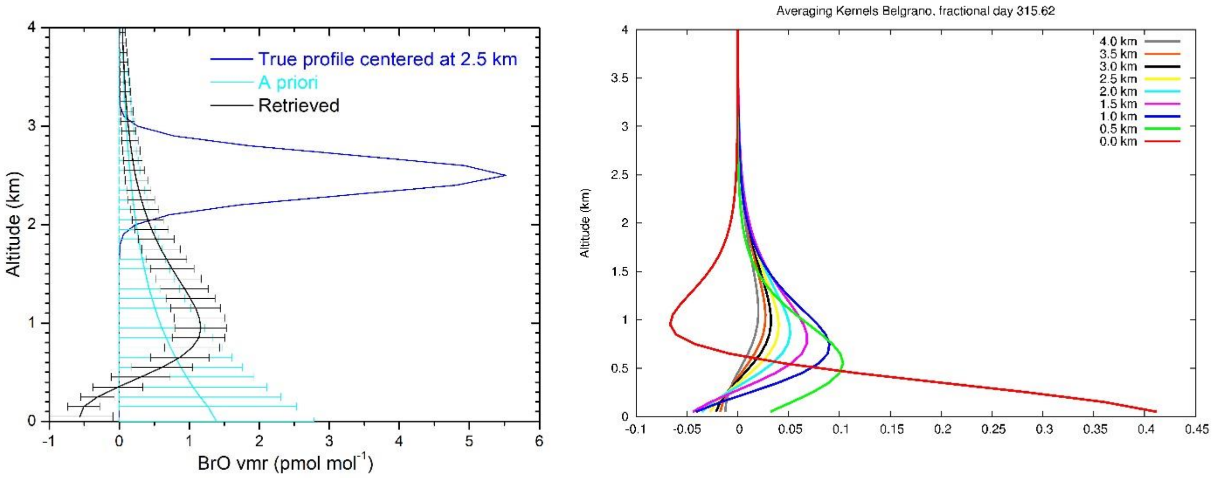

Figure S10: Sensitivity test of an uplifted BrO layer. (Left) Comparison of a true profile of an uplifted BrO layer centered at 2.5 km (dark blue) with the retrieved one (i.e., smoothed true profile, in black). No aerosol load was included on the simulation. The a priori BrO profile used in the inversion is shown in cyan. The scan of the test corresponds to Belgrano, 11th November (14:52 UTC). (Right) Averaging kernel of the retrieval.