

Interactive comment on Hemispheric asymmetry in stratospheric NO₂ trends by M. Yela et al.

Reply to Interactive comments from reviewer #1

We strongly appreciate the reviewer for his/her helpful and supportive comments. For clarity, our responses to the reviewer comments are in blue.

Anonymous Referee #1

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Review of “Hemispheric asymmetry in stratospheric NO₂ trends” by M. Yela et al. In this paper, the authors report on long-term ground based zenith-sky observations of stratospheric NO₂ columns at four stations and how they changed over the last 20 years. Interestingly, trends are of the order of 10% per decade at all stations but have opposite signs for the NH sub-tropical station and for the SH high latitude stations.

The stability of the trends with respect to time interval and parameters included in the trend model is evaluated, the difference between AM and PM trends discussed and the change in diurnal build-up of NO₂ evaluated. For Izana, DOAS NO₂-trends are also compared to other data sources from FTIR and satellite observations and qualitative but not quantitative agreement is found. In my opinion, this is an interesting and thorough analysis of stratospheric NO₂ trends which provides interesting data and results. While interpretation is mostly limited to qualitative discussion, and detailed comparison to dedicated model runs for the locations of the instruments is needed for a more quantitative evaluation, the study is relevant enough as it is to warrant publication. The manuscript is clearly structured, well written and the figures are clear and useful. As I have only few comments and suggestions, I recommend publication of this paper after minor revisions.

Major Comments

In the discussion of the difference in NO₂ trends between Marambio and Ushuaia, it is stated that the months with large differences are linked to the presence of the polar vortex. While this sounds plausible, it is not really supported by Fig. 8 which shows large differences already in April. To me this appears more like a latitudinal dependence which is more pronounced in winter than in summer. It is also stated that the trend in NO₂ columns could be linked to changes in vortex position and the resulting change in statistics.

This makes sense, and at least for Ushuaia, it would be relatively simple to check this assumption by repeating the analysis but excluding all measurements where the station was influenced by polar vortex air. I'd suggest adding this analysis to the paper.

Following the referee suggestion we have excluded the days inside the vortex from Ushuaia data series. Results show that, as expected, the trend decrease slightly (less negative) but the contribution to general trend is very small probably due to the fact that the days inside the vortex at Ushuaia, while increasing along time, are still very small compared with the total number of days. Even excluding these data the wavy pattern occurring in winter (reduction of the negative trend in July-August and increase in September-October) are mainly due to mid latitude dynamics. As a consequence we have reformulated the text in the following way:

Line 327 after “(Fig. 9)”. Removed the sentence starting after (Fig.9).

Line 327 after “(Fig. 9)”. Added the following paragraph: *“To test that the impact of the vortex position drifting is the main cause of the wavy structure in the trend observed in the Ushuaia winter (small trends in July-August large ones in September–October, see Fig. 8) we have repeated the monthly trend analysis excluding the days when the station was inside the vortex. Results show that while, as expected, negative trends are reduced, the magnitude is not enough to justify the observed trends. In fact, the changes are of only few tenths of a percent, probably due to the fact that the days inside the vortex at Ushuaia, while increasing along time, are still very small compared with the total number of days. In summary, when only extra-vortex*

data are used the winter wavy structure remains providing evidence that the evolution of the seasonal NO₂ trend is dominated by the mid-latitude dynamics along the year.”

In the comparison to satellite data, it would be good to add some information on collocation criteria used and the respective overpass times of the satellites. I think it would also be interesting to compare the satellite data to the PM DOAS measurements. Although the time difference between satellite observations and AM data is usually shorter, the AM measurements are strongly impacted by night-time chemistry whereas the satellite data at least over sub-tropical regions are more representative for daytime chemistry. In my experience, correlation of ground-based and satellite NO₂ data is better when using PM observations at least at low latitudes.

The purpose of considering all data available, including GB-FTIR and satellite for the Izaña station is to support, through additional and independent measurements, the genuine character of the trend. For that reason in this particular work no collocation has been applied since the absolute magnitude does not affect the trend. On the other hand, at Izaña, the ENVISAT overpassing time coincides with the effective SZA at which AM DOAS measurements are taken thus the photochemical correction has an almost negligible impact in the intercomparisons. OMI overpassing is later, and the NO₂ column is some 10% larger due to the diurnal build-up but, as mentioned, our interest lies in the trend rather than in absolute values. Recently a detailed intercomparison at Izaña considering collocation and “effective SZA” have been published (AMT Robles et al. 2016).

Minor comments

Line 38: I think the reactions listed do not lead to catalytic ozone destruction; for this reaction of NO₂ with O needs to be included.

We have improved the sentence: Nitrogen oxides interact with ozone both directly and indirectly. Nitric oxide (NO) reacts with ozone, forming NO₂ and O₂. NO is recovered by NO₂ reaction with atomic oxygen and, in day time, by NO₂ photolysis. This catalytic reactions result in ozone reduction.

Line 56: major source of NO₂ => major source of NO₂ in the stratosphere.

Done

Line 93: was installed Antarctica => was installed in Antarctica.

Done

Line 116: were derived from 6 typical individual measurements => were typically derived from 6 individual measurements (?).

We have modified the sentence: “...were derived from all available measurements between 89° and 91° SZA, typically 5-6 data per twilight”.

Line 134: effect on the cross-sections => effect on the effective cross-sections.

Done

Line 141: For monthly data – do you mean the fraction of months for which you have no data at all?

We clarified this point: “For monthly mean data, the rates of failures are 3.45 %, 0.40 % and 0.79 % of the total dataset for Izaña, Ushuaia and Marambio, respectively”.

Line 160: alpha > 0.1 – alpha not defined.

Alpha refers to the significance level. We simplified the sentence “to exclude the proxies exceeding $\alpha > 0.1$, corresponding to significant values of less than 90%”. Now it stands as “to exclude proxies with confidence intervals below 90%”

Line 160: significant values of less than 90% => significance values of less than 90%.

Changed. See above

Line 266: Both halogens should result => The observed changes in both halogens should result.

Done

Line 292: thus there was less N₂O₅ – while this is a reasonable explanation, I think other explanations cannot be completely excluded.

In lines 277-285 we argue that DBU is a good index to estimate changes in N₂O₅. However, as the reviewer points out, other explanations could be possible, particularly a change in the vertical distribution of the NO₂ column. Therefore we have modified the sentence as follows:

“In summary, all SH stations exhibit a negative decadal trend in their DBUs, ranging from -8 to -14 %, revealing either a reduction of N₂O₅ in the past few years at the middle and high latitudes of the Southern hemisphere or dynamically induced changes in the NO₂ vertical distribution ”.

Line 364: N₂O oxidation is not the cause of the observed trend, nor of other global parameter changes. This sentence sounds odd, please rephrase.

Global NO₂ increase was expected at the beginning of the analysis due to the very long N₂O lifetime at a maintained increasing rate of 2.5%/decade. We have reformulated the sentence to make it clearer:

”The opposite sign in the NO₂ trends observed at the NH and SH stations shows that the NO_x distribution in the stratosphere does not directly reflect the increasing N₂O in the atmosphere, at least when individual stations are analyzed.”

Figure 10: Please add that these are AM DOAS measurements (see also my comment above).

Done

NOTE: Ushuaia data in figure 2, 4, 5, 6 and 8 are slightly different than in previous version due to the correction of few data from a recent quality control.

Reply to Interactive comments from reviewer #2

We thank you the reviewer for his/her helpful comments. For clarity, our responses to the reviewer comments are in blue.

Anonymous Referee #2

Received and published: 8 August 2017

This paper presents sound analysis of four data series that, in keeping with NDACC requirements, have measured stratospheric species to the best available standards over decades. The literature is well surveyed, and the analysis techniques follow established practice, but in doing so the paper does not add much new insight. The results are at odds with cited previous studies, and that should be discussed further. My main criticism is that, starting with the title, the representativeness of the sites seems to be exaggerated; one site in the Canary Islands serves as a proxy for the northern hemisphere, while three sites in Tierra del Fuego, the Antarctic Peninsula, and the southern Weddell Sea purportedly represent the southern hemisphere. It

would be better to acknowledge the respective limitations, especially as the NDACC as a whole gives much wider (if still irregular) coverage.

While certainly a subtropical station is not representative of the NH, all 4 NDACC GB stable instruments with long data series support the hemispheric asymmetry in stratospheric NO₂ at different latitudes previously observed by satellite instrumentation. The title highlight what we think is the major outcome of the paper: The changing behavior of the stratospheric dynamics in last decades. The stations are already enumerated in the abstract, so we think there is no misunderstanding.

Both latitudinal and longitudinal gradients may be present, as implicit for Antarctic vortex displacement toward South America, but also cited as a feature of Gruzdev's 23-station analysis in 2009 ("Trends were found to be mostly positive in the middle and low latitudes of the SH and mostly negative in the European sector of the middle latitudes of the NH" - both different from this study).

Latitudinal and even longitudinal gradients in the tracers distribution in the stratosphere are a well known feature. NO₂ display a strong meridional gradient during solstice due to differences in illumination time. Longitudinal small gradients can be present as well due to the quasi-stationary planetary waves, but we don't see the reason why this should affect the long-term trends. On the other hand Gruzdev data analysis ends in 2007 and we found that last years have a strong contribution to the observed trend.

It may also be that the difference depends heavily on the analysis period. The Izaña residuals in Fig 2 to 2008, as comparable to a 2009 analysis, show no upward trend, and the Ushuaia and Marambio data to the same time show indistinct trends.

Time period determine the magnitude in any analysis trend. In figure 5 the Izaña trend resulting from calculation using different time periods show that the trend remains essentially unchanged if the data series is shortened by up to 5 years at the start and up to 4 at the end, but also that most of the trend resulted from the increase in last decade. A similar situation occurred in the SH. (See Fig.2 and text in lines 255-256).

On the subject of time periods, the authors should perhaps also mention why their paper in mid 2017 only includes data to the end of 2014. My guess is that it represents a lengthy period of trying different analyses in what is routinely a frustrating attempt to tease meaning from such datasets, but it would still be better for the 25 years of NDACC special issue to use the 24 years of data from Izaña and 23 from the others.

The reason why the data series ends at the beginning of 2015 is that the work was mostly elaborated during 2015 and delayed later on due to a number of reasons. Adding 2 more years of data (10%) at the present time implies a complete recalculation that authors do not consider justified enough since it would produce only small changes in the magnitude of the results not compromising the main results of the paper.

Specific points:

Lines 41-43: The technique of zenith-sky DOAS was pioneered by Noxon, and the first regular monitoring was at Lauder, continuous from 1980, and later from Scott Base.

We corrected this omission. Authors are well aware that Lauder station is the first regular NO₂ monitoring station. The sentence now stands as: "*Regular monitoring of stratospheric NO₂ started in 1980 with the deployment of Zenith DOAS (Differential Optical Absorption Spectroscopy) scanning spectrometers at Lauder, New Zealand by Mckenzie and Johnston, 1982 followed by two Antarctic stations (Scott Base at 78° S by Mckenzie and Johnston, 1984 and Dumont D'Urville at 66° S by Pommereau and Goutail, 1988)*".

We have included reference: McKenzie, R., L. and Johnston, P.V.: Seasonal variations in stratospheric NO₂ at 45° S, Geophys. Res. Lett., V9, p. 1255-1258, 1982

Line 106: "... degradation ... at a rate of 4.33%/year." Confidence limits on this figure are relevant to the inferred trends.

The scanning spectrometer initially installed in 1993 is still in operation. We added the PDA and CCD to improve the accuracy and to extend the spectral range toward the UV and IR. We do not estimate a larger error due to degradation since it was a very slow and linear effect, and was corrected with the scanning-photomultiplier spectrometer operating in the same site (430-450 nm band).

Line 147: The second beta terms should be subscripted 2k, not 2k-1.

Corrected.

Line 154: "... since the start of measurements, in months". The scaling of t by $2\pi/12$ in the trigonometric terms of the equation means that t must be expressed in months.

Added

Line 156: "annual, semi-annual, and four-monthly waves". A quarterly term would have $k=4$.

Quarterly term has been removed from the analysis and text since it has no impact at all.

Line 160: " $\alpha > 0.1$ " is less conventional than $p > 0.1$ to express significance level.

We simplified the sentence "*to exclude the proxies exceeding $\alpha > 0.1$, corresponding to significant values of less than 90%*". Now it stands as "*to exclude proxies with confidence intervals below 90%*"

Line 178: "in the first few years of the time series, strongly affected by Pinatubo, which would otherwise bias the trend" would make it clearer that the bias was a genuine geophysical effect rather than a measurement or statistical artefact.

The sentence has been modified: "*SA proxy accounts for the short-range contribution of the volcanic aerosols on the NO_2 column which would, otherwise, affect the long term trend*".

Line 197: "negative trend (Schwarzkopf and Ramaswamy, 2006)", rather than "i.e." Alternatively, "e.g." might have been meant here.

Corrected.

Line 244: "large nitrate aerosols load injected following Pinatubo's eruption". Pinatubo injected 20 Mt of sulphur dioxide, which was oxidised to sulphate aerosol over a few weeks. There was no large injection of nitrate aerosols by Pinatubo, or following it.

This is a miswriting. It is obviously sulphate.

Line 247: "quarterly" is "four-monthly".

The $K=3$ term does not affect anything and has been removed.

Line 265: "negative decadal trend of $-5.9 \pm 1.5\%$ " would be clearer, without any risk of tautology.

Changed.

Lines 303-306: "The negative trend in the SH increases ... At Ushuaia, the negative trend is reduced to values close to the annual minimum (-7%), whereas in Marambio, the trend increases with respect to previous months". Talking of minima, and reductions, in negative trends is unnecessarily ambiguous. While the reader can perhaps correctly assume a reduction in the absolute value of a negative trend is meant, it is better to choose different words: "The downward trends in the SH become more negative further south ... At Ushuaia, the trend is less negative ...".

The proposed sentence is clearer. We have modified it.

Line 340: "The MIPAS data have been combined with the DOAS averaging kernels ...", or "converted", rather than "corrected".

Changed

Line 348: Fig 10, lower panel, does not show similar seasonalities; that would require a monthly plot like Fig 8.

"*annual means*" in line 347 should read "*monthly means*". Lower plot displays the monthly means. This has been corrected.

Line 351: "MIPAS decadal trend of $+3.0 \pm 0.4\%$ " appears as 5.0 ± 3.5 in Table 5. Please check all such figures.

Figures in Table 5 are correct. We have corrected the text in line 351.

Line 364: "... evidence that N₂O oxidation is not the cause ..." Please clarify. Is that argument that N₂O is sufficiently well mixed that any change would expect both hemispheres the same?.

Global NO₂ increase was expected at the beginning of the analysis due to the very long N₂O lifetime at a maintained increasing rate of 2.5%/decade. We have reformulated the sentence to make it clearer: "*The opposite sign in the NO₂ trends observed at the NH and SH stations shows that the NO_x distribution in the stratosphere does not directly reflect the increasing N₂O in the atmosphere, at least when individual stations are analyzed*".

Line 369: "Negative trends were found in the lower stratosphere ..."

Corrected

Line 391: "... change of sign between hemispheres in the stratospheric trend" would be better, except for comments above about whether the four sites really represent their respective hemispheres.

Corrected.

In Table 5, please check the calculation of the "T statistic" (usually "t statistic") as the values appear to be at odds with the trends and their standard errors.

The stated errors are not the standard errors but the trend estimate errors based on Weatherhead et al, 1998 which account for the data autocorrelation. Since the t-statistics only contributes to generate confusion, we have removed that column from the table.

NOTE: Ushuaia data in figure 2, 4, 5, 6 and 8 are slightly different than in previous version due to the correction of few data from a recent quality control.

Hemispheric asymmetry in stratospheric NO₂ trends

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Abstract. Over twenty years of stratospheric NO₂ vertical column density (VCD) data from ground-based zenith DOAS
15 spectrometers was used for trend analysis, specifically, via multiple linear regression. Spectrometers from the Network for the Detection of Atmospheric Composition Change (NDACC) cover the subtropical latitudes in the Northern Hemisphere (Izaña, 28°N), southern Subantarctica (Ushuaia, 55°S) and Antarctica (Marambio, 64°S and Belgrano, 78°S). The results show that for the period 1993-2014, a mean positive decadal trend of +8.7% was found in the subtropical Northern Hemisphere stations, and negative decadal trends of -8.7% and -13.8% were found in the Southern Hemisphere at Ushuaia and Marambio,
20 respectively; all trends are statistically significant at 95%. Belgrano only shows a significant decadal trend of -11.3% in the summer/autumn period. Most of the trends result from variations after 2005. The trend in the diurnal build up per hour (DBU) was used to estimate the change in the rate of N₂O₅ conversion to NO₂ during the day. With minor differences, the results reproduce those obtained for NO₂. The trends computed for individual months show large month-to-month variability. At Izaña, the maximum occurs in December (+13.1%), dropping abruptly to lower values in the first part of the year. In the Southern
25 Hemisphere, the polar vortex dominates the monthly distributions of the trends. At Marambio, the maximum occurs in the mid-winter (-21%), whereas at the same time, the Ushuaia trend is close to its annual minimum (-7%). The large difference in the trends at these two relatively close stations suggests a vortex shift towards the Atlantic/South American area over the past few years. Finally, the hemispheric asymmetry obtained in this work is discussed in the frame of the results obtained by previous works that considered tracer analysis and Brewer-Dobson circulation. The results obtained here provide evidence that the NO₂
30 produced by N₂O decomposition is not the only cause of the observed trend in the stratosphere and support recent publications pointing to a dynamical redistribution starting in the past decade.

1 Introduction

Stratospheric nitrogen dioxide (NO₂) has been a subject of interest since the late sixties, when the use of supersonic aircraft flying at stratospheric levels was being considered. At that time, studies on the impact of nitrogen oxides on the ozone in the stratosphere were initiated (Johnston, 1971). The interest in this atmospheric layer was enhanced in the mid-seventies, powered by the discovery of the ozone depletion potential of halogenated compounds (Stolarski and Cicerone, 1974).

Nitrogen oxides interact with ozone both directly and indirectly. Nitric oxide (NO) reacts with ozone, forming NO₂ and O₂. NO is recovered by NO₂ reaction with atomic oxygen and, in day time, by NO₂ photolysis. This catalytic reactions result in ozone reduction. On the other hand, NO₂ reacts with BrO and ClO, mitigating the ozone depletion potential of halogenated compounds. NO_x oxidation products, such as HNO₃ and N₂O₅, have relatively long lifetimes and therefore act as NO₂ reservoirs.

Regular monitoring of stratospheric NO₂ started in 1980 with the deployment of Zenith DOAS (Differential Optical Absorption Spectroscopy) scanning spectrometers at Lauder, New Zealand, by Mckenzie and Johnston, 1982 followed by two Antarctic stations (Scott Base at 78° S by Mckenzie and Johnston, 1984 and Dumont D'Urville at 66° S by Pommereau and Goutail, 1988). In the following decades, instruments were installed at remote, unpolluted sites for monitoring NO₂, O₃ and other stratospheric gases suitable for ground-based measurements.

Recently, the interest in trends of stratospheric trace gases has increased, since global circulations models predict an acceleration of the stratospheric residual circulation (or Brewer-Dobson circulation, BDC hereafter) of 2-3.2 %/decade as a consequence of the temperature changes in the atmosphere due to human activities (Butchart, 2014). The speed of the BDC circulation influences the concentrations of long-lived trace gases with sources in the troposphere (e.g., CFCs, CH₄, N₂O), as well as their eventual stratospheric products (Cook and Roscoe, 2009). In particular, N₂O, which is the primary source of NO_x, dissociates in the stratosphere via a reaction with excited atomic oxygen (¹D) and produces NO. NO₂ is mainly formed by the NO+O₃ reaction. An accelerated BDC implies a lower mean residence time of N₂O in the stratosphere and, consequently, a lower N₂O to NO₂ conversion.

On the other hand, the emissions of N₂O to the atmosphere are steadily growing, with the concentration increasing at a rate of 2.5 % / decade and more in recent years (IPCC, 2013). Since the N₂O lifetime in the troposphere is approximately 120 years and N₂O is the major source of NO₂ in the stratosphere, a tropospheric increase will result in an NO₂ increase in the stratosphere.

These two counteracting processes could minimize or even cancel the potential changes in the stratospheric concentration of NO₂. However, the observational evidence of a trend in the BDC speed remains inconclusive (Butchart, 2014, Fu et al., 2015). Oberländer-Hayn et al., (2016) suggest that, even though the stratosphere is changing substantially in response to Greenhouse Gases (GHG) increases, most of the BDC trend is associated with a lifting of the entire atmospheric circulation instead of an accelerating flow. If this is the case, a NO₂ increase should be seen in the long term, given that all other factors remain the same.

65 Previous studies to establish a trend in stratospheric NO₂ based on the DOAS data from the stations with long data
availability, however, did not yield conclusive results on the global scale. A first attempt was undertaken by Liley et al., (2000)
using the longest data series available, who found an approximate 5 % increase at Lauder (45°S) for the period 1981-1999.
Fish et al., (2000) found no explanation related to the changes in O₃, temperature or water vapour, concluding that only changes
in the stratospheric aerosol load could explain the observations. Later, McLinden et al., (2001) reproduced the observations of
70 Liley et al. (2000) using a 3D CTM model, including halogen chemistry and assuming a negative trend in temperature of
0.5°/decade. A few years later, Gruzdev (2009) analysed 23 stations from the NDACC database. Trends were found to be
mostly positive in the middle and low latitudes of the Southern Hemisphere (SH) and mostly negative in the European sector
of the middle latitudes of the Northern Hemisphere (NH). In the high and polar latitudes of both hemispheres, the annual
estimates of the trends were mostly statistically insignificant. In Antarctica, a positive NO₂ trend was observed at 78° S, while
75 in the NH high latitudes, both positive and negative trends were observed. A detailed study of the Jungfraujoch station (55° N,
3550 masl), including DOAS plus FTIR data and satellite composites (Hendrick et al., 2012), found negative trends ranging
from -2.4 % to -4.3 %, depending on the instrument and selected period. In summary, until now, the global NO₂ trend over the
past few decades has not been accurately established. One important difficulty in comparing the trends at different latitudes is
that the stations do not cover the same periods. In addition, the trends can be the result of multiple factors that do not behave
80 linearly.

The purpose of this work is to contribute to the knowledge of the long-term NO₂ evolution by searching for significant
trends in the stratospheric NO₂ using the INTA NO₂ DOAS records in combination with a multiple regression model. Such
models have been extensively used in recent years to infer trends in long-term atmospheric time series of ground-based
instruments; in particular, they have been used to study the evolution of stratospheric ozone (Bodeker et al., 1998; Wohltmann
85 et al., 2007; Fioletov 2008; Mäder et al., 2010), NO₂ (Van der A et al., 2006 and 2008; Gruzdev, 2009, Hendrick et al., 2012)
and other species (i.e., Remsberg, 2015).

The paper is organized as follows: In section 2, the instruments and data are described. In section 3, the regression
model and explanatory variables are presented. Section 4 addresses the results and is composed of 3 subsections. In 4.1, the
general results are shown. Section 4.2 addresses a more detailed analysis of the subtropical case and, in section 4.3, the
90 interhemispheric asymmetry is discussed. Finally, the conclusions are shown in section 5.

2 Instrumentation, stations, techniques and database

In the year 1993, INTA installed a scanning spectrometer at the subtropical high mountain observatory of Izaña (28° N, 16°
W, 2370 masl) for long term measurements of stratospheric NO₂. In 1994, two identical instruments were deployed in
Subantarctica (Ushuaia station; 55° S, 68° W) and Antarctic Peninsula (Marambio station; 64° S, 56° W). Then, in 1995, a
95 fourth instrument was installed in Antarctica at a higher latitude (Belgrano station; 78° S, 35° W). The three instruments cover

the latitudinal belt from the outside to the inside of the Antarctic vortex. Since installation, all instruments have been operated without interruption.

100 Belgrano (in continental Antarctica) is usually closest to the core of the polar vortex and hence is representative of the in-vortex air. Marambio (Antarctic Peninsula) is frequently located at the edge of the vortex region and alternates between measuring the vortex and the mid-latitude air masses. Ushuaia is, essentially, a mid-latitude station and only occasionally is reached by in-vortex air

105 The instrumentation consists of spectrometers covering the visible range, and the retrieval is based on the DOAS technique. At all four stations, identical scanning spectrometers (EVA) were initially installed. In Izaña, a second spectrometer (RASAS), based on a diode array detector, covering a wider range was added in 1999. Then, in 2010, the PDA was replaced by a CCD (RASAS-II), including MAXDOAS capability. All instruments were developed at the INTA laboratories. Data merging was carefully carried out after a period of overlap to assure the smooth transition between the instruments. The transition between EVA and RASAS has been previously reported (Gil et al., 2008). The transition between RASAS and RASAS-II required a RASAS correction due to a degradation of the detector response since mid-2006, at a rate of 4.33 % / year. The details of the RASAS-II instrument have been previously published in Puentedura et al., (2012) and Robles-Gonzalez et al., (2016). The spectrometers were installed in the top terrace of the Izaña Atmospheric Observatory, run by the CIAI (Centro de Investigación Atmosférica de Izaña), belonging to the Agencia Estatal de Meteorología (AEMET, Spain), on the slopes of the Teide volcano, Tenerife, Canary Island. The Izaña Atmospheric Observatory is a high mountain station, part of the Global Atmospheric Watch (GAW) programme and managed by the CIAI.

115 The EVA instrument is a scanning spectrometer for twilight measurements between 88-92° solar zenith angles (SZA) in the 430-450 nm spectral range, with a spectral resolution of 1 nm. These instruments are located outdoors in thermostatic housings. The three Southern Hemisphere spectrometers were compared to each other after one year of measurements with the help of a NO₂ cell containing a known amount of gas. The discrepancies among them were found to be below 4 % (Yela et al., 2005). Twilight (AM and PM) vertical column densities were derived from all available measurements between 89° and 91° SZA, typically 5-6 data per twilight. New MAXDOAS instruments have been installed at the three stations, in 2011 at Belgrano, 120 in 2015 at Marambio and in 2016 at Ushuaia. Both, DOAS and MAXDOAS instruments are simultaneously measuring for data serie homogenisation.

125 The NO₂ column retrieval is based on the standard DOAS spectral analysis (Platt and Stutz, 2008), performed using software developed at INTA. The DOAS settings for the NO₂ column retrieval follows the NDACC UV/Vis Working Group recommendations (Van Roozendaal and Hendrick, 2012) whenever possible. Absorption cross sections O₃, NO₂, H₂O and O₄ have been also included in the analysis. Raman scattering cross section was generated by the Win-DOAS package (Fayt and Van Roozendaal, 2001), calculated from Raman theory. Finally, the inverse of the reference spectrum was included as a pseudo cross section to account for stray light inside the spectrograph and the residual dark current of the detector. The air mass factor (AMF) used for the conversion of the NO₂ slant columns to vertical columns is the NDACC NO₂ standard AMF, available on the NDACC UV-Vis web page (<http://ndacc-uvvis-wg.aeronomie.be/>) and based on the Lambert et al., 1999 and 2000

130 climatology of the NO₂ profiles. This climatology consists of a Fourier harmonic decomposition of the UARS HALOE v19 and SPOT-4 POAM-III v2 NO₂ profile data. The cross sections and other parameters used in the analysis are shown in Table 1.

The estimated overall errors in the individual measurements are, on average, approximately 12 % (1-2 % fit analysis; < 2 % cross-sections; 2 % reference spectrum; 2-3 % AMF; 2 % stratospheric temperature). For details, see Gil et al., (2008).
135 Fit analysis, cross-sections and reference spectra do not affect the trends. Potential long-term changes in the stratospheric temperature could have a minor effect on the **effective** cross-sections, but no statistically significant changes in the stratospheric temperature have been observed during the data period. Only differences in the NO₂ profiles with respect to the AMF climatology used, could have an effect of a few tenths of a percent.

The spectrometers are NDACC-qualified instruments (more information is available at
140 <http://www.ndsc.ncep.noaa.gov/data/>) and have been successfully intercompared for NO₂ in ad hoc international exercises (Roscoe et al., 1999 and 2010, Vandaele et al., 2005).

The DOAS technique at the zenith during twilight is slightly sensitive to clouds. Gaps in the data are mostly due to instrumental malfunctions. **For monthly mean data, the rates of failures are 3.45 %, 0.40 % and 0.79 % of the total dataset for Izaña, Ushuaia and Marambio, respectively.**

145 **3 Multiple regression and proxies.**

In the present work, a multiple linear regression model of the following form was used:

$$Y(t) = a + \sum_{k=1}^2 \left[\beta_{2k-1} \sin \left(2 \pi t \frac{k}{12} \right) + \beta_{2k} \cos \left(2 \pi t \frac{k}{12} \right) \right] + \sum_{j=5}^{m+4} \beta_j X_j(t) + \varepsilon(t) \quad (1)$$

150

where,

$Y(t)$ = NO₂ column at time t

a = constant

X_j = each of the explanatory functions

155 β_j = coefficient of the corresponding explanatory function X_j

t = time since the start of the measurements, **in months**

ε = noise as a function of time t

m = number of explanatory functions

The bracketed terms represent the harmonic functions accounting for the annual **and semi-annual** waves, whereas the
160 βX terms include all explanatory variables. In the first run, 7 proxies that could potentially affect the NO₂ distribution are used

(the trend, stratospheric aerosols, solar cycle, Quasi-Biennial Oscillation (QBO), stratospheric temperature, stratospheric circulation, and El Niño Southern Oscillation (ENSO)). Following Mäder et al., (2007), an iterative process was used [to exclude proxies with confidence intervals below 90%](#). For details, see Mäder et al., (2007) and Knibbe et al., (2014). In this way, the degrees of freedom of the regression increase.

165 Autocorrelation affects the linear trend calculation by increasing the uncertainty. If autocorrelation of the data noise is not included, the standard deviation of the trend estimate will substantially underestimate the actual uncertainty. According to Weatherhead et al., (1998), the standard deviation of the trend per year to be used to describe the precision of the trend estimate can be approximated quite accurately by:

$$\sigma_{\beta} \approx \frac{\sigma_N}{n^{3/2}} \sqrt{\frac{1+\phi}{1-\phi}} \quad (2)$$

170 where σ_N is the standard deviation of the residuals (differences between the NO_2 data series and the modelled one), and n is the length of the data series in years and ϕ is the autocorrelation in the residual for time lag 1, defined as $\text{Corr}(N_t, N_{t-1})$. This formula has been previously used for trends in NO_2 (Van der A et al., 2006 and 2008, Hendrick et al., 2012).

Stratospheric aerosols. Stratospheric aerosols (SA) affect the amount of available NO_x . An increase in the aerosol loading due to volcanic eruptions reduces the NO_x/NO_y partitioning through the heterogeneous hydrolysis of N_2O_5 on the aerosol surfaces (Fahey et al., 1993). The eruption of Mount Pinatubo in 1991 produced a reduction in the total NO_2 column of 19-34 %, depending on the station, in the following years (Gruzdev, 2014). Therefore, SA have been included as a proxy in the analysis. The dataset is the monthly aerosol optical depth (AOD) for the NH at $0.55 \mu\text{m}$, compiled at NASA's Goddard Institute for Space Studies (GISS). The dataset ending in September 2012 has been extended in time to April 2014 by the optical spectrograph and infrared imaging system (OSIRIS) data and to the end of 2014 by the white light optical particle
175
180 counter (WOPC) data (Kremser et al., 2016). For the analysed period, [SA proxy accounts for the short-range contribution of the volcanic aerosols on the \$\text{NO}_2\$ column which would, otherwise, affect the long term trend.](#)

Solar cycle. The solar radiation flux at 10.7 cm (2800 MHz) is an excellent indicator of solar activity. The data used are from the Penticton Radio Observatory in British Columbia. Unlike many solar indices, it can be easily and reliably measured on a day-to-day basis from the Earth's surface in all types of weather. The 11-year solar cycle proxy is included to
185 account for potential chemical changes due to variations in UV-radiation.

QBO. The Quasi Biennial Oscillation (QBO) affects the circulation in the lower stratosphere and hence the species distribution (Gray and Russell, 1999). Recently, QBO signatures in the variability of the middle to upper stratosphere NO_2 where detected (Liu et al., 2011). We employ a commonly used monthly index, built using the mean of the zonal winds averaged from 3 equatorial stations (Canton islands, Singapore and Gan/Maldives) compiled by the Berlin Free University
190 for 50 and 10 hPa.

ENSO. The El Niño/Southern Oscillation (ENSO) has been found to influence the distribution of minor species in the tropical lower stratosphere up to 27 km (Randel et al., 2009). We have included as a proxy/predictor the multivariate

195 ENSO Index (MEI) based on the six main observed variables over the tropical Pacific: the sea-level pressure (P), zonal (U) and meridional (V) components of the surface wind, sea surface temperature (S), surface air temperature (A), and total cloudiness fraction of the sky (C). Negative values of the MEI represent the cold ENSO phase (La Niña), while positive MEI values represent the warm ENSO phase (El Niño). For details, see Wolter and Timlin, (2011). A time lag of one to six months has been tested since the middle stratosphere may take time to respond to tropical sea surface temperature anomalies (Sioris et al., 2014).

200 **Stratospheric temperature.** There is a growing consensus that the global temperatures in the stratosphere [show a negative trend \(Schwarzkopf and Ramaswamy, 2006\)](#); however, its magnitude is still under debate (Seidel et al., 2016). A recent study by Randel et al., (2016) based on satellite data shows a cooling trend of -0.1 to -0.2 K decade⁻¹ in the lower stratosphere and up to -0.5 to 0.6 K decade⁻¹ in the middle stratosphere for the period 1979-2015, but most of this trend is due to the large decrease prior to 1995. After that date, there is no significant trend observed (Seidel et al., 2016).

205 Temperature variations in the stratosphere modify the NO₂ concentration by changing the reaction rates. To account for the potential trends related to this effect, the stratospheric temperatures over the stations extracted from the Interim European Centre for Medium-Range Weather Forecasts (ECMWF) Re-Analysis (ERA-Interim) (Dee et al., 2011) have been used as a proxy. Temperature data are extracted from the 0.25° x 0.25° grid at levels corresponding to the height of the NO₂ maximum at each station, as obtained by the NO₂ harmonic climatology based on HALOE v19 and POAM-II data (Lambert et al., 1999), that is, 10 hPa for Izaña, 20 hPa for Ushuaia and 30 hPa for Marambio and Belgrano. We used the monthly mean
210 of the average of the 00:00 h and 12:00 h UT values as a proxy.

Stratospheric circulation. Changes in BDC induce changes in the concentration of stratospheric species with tropospheric origins. Recent climate studies have found that BDC will intensify with the increase in greenhouse gases (Butchart, 2014). With a faster meridional circulation, N₂O of tropospheric origin has a shorter lifetime in the stratosphere, and, as a consequence, less N₂O would be oxidized to NO (Cook and Roscoe, 2009). To identify potential changes in the long-
215 term NO₂ evolution associated with this effect, the Eddy heat flux (EHF) ($v'T'$) at 100 hPa, averaged over 45°-75° S of the hemisphere, where the observational stations are located, has been included as a proxy in the multiple regression analysis. EHF is proportional to the vertical component of the Eliassen-Palm (EP) flux (Fosco and Salby, 1999, Salby and Callaghan, 2004), which has been found to have good correlation/anticorrelation with the extratropical/tropical O₃ (Randel et al., 2002, Weber et al., 2011). Data for the calculation of EHF were obtained from the ERA-Interim data, averaged for every month of
220 the time series. The cumulative effects of the total NO_x/NO₂ concentration were approximated by considering a delayed response in the EHF time series as follows (Brunner et al., 2006):

$$\text{EHF}(t) = \text{EHF}(t - 1)e^{\frac{\Delta t}{\tau}} + \text{EHF}(t) \quad (3)$$

where EHF(t) is the data obtained from the ERA-Interim winds and temperatures and Δt is the data time unit. For the Antarctic/Subantarctic stations τ was set to 12 for months from April to September and was set to 3 for the rest of the year. For Izaña subtropical station it is set to 3 for the whole year.

In Table 2, the source of each proxy is summarized.

4 Results

4.1 General

The multiple regression fit is shown in Fig. 1 for Izaña, Ushuaia and Marambio. The model explains between 86 to 96 % of the observed variance in all cases. The dominant pattern is, as expected, the seasonal wave, explaining between 57 to 85 % of the variance, followed by the linear trend, explaining from 6 to 27 % of the variance. The rest of the explanatory variables have modest contributions. The residuals and the trend were plotted together to search for common structures that could represent anomalies not captured by the model (Fig. 2). The morning and evening residuals look very similar, showing the non-random character of the departures of the model. Cross-correlation between the stations shows independent residuals (correlation coefficients: IZO/USH = +0.01, IZO/MAR=-0.08, and USH/MAR=+0.13). The trend is significant at 99 %.

The results of the analysis show that the seasonal waves and trend are the major contributors to the variance, explaining 84.3/83.4 %, 91.0/92.2 % and 89.2/94.8 % of the variance for AM/PM at Izaña, Ushuaia and Marambio, respectively. As an example, Fig. 3 shows the individual contributions of the less relevant proxy terms (other than the seasonal and trend terms) for Izaña. They all maintain standard deviations below 5×10^{13} molec.cm⁻², representing less than 2 % of the NO₂ data series mean value (2.45×10^{15} molec.cm⁻²). The details of the trend analysis are summarized in Table 3.

To further explore the contributions of each proxy to the retrieved trend, a sensitivity test has been performed for data of the three stations. The results are shown in Fig. 4. Each data point represents the trend obtained when different proxies are excluded from the analysis. The first data point is the trend inferred considering all proxies from the monthly data series. The next six data points represent the trends when single proxies are excluded from the analysis, followed by the results obtained when excluding successively more proxies in order of their significance. Finally, the last data point represents the result of a simple linear regression. The results show that only stratospheric aerosols have a large impact at all three stations. Although the influence was restricted to the first years of the data (1993-1995), before the decay of the large sulphate aerosols load injected in the stratosphere following Pinatubo's eruption in 1991, this influence does affect the trends of the complete series by 14 to 22 %. Since the stratospheric aerosols reduce NO₂, when removing the aerosols proxy, the trend increases with a positive trend (NH) and decreases when the trend is negative (SH). The EHF have no impact or significance and was removed from the final analysis. The impact of the stratospheric temperature is also very small, probably because the impact is accounted for by the seasonal waves. The rest have minor impacts (<5%).

Next, we explored the trend sensitivity to the data series length by reducing the period both at the starting and ending months. For this exercise, we chose the Izaña PM series. The results (Fig. 5) show that the trend remains essentially unchanged

255 if the data series is shortened by up to 5 years at the start and up to 4 at the end, providing confidence in the stability of the trend. It can also be seen that the trend is largest during the last decade (2003-2014).

The decadal trends obtained from the mean AM and PM values for Izaña, Ushuaia and Marambio are $+8.7 \pm 1.2 \%$, $-8.7 \pm 1.4 \%$ and $-13.7 \pm 2.2 \%$, respectively. Most of the observed trends occurred in the last decade (after 2003-2006), as revealed by Fig. 2. At Izaña, the AM decadal trend is larger than the PM trend, $+9.5 \pm 1.2 \%$ vs. $+7.9 \pm 1.1 \%$, respectively. 260 McLinden et al. (2001), using a chemical transport model (CTM) to explain the NO₂ trend observed at Lauder (Liley et al., 2000), found that the larger trends derived from the AM data are caused by decreasing O₃, which, in turn, reduces the rate of NO₂+O₃, allowing for more NO₂ to be present the next morning. At Izaña, the different AM and PM trends cannot be explained by changes in O₃ since a non-significant decadal trend of $+0.5 \pm 1.2 \%$ is obtained for the period of 1999-2012 by the FTIR instrument (Vigouroux et al., 2015). However, McLinden et al., (2001) predicted a decrease in the NO₂ trend of approximately 265 1 %, when exclusively considering the increasing halogens in the stratosphere between 1980-2000. Data from the past few decades show the opposite trend. Equivalent effective stratospheric chlorine (EESC) gas concentrations in the mid-latitudes have declined by 15 % from their peak values in the year 2000. In particular, HCl, the main reservoir of inorganic chlorine, displays a negative decadal trend of $-5.9 \pm 1.5 \%$ between 1997 and 2012. The same declining rate is observed for bromine between 2000 and 2012 (WMO, 2014). The observed changes in both halogens should result in an increase in the NO₂ trend. 270 Moreover, the halogen decline would modify the daytime NO_x partition, since NO₂ would increase during the illuminated hours and decrease in darkness (McLinden et al., 2001), creating a larger trend at dawn than at dusk, as is observed. In the SH, the AM and PM decadal trends are closer, $-8.7 \pm 1.4 \%$ and $-8.7 \pm 1.3 \%$ for Ushuaia, $-13.8 \pm 2.1 \%$ and $-13.6 \pm 1.9 \%$ for Marambio, for AM and PM, respectively. At these stations, the decrease in halogens is probably compensated by an increase in O₃. Details of the trend analysis are summarized in Table 3.

275 At Belgrano, the trend has been obtained by averaging the decadal trends for the individual months, when data are available. Since DOAS requires SZAs close to 90°, only the Feb-April and Aug-Nov periods are suitable for measurements. For the sake of simplicity, we will refer to these periods as the summer and winter seasons, respectively. During the winter, the NO₂ column reaches values close to zero, and its trends are non-significant. The mean summer decadal trend is $-11.3 \pm 4.0 \%$ ($-10.9 \pm 4.1 \%$ and $-11.7 \pm 4.0 \%$ for AM and PM, respectively). In Fig. 6, these results are summarized.

280 An alternative way to analyse the trends of the twilight data is to consider the evolution of the NO₂ diurnal build-up per hour (DBU). The DBU is essentially due to the N₂O₅ photodissociation, which is dependent on temperature, O₃, and hours of the night and can be expressed as:

$$\text{DBU} = \frac{\text{NO}_{2\text{PM}} - \text{NO}_{2\text{AM}}}{24 \cdot \Delta t} = \frac{\text{NO}_{2\text{PM}}}{24 \cdot \Delta t} \left(1 - \frac{\sum_{\text{base}}^{\text{toa}} [W(z)R(z)]}{\sum_{\text{base}}^{\text{toa}} W(z)} \right) \quad (4)$$

where NO_{2AM} and NO_{2PM} are the columns at sunrise and sunset, respectively, and Δt is the monthly mean of the diurnal night 285 hours. R is the AM-to-PM ratio at a given height, and W(z) is a NO₂ climatological profile acting as weighting factor. R can be computed (Senne et al., 1996) from:

$$R(z) = \frac{NO2_{AM}(z)}{NO2_{PM}(z)} = e^{-2K(z)O_3(z)\Delta t} \quad (5)$$

where K is the $NO_2 + O_3$ reaction rate constant and $O_3(z)$ is the ozone concentration at height z .

At Izaña, the DBU obtained from Eq. (4) using the O_3 and temperature profiles from the local ozonesounding agree well with the observations (Fig. 7). The resulting decadal trend for the period is of $+5.5 \pm 1.6 \%$, which provides a hint of the trends in the reservoirs. In the Subantarctic/Antarctic stations, the DBU displays negative decadal trends of $-8.4 \pm 1.8 \%$ and $-13.8 \pm 2.4 \%$ for Ushuaia and Marambio, respectively. In Belgrano, the values are too low (winter) or the AM and PM data are too close (February) to obtain the DBU, except in March and April. The BDU decadal trends for these months are $-13.0 \pm 7.3 \%$ and $-10.6 \pm 2.9 \%$, which is probably not representative of the mean annual trend. In summary, all SH stations exhibit a negative decadal trend in their DBUs, ranging from -8 to -14 %, revealing either a reduction of N_2O_5 in the past few years at the middle and high latitudes of the Southern hemisphere or dynamically induced changes in the NO_2 vertical distribution.

To investigate the variability of the NO_2 trend with the season, the calculations were performed on a month-by-month basis. Even though the contributions of proxies other than seasonal waves are small ($<1 \%$ in most cases), the same proxies and lags were applied in the multiple regression as in the previous cases. The results are shown in Fig. 8. The AM and PM trends were plotted separately for each station, along with their mean value. At Izaña, during the winter and spring, both trends agree well. From July to the end of the year, as the trend increases, there is also a progressive increase in the AM-PM difference that clearly exceeds the error bars. O_3 trends in individual months (not shown) are too small and do not change much throughout the year. A seasonality in the decreasing halogen trend could be a possible explanation, but, for the moment, we have no satisfactory explanation for this behaviour. At Izaña, the monthly mean trends are largest in the autumn and beginning of the winter and are mainly forced by a faster increase in the AM trends. The annual excursion ranges from 4.4% at its minimum in February to 13.1% in December. The downward trends in the SH become more negative further south. At Ushuaia, the trend is less negative to values close to the annual minimum (-7%), whereas in Marambio, the trend increases with respect to the previous months (-21%). The time when the trends diverge coincides with the formation of the Antarctic Polar Vortex (APV), and this divergence extends for a period coincident with the coldest temperatures and polar stratospheric cloud (PSC) formation. In Fig. 8, the 2006 - 2016 mean area covered by temperatures low enough for PSC formation, as obtained by the Climate Prediction Center (CPC) (<http://www.cpc.ncep.noaa.gov/products/stratosphere/polar/polar.shtml>) is shown in grey. In September, the absolute maximum of the negative trends is reached at both stations as a result of an increase in the number of days that the stations were inside the APV. We will come back to this point later.

During the autumn and winter, there is meridional transport towards the Pole. Once the Antarctic vortex is established, O_3 and NO_2 transported from lower latitudes accumulate outside the vortex, since the vortex edge acts as a barrier for mass exchange. Marambio is generally at the edge of the vortex, whereas Ushuaia remains outside, with very few exceptions. The observed behaviour could be explained by a positive trend in the size of the vortex area, such that Marambio remains inside the vortex longer, thus reducing its NO_2 column year by year. Conversely, larger NO_2 masses transported from lower latitudes would accumulate above Ushuaia, somehow compensating for the negative trend. Alternatively, the same effect could be caused

320 by a drift of the average vortex position towards the Atlantic/Argentinean sector. The drifting of the APV during the spring has
been studied over the past decade (Hassler et al, 2011, Grytsai et al., 2017) using both observations and models. The results
show longitudinal displacements of the APV across the years. In particular, the minimum of the planetary wavenumber 1,
centred at latitudes of approximately 65° S, has shifted westward since 2003, thus increasing the time of the stations in the
Argentinean sector under the influence of the PVA. To confirm this effect over Ushuaia and Marambio, the NO_2 representative
325 potential temperature level of 530 K between days 150 and 330 (May through November) has been used to calculate the position
of the station with respect to the vortex according to the widely accepted Nash et al. criteria (Nash et al., 1996), based essentially
in finding the maximum PV gradient at equivalent latitudes to define the vortex edge. ERA-Interim data were used for this
purpose. The results show an increasing number of days inside the vortex both in Ushuaia and Marambio in previous years
(Fig. 9). To test that the impact of the vortex position drifting is the main cause of the wavy structure in the trend observed in
330 the Ushuaia winter (small trends in July-August large ones in September –October, see Fig. 8) we have repeated the monthly
trend analysis excluding the days when the station was inside the vortex. Results show that while, as expected, negative trends
are reduced, the magnitude is not enough to justify the observed trends. In fact, the changes are of only few tenths of a percent,
probably due to the fact that the days inside the vortex at Ushuaia, while increasing along time, are still very small compared
with the total number of days. In summary, when only extra-vortex data are used the winter wavy structure remains providing
335 evidence that the evolution of the seasonal NO_2 trend is dominated by the mid-latitude dynamics along the year.

The trends at Belgrano in the summer are lower than those at Marambio, with values close to those at Ushuaia. The
winter data are not significant. The NO_2 concentration in the stratosphere during these months is very low and very dependent
on the time of the last warming, which is highly variably from year to year.

4.2 The subtropical case: comparisons with other observations

340 DOAS trends at Izaña have been compared with the ground-based NDACC FTIR data located in the same station and with 3
satellite instruments: nadir SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartography) and
OMI OMI (Ozone Monitoring Instrument), both DOAS spectrometers, and the limb sounding FTIR MIPAS (Michelson
Interferometer for Passive Atmospheric Sounding). The SCIAMACHY stratospheric data are produced by the IUP-Bremen.
The data used here are the improved version V3.0 released in 2016. The MIPAS NO_2 profiles are from (IMK/IAA data version
345 v5h NO_2 20/v5r NO_2 220) at the station's location converted to VCD. Only the daytime data (10 AM overpasses) were
considered. The MIPAS data have been combined with the DOAS averaging kernels to make them comparable. The basic
instruments are shown in Table 4. Further details can be found in the corresponding web pages. Figure 10 shows the annual
mean values (upper panel) obtained from the monthly means (lower panel) to avoid potential biases due to a non-uniform
distribution of data available across the year. This is particularly important for the ground-based FTIR data, since there are
350 many more daily measurements during the summer months, when NO_2 is at maximum, than in other months. Only in the few
cases when the monthly data were not available were the corresponding climatological values used. No photochemical
correction has been applied to the satellite data to refer them to the same SZA because the purpose is to compare the NO_2

column trends. The differences between the instruments for the [monthly](#) means are within 5 % and exhibit similar seasonalities (Fig. 10, lower panel). There are multiple causes affecting the magnitude of the measured column, namely, the hour of the measurements, field of view, vertical sensitivity, etc. (Piters et al., 2011, Robles-Gonzalez et al., 2016); however, these factors should not affect the observed trends. Table 5 displays the results of the trends from the regression model using the monthly data. There is a large scatter in the trends. The MIPAS decadal trend is of $+5.0 \pm 3.5$ %, close to that of FTIR ($+3.6 \pm 2.7$ %). SCIAMACHY provides a low trend but is statistically non-significant. OMI shows a decadal trend of $+7.5 \pm 2.2$ %, not far from that obtained from DOAS but for the 2002-2014 period. MIPAS and OMI are significant at the 90% confidence level. In summary, at present, there is no agreement between the instruments and the actual trend over Izaña. To further complicate the interpretation, McLinden et al., (2001), using a 3-D CMT model, found that the trend can be highly dependent on the time of day of the measurement. For the case shown in their paper, i.e., with decreasing O₃ and increasing halogens, there is almost a factor of 2 between the maximum trend at sunrise and the trend minimum at sunset. In the late morning and around noon, when the satellites and FTIR measurements are taken, the trend is much lower than that at SZA=90° AM, when the DOAS takes its measurement. Therefore, unless careful analyses of the CTM models are carried out for the exact periods of the measurements, the trend intercomparisons of a set of measurements obtained at different times of day has been found to be of little use for the confirmation of the DOAS trend. There is little doubt, however, of the sign of the trends since all instruments show a positive trend.

4.3 Discussion of the hemispheric asymmetry

The opposite sign in the [NO₂ trends](#) observed at the NH and SH stations shows that the [NO_x distribution in the stratosphere does not directly reflect the increasing N₂O in the atmosphere, at least when individual stations are analyzed](#). Stratospheric temperatures from the ECMWF ERA-Interim data above the NH and SH stations show no statistically significant trends during the period of observation. The EHF has been used as a proxy for the meridional transport as a possible explanatory variable for the trends observed in the analysis, but no significant correlation has been obtained. Eckert et al., (2014) found a similar hemispherically asymmetric pattern when analysing the global ozone trends from MIPAS. [Negative trends](#) were found in the northern lower stratosphere, whereas positive values were observed in the Southern Hemisphere. These authors suggested a meridional displacement of the subtropical barriers as the cause of the hemispheric asymmetry, since they could mimic the observed trends by shifting the subtropical mixing barriers to the south by 5° at altitudes below 30 km, although no explanation was provided for the displacement beyond what is possible due to low-frequency natural variations. Previously, Stiller et al., (2012) computed the age of stratospheric air (AoA) in the stratosphere using MIPAS sulphur hexafluoride (SF₆) measurements, finding a positive trend in the Northern Hemisphere, centred at 20 km from 20° to 60° N and a negative trend in the tropics and the Southern Hemisphere. In particular, the increasing AoA was observed at heights from the tropopause to the upper limit of MIPAS (38 km). The MIPAS AoA has been reassessed (Haenel et al., 2015), but the hemispheric asymmetry remains. Total positive reactive NO_y trends in the Northern Hemisphere and the negative trends in the Southern Hemisphere in the lower stratosphere (~25 km) have been reported by Funke et al., (2015), using the MIPAS data from the period 2002-2012. A more

detailed meridional structure of the NO₂ trends was obtained by Burrows et al., (2016) by analysing the SCIAMACHY NO₂ limb measurements in 2003-2011. They find a well-defined region with positive/negative trends extending from the equator to the high latitudes in the Northern/Southern Hemispheres, with a maximum at 26-27 km in the subtropics.

390 Since the global NO_y remained almost constant during this period, the observed behaviour should be the result of a meridional redistribution. Recently, Stiller et al., (2017) found the same meridional pattern in N₂O from the CLaMS CTM model, driven by the ERA-Interim reanalysis, and explored the hemispheric symmetry in the AoA, confirming a southward displacement of the stratospheric circulation pattern between the potential temperature levels of 500 and 800 K. Additionally, Garfinkel et al., (2017), using the GEOSCCM model, also found an increase in the Northern Hemisphere AoA for the period after 1992 when including the stratospheric aerosols and ODS evolution in the simulation. The positive trend peaks between
395 20-30° N and extends from 20 to 40 km.

In summary, previous works exhibit discrepancies in the heights where the stratospheric trends peak (AoA, ozone and NO₂) but agree on the existence of a [change of sign between hemispheres in the stratospheric trend](#). Although the search for an explanation of the observed hemispheric asymmetry patterns is outside the scope of this paper, there is growing evidence based on observational analysis and modelling of a redistribution of tracers in the stratosphere in the past few decades. The results
400 presented here provide an additional confirmation of the changes in the dynamics of the lower/middle stratosphere based on data from an independent source.

5 Conclusions

Long-term datasets from the DOAS spectrometers located at remote stations (Izaña, 28° N, Ushuaia, 55° S, Marambio, 64° S and Belgrano, 78° S) have been used to calculate the trends in the NO₂ stratospheric column over the 1993/94-2014 period.
405 Seasonal cycles, stratospheric aerosols, solar cycle, ENSO, QBO, stratospheric temperature, and eddy heat flux were included as explanatory variables. The results show a positive mean NO₂ decadal trend of 8.7 ± 1.2 % over the past 23 years at the northern subtropical station at Izaña, surpassing the expected 2.5 % increase due to the positive N₂O trend. The observed trend is larger at dawn (9.5 ± 1.2 %) than at dusk (7.9 ± 1.1 %). The attempt to compare other available databases does not provide confirmation of the observed DOAS trend, either due to the shorter time series, larger uncertainties, or different diurnal
410 sampling. The same analysis applied to the Antarctic/Subantarctic stations displays the opposite trends. The NO₂ stratospheric column has been found to decrease at a mean rate of -8.7 ± 1.4 %. decade^{-1} and -13.8 ± 2.2 %. decade^{-1} for Ushuaia and Marambio, respectively. Most of the observed trends occurred in the last decade (after 2003-2006). Belgrano also displays a negative trend of -11.3 ± 4.0 % for the summer/autumn season, which is the only period that is statistically significant. The trend in the NO₂ diurnal build up (DBU) rate is essentially due to N₂O₅ photolysis and is $+5.5 \pm 1.6$ % at Izaña, -8.4 ± 1.8 % at
415 Ushuaia and -13.8 ± 2.4 % at Marambio, providing a hint about the NO_y trend.

The analysis of individual months shows that the trend is largely dependent on the season. The decadal trends annual excursion at Izaña ranges from 4.4 ± 1.8 % at its minimum in February to 13.8 ± 2.8 % in December. The Southern Hemisphere

station trends are strongly influenced by the Antarctic polar vortex. The negative trend at Marambio increases in mid-winter (-21 %), whereas at Ushuaia, the decadal negative trend is reduced to values close to its annual minimum during the same time
420 (-7 %). The largest trend is observed in September. The considerable difference in the trends can be explained by a shift of the APV towards the South America sector during the winter. The analysis of the trends, given the position of the stations with respect of the Antarctic polar vortex (APV) over the Antarctic region, supports this explanation.

The results presented here provide an additional confirmation of the changes in the lower/middle stratosphere dynamics based on data from an independent source and provide further observational evidence of the recent findings on the
425 hemispheric asymmetry in stratospheric NO₂ and the age of air during the past decades.

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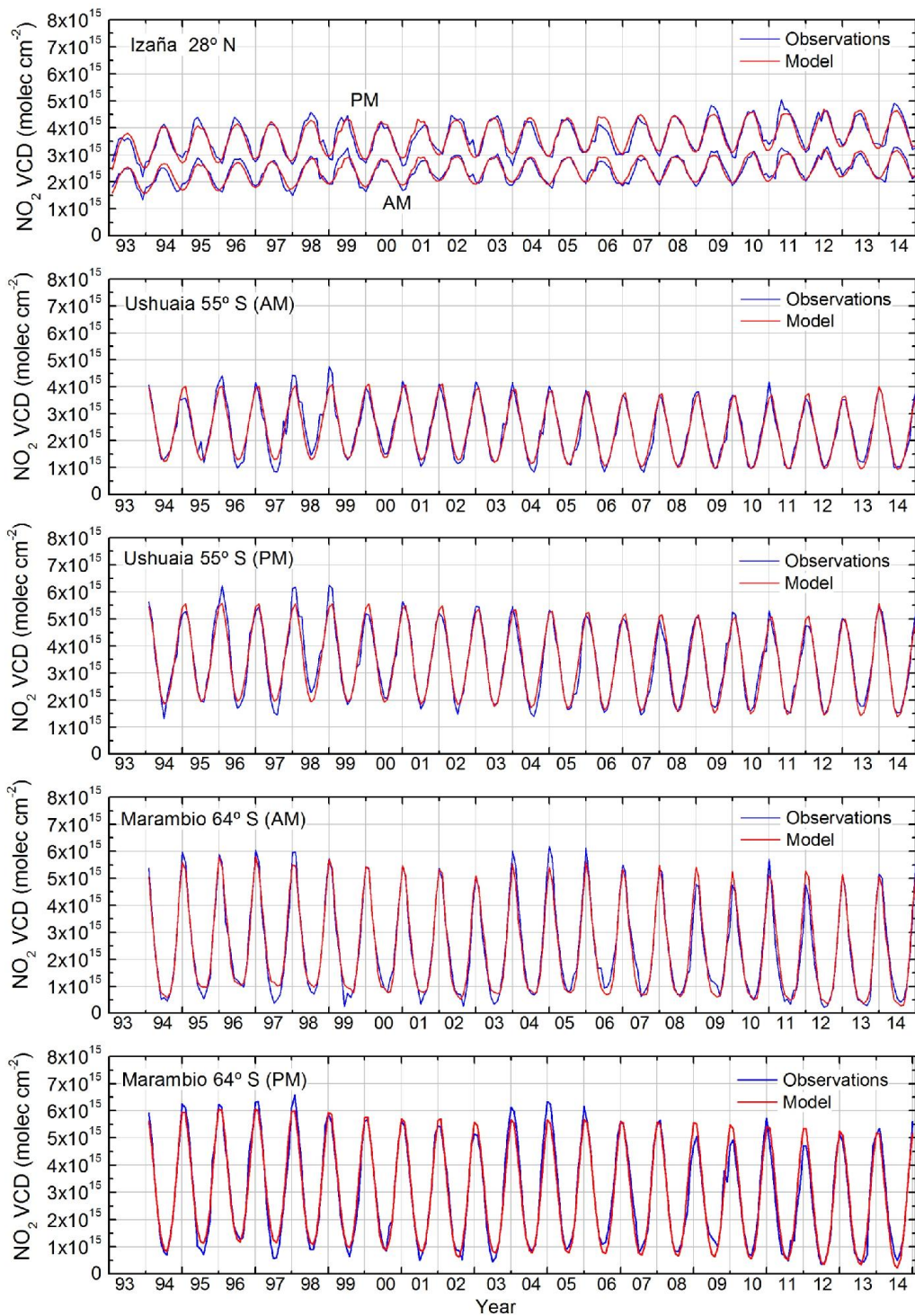
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Figure 1: NO₂ vertical column density time series (blue lines) and fit obtained using the multiple linear regression model (red lines)

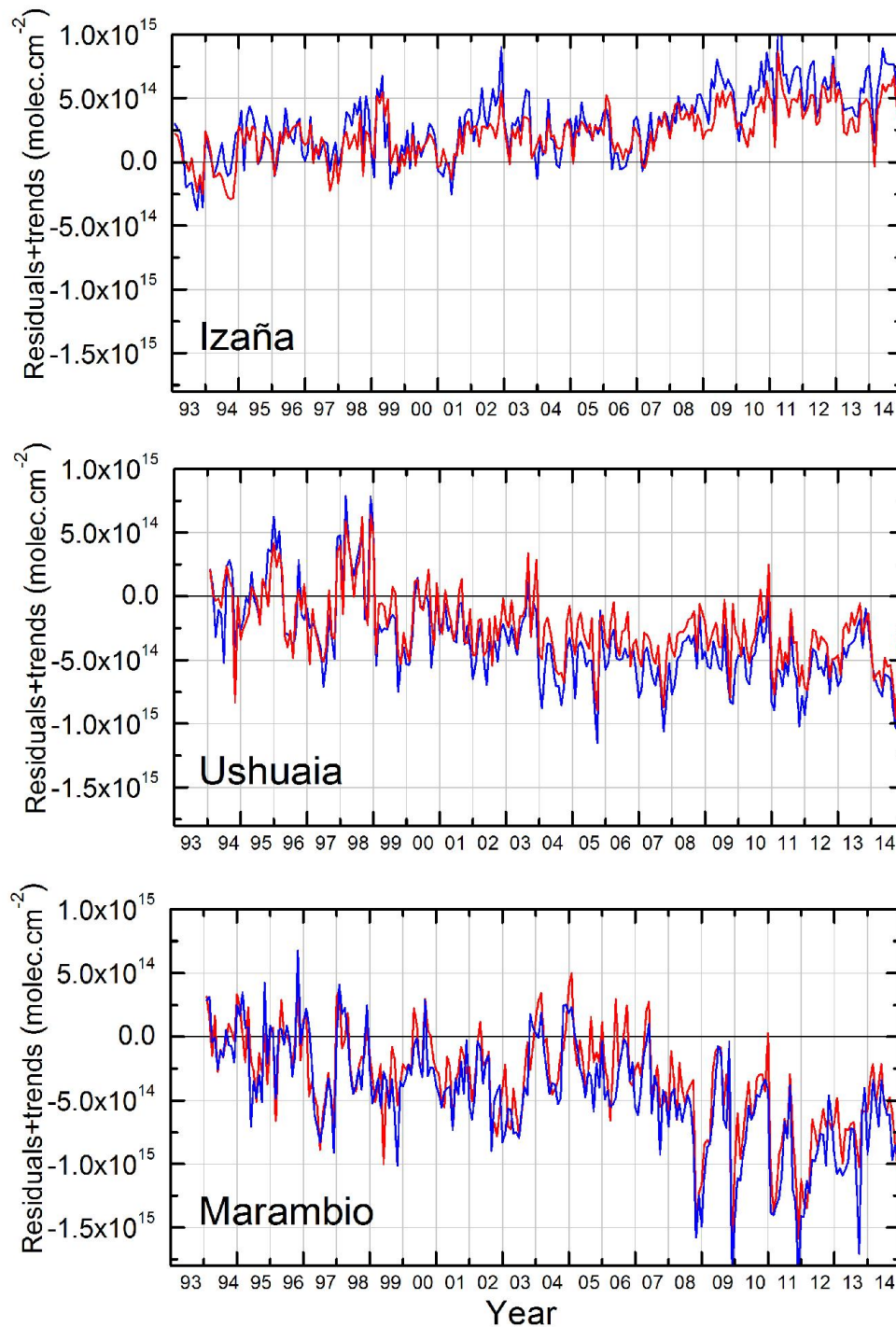


Figure 2. Fit residuals: observations minus models without trends. Red lines: AM data. Blue lines: PM data.

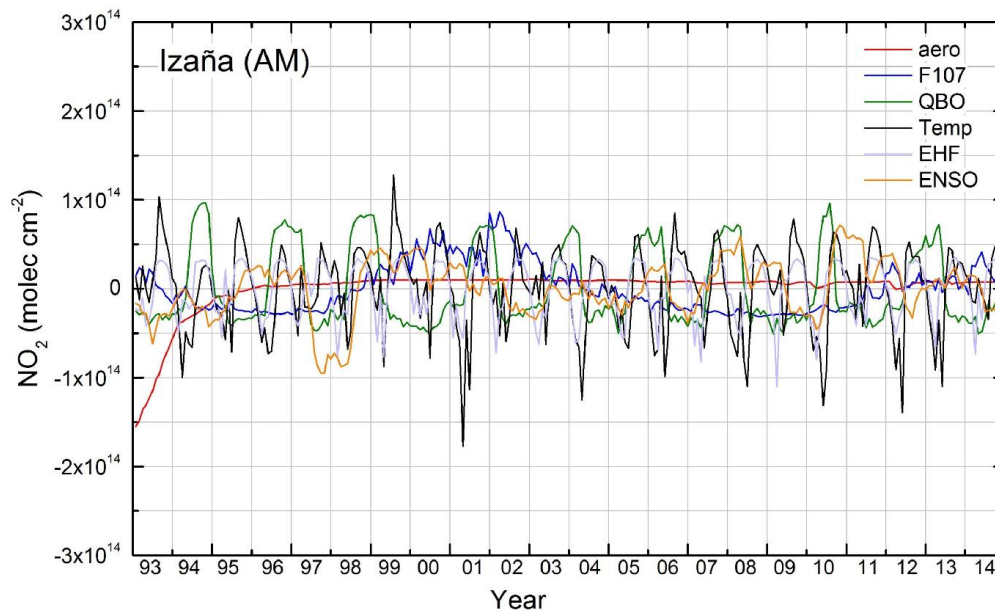


Figure 3. Example of the contributions of the proxies other than the seasonality and trends to the modeled NO_2 time series for Izaña.

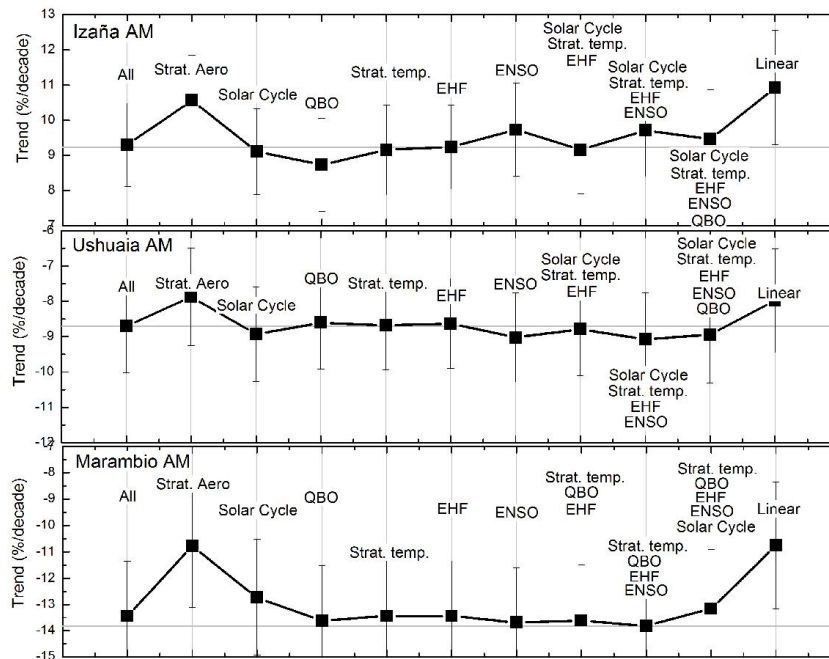
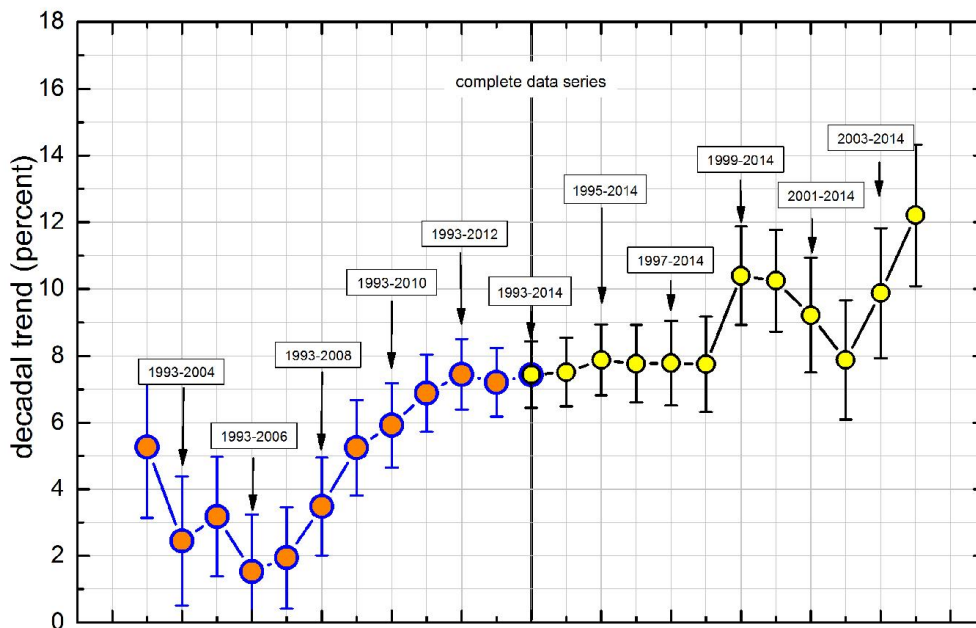
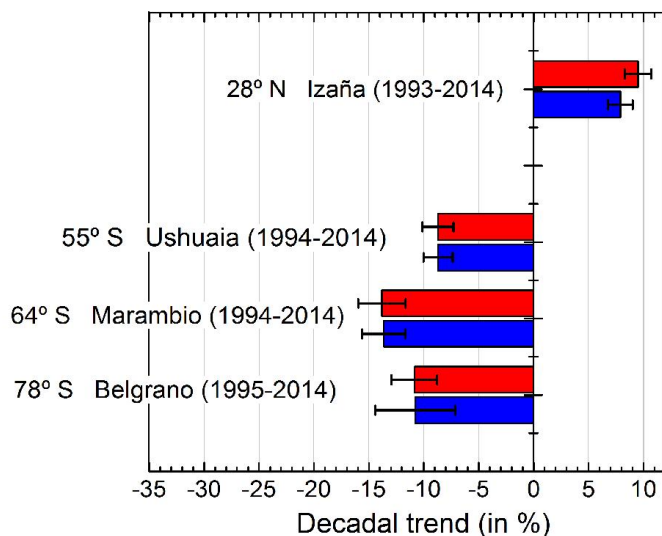


Figure 4. Impact of the computed trends per month depending on the selected proxies. Case “All” = all proxies included. Labels indicate the proxy/ies excluded from the analysis. Trend obtained in the final analysis is plotted as a reference (grey line). See text for details.



660

Figure 5. Dependency of the Izaña PM trend on the selected period. In the central point, the complete 1993-2014 time series is used. Each point to the left (orange circles) is the trend after reducing the time series by one year before 2014. Each point to the right (yellow circles) is the trend after reducing the time series by one year after 1993.



665

Figure 6. AM (red) and PM (blue) decadal trends obtained for the DOAS stations. The trend at Belgrano was obtained for the Feb-March-April period. See the text for details.

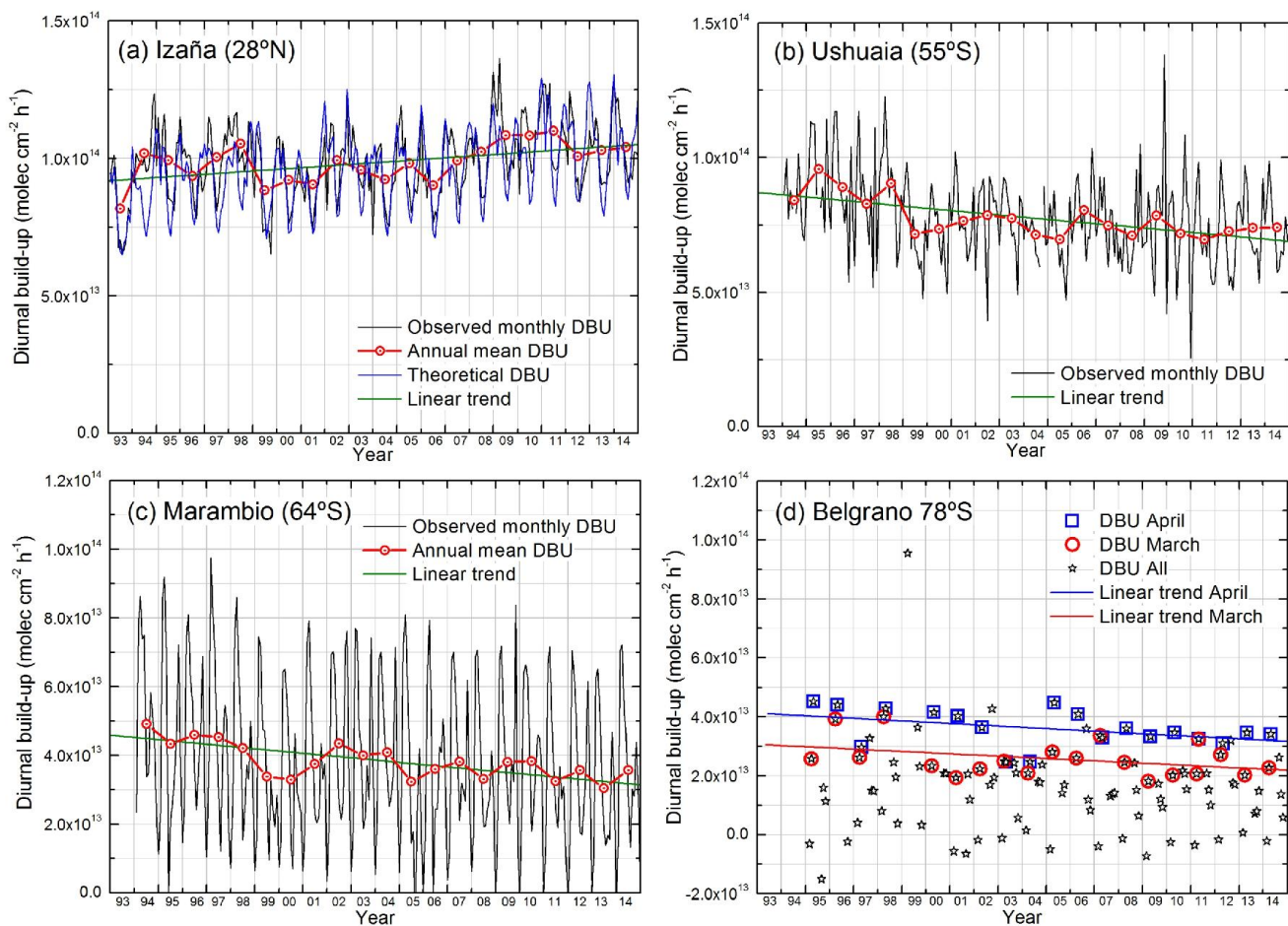


Figure 7. Diurnal NO₂ build-up in molec.cm⁻².h⁻¹ for the 4 DOAS stations. a)-c) Observed DBU (black lines). Annual means (red lines). Linear trends (dotted lines). The computed DBU is plotted in a) (blue line). d) The Belgrano DBU for all available months (black stars). Months of March and April are highlighted with red circles and blue squares, respectively.

670

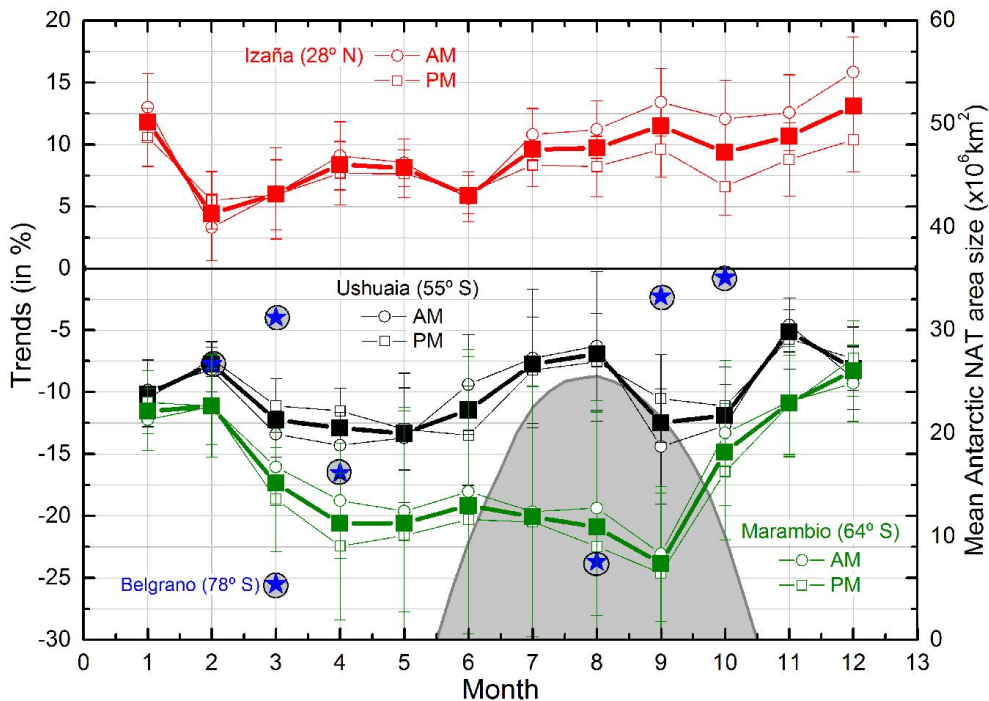


Figure 8. NO₂ decadal trends for the individual months at Izaña, Ushuaia, Marambio and Belgrano. Open circles and open squares represent the AM and PM data, respectively. Solid squares are the monthly means. The Belgrano trends are from the diurnal means. The shadowed area is the mean size of the area of the potential NAT PSCs (right scale).

675

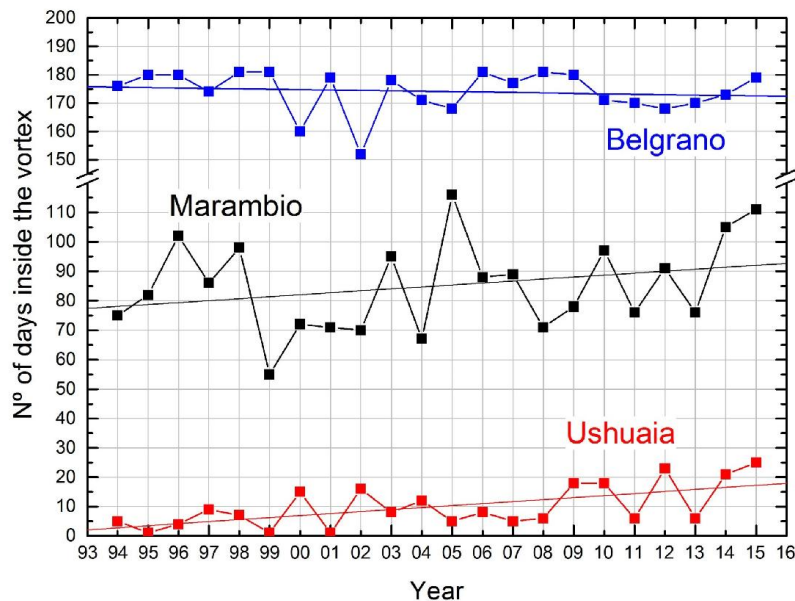
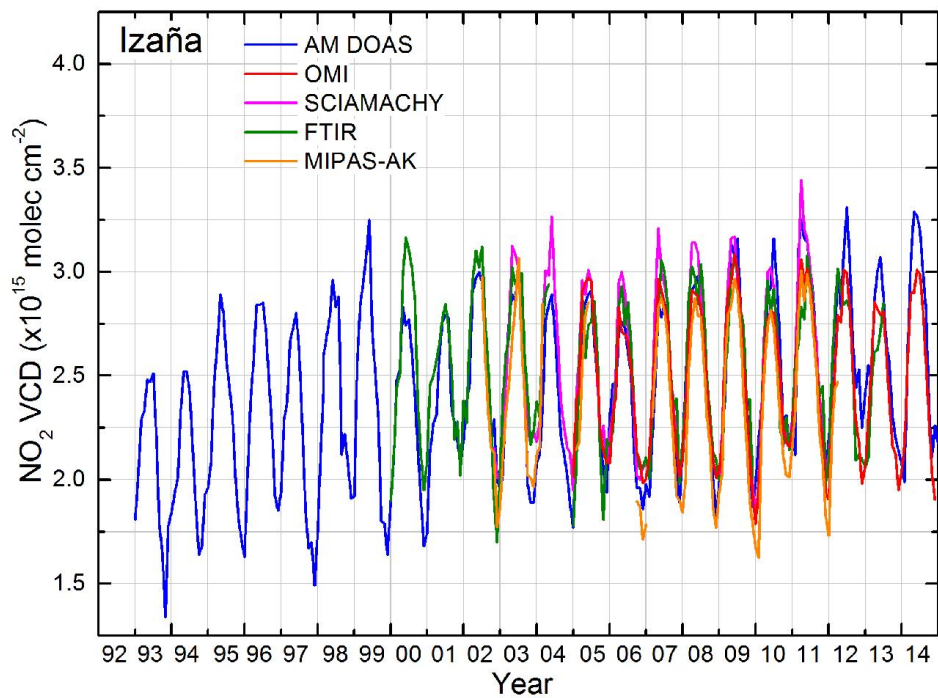
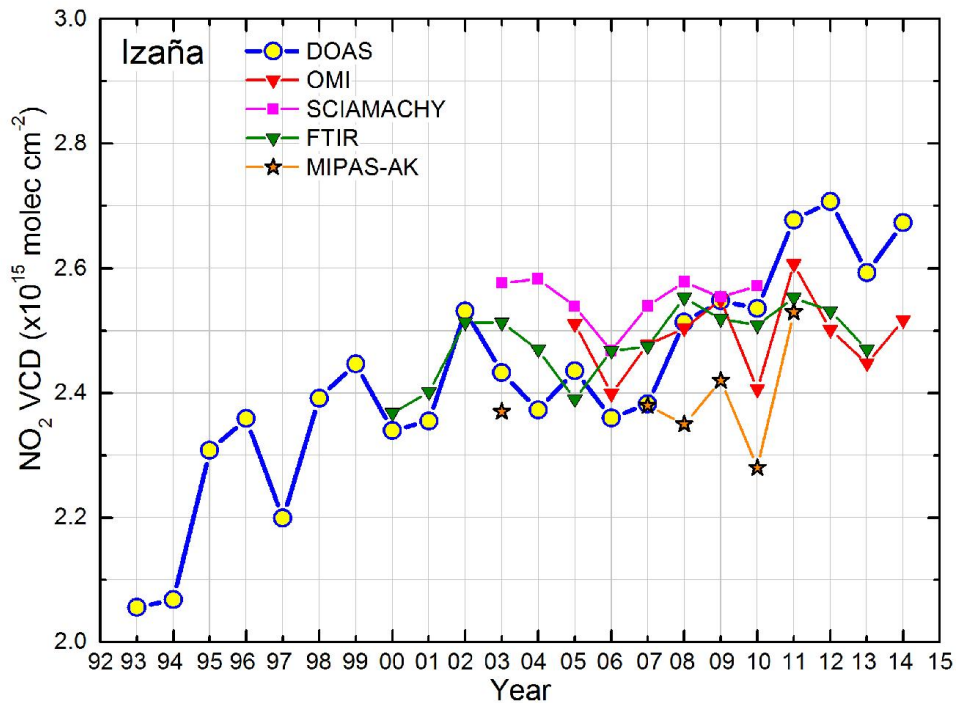


Figure 9. Annual evolution of the number of days that the stations spent inside the polar vortex at 530K according to the Nash et al. (1996) criteria.



680

Figure 10. NO_2 VCD annual means at Izaña from the available datasets (upper panel) obtained as monthly averages (lower panel).

Table 1. DOAS retrieval settings.

	Izaña: EVA/ RASAS / RASAS-II	EVA: Ushuaia/Marambio/Belgrano
Fitting interval	EVA: 430-450 nm RASAS-I: 450-533 nm RASAS-II: 430-520 nm	430-450 nm
NO ₂ cross-section	Vandaele et al. (1998), 220K	Vandaele et al. (1998), 220K
O ₃ cross-section	Bogumil et al. (2001), 223K	Bogumil et al. (2001), 223K
H ₂ O cross-section	Hitran (Rothman et al., 2008)	Hitran (Rothman et al., 2008)
O ₄ cross-section	EVA/RASAS. Greenblatt (1990), room temp. RASAS-II. Hermans (1999), room temp.	Greenblatt (1990), room temp.
Ring effect	Chance and Spurr (1997)	Chance and Spurr (1997)
Orthogonalization Polynomial	EVA: 2 nd degree RASAS/RASAS-II: 3 rd degree	2 nd degree
Offset correction	Inverse of the reference	Inverse of the reference
AMF calculation	NDACC NO ₂ AMF LUTs	NDACC NO ₂ AMF LUTs
Determination of the residual amount in the reference spectrum	Modified Langley plot (Vaughan et al., 1997)	Modified Langley plot (Vaughan et al., 1997)
SZA range for the twilight averaging of the vertical columns	EVA: 88 – 91° SZA RASAS/RASASII: 89 – 91° SZA (Approx. 6 measurements)	88 – 91° SZA (Approx. 6 measurements)

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Table 2. Source of the explanatory variables of the multiple regression.

Description	Source
Stratospheric aerosols	http://data.giss.nasa.gov/modelforce/strataer/
Solar cycle	http://umbra.nascom.nasa.gov/sdb/ydb/indices_flux_raw/Penticton_Observed/monthly/MONTHPLT.OBS.
Quasi Biennial Oscillation (50 and 10 hPa)	http://www.geo.fu-berlin.de/met/ag/strat/produkte/qbo/qbo.dat .
El Niño Southern Oscillation	http://www.esrl.noaa.gov/psd/enso/mei/table.html .
Strat. temperature and wind for the Eddy heat flux calculation	http://apps.ecmwf.int/datasets/data/interim-full-daily

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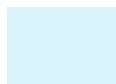
Table 3. Summary of the trend analysis for the DOAS stations. In the lower part, the contribution of each explanatory variable to the total variance is given in %. The colors denote the significance (blue 99%, pink 95% and green 90%). “Not” means it has been excluded from the definite analysis.

	IZAÑA (28° N)		USHUAIA (55° S)		MARAMBIO (64° S)	
	AM	PM	AM	PM	AM	PM
Trend (in %)	+9.51	+7.89	-8.72	-8.71	-13.94	-13.66
Uncertainty (in %)	1.19	1.11	1.42	1.33	2.09	1.95
Uncertainty (in mol.cm ⁻² .decade ⁻¹)	2.61x10 ¹³	3.79x10 ¹³	3.73E+13	5.02E+13	5.95E+13	6.75E+13
Autocorrelation coeff.	0.478	0.525	0.371	0.526	0.457	0.555
Residual Standard dev.	1.53x10 ¹⁴	2.08x10 ¹⁴	2.42E+14	2.67E+14	3.50E+14	3.43E+14

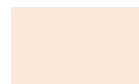
Contribution to the variance and confidence level (in %)

Trend	27.82	26.96	6.89	13.33	8.50	10.47
Annual wave	56.61	55.59	85.07	76.48	80.74	84.37
Semiannual wave	Not	Not	0.62	0.55	6.09	1.08
Strat. Aerosols	0.29	0.75	0.12	0.17	0.34	0.24
Solar Cycle	0.24	0.01	0.32	0.03	0.18	0.20
QBO	0.51	0.95	0.29	0.30	Not	Not
Strat. Temperature	0.95	1.19	0.83	4.97	Not	Not
EHF	0.00	1.28	Not	Not	Not	Not
ENSO	0.41	0.08	0.00	0.06	Not	Not
TOTAL variance explained (%)	86.83	86.81	94.14	95.89	95.84	96.37
Contributions other than those of season and trend (%)	2.40	4.26	2.55	2.88	0.52	0.44

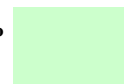
99%



95%



90%



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Table 4. Instrument information.

Instrument	Platform	Technique	Data	Period	Data availability
FTIR	Ground-based	FTIR		1/2000-12/2013	IMK/ASF NDACC-Izaña FTIR team https://www.imk-asf.kit.edu/english/201.php
MIPAS	ENVISAT	FTIR		7/2002-4/2012	IMK/IAA MIPAS team http://www.imk-asf.kit.edu/english/308.php
SCIAMACHY	ENVISAT	DOAS		8/2002-3/2011	http://www.iup.uni-bremen.de/does/scia_no2_data_acve.htm
OMI	AURA	DOAS	V3.0	1/2005-12/2014	http://avdc.gsfc.nasa.gov/pub/most_popular/overpass/OMI/OMNO2/

760

Table 5. Decadal trends in available datasets at Izaña.

Technique	Measurements	Period	Total months	Gaps	Trend %/decade	Error %/decade	Significance 90%	Residual Standard Dev	Proxies significance						
									SA	SC	TEM	ENS	NAO	QBO	EHF
DOAS	AM(SZA=89-91°)	3/1993-12/2014	264	9	+ 9.24	± 1.20	YES	1.51x10 ¹⁴	x	x	x	x		x	
	PM(SZA=89-91°)	3/1993-12/2014	264	9	+ 7.53	± 1.12	YES	2.06x10 ¹⁴	x	x	x	x		x	
	Diurnal build-up/hour	1/1993-12/2014	264	12	+ 5.46	± 1.67	YES	9.54x10 ¹²	x	x				x	
SCIAMACHY	≈ noon	8/2002-3/2011	116	0	+ 1.34	± 2.25	NO	1.09x10 ¹⁴		x		x			
OMI	≈ noon	10/2004-12/2014	123	0	+ 7.53	± 2.24	YES	1.39x10 ¹⁴				x		x	
FTIR	SZA<60°	1/2000-12/2013	168	21	+ 3.61	± 2.73	NO	2.37x10 ¹⁴		x	x	x			
MIPAS	≈ 10 am	7/2002-4/2012	119	25	+ 5.02	± 3.54	NO	1.20x10 ¹⁴		x		x		x	

765