

SAOZ measurements of NO₂ at Aberystwyth

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We present in this paper fifteen years' measurements, from March 1991 to September 2005, of stratospheric NO₂ vertical columns measured by a SAOZ zenith-sky visible spectrometer. The instrument spent most of its time at Aberystwyth, Wales, with occasional excursions to other locations. The data have been analysed with the WinDOAS analysis program with low-temperature high-resolution NO₂ cross-sections and fitting a slit function to each spectrum. Because of a change in detector in May 1998 there is some uncertainty about the relative changes before and after this date, which are partially constrained by the results of an intercomparison exercise. However, the effect of the Mt Pinatubo aerosol cloud is very evident in the data from 1991–94, with a decrease of 10% in NO₂ in the summer of 1992 (the SAOZ was located in Lerwick, Scotland during the winter of 1991–92 and observed very low NO₂ values but these cannot be directly compared to the Aberystwyth data). To focus more on interannual and long-term variations in NO₂, a seasonal variation comprising an annual and semi-annual component was fitted to the morning and evening twilight separately from 1995 to the present. This fit yielded average NO₂ columns of $4.08 \times 10^{15} \text{ cm}^{-2}$ and $2.68 \times 10^{15} \text{ cm}^{-2}$ for the evening and morning twilight, respectively, with a corresponding annual amplitude of $\pm 2.08 \times 10^{15} \text{ cm}^{-2}$ and $\pm 1.50 \times 10^{15} \text{ cm}^{-2}$. Departures from the fitted curve show a trend of 6% per decade, consistent with that reported elsewhere, for the period 1998–2003, but in the past two years a distinct interannual variation of amplitude of $\sim 8\%$ has emerged.

Introduction

Nitrogen dioxide (NO₂) is an important trace gas in the stratosphere due to its significant role in the photochemistry of ozone. Stratospheric ozone plays a critical role in the atmosphere by absorbing most of the biologically damaging ultraviolet radiation from the sun before it reaches the Earth's surface. Between around 25 km and 40 km altitude NO₂ is involved in a catalytic cycle that accounts for almost half the ozone removed by gas-phase reactions.¹ Below 25 km NO₂ moderates ozone loss caused by active chlorine and hydrogen by converting them into their inactive reservoir forms. Thus, monitoring of stratospheric NO₂ is an important adjunct to international efforts to monitor the health of the ozone layer. One of the longest duration time series of stratospheric NO₂ measurements is that from Lauder, New Zealand, which extends from 1980 to the present. Analysis of this record shows that the atmospheric column of NO₂ is increasing at approximately 5% per decade at 45°S.² Measurements from

similar latitudes in the Northern Hemisphere (using infrared spectroscopy) show a similar trend.^{3,4} This is twice the rate of increase of nitrous oxide (N₂O), its main source gas, and could be an indication of changes to the overall atmospheric circulation.⁵ Using a combination of photochemical and 3-D chemistry transport models, McLinden *et al.*⁶ were able to show that the Lauder trend can be understood if the increase in N₂O is combined with the decrease in ozone, the change in odd nitrogen partitioning due to increased chlorine concentrations, and variations in volcanic aerosols. Continued measurements of NO₂ are therefore necessary both to improve understanding of the photochemistry of ozone, and to help monitor and understand other critical atmospheric processes.

NO₂ is one of a family of odd nitrogen compounds in the stratosphere with a complex diurnal variation in concentration. During daylight a balance is established between NO and NO₂ concentrations through the reaction of the former with ozone and the rapid photolysis and reaction with atomic oxygen of the latter:



Reaction (3) effectively determines the rate at which these reactions destroy odd oxygen (O + O₃) since the first two constitute a null cycle. At night, photolysis of NO₂ ceases and all the odd oxygen in the stratosphere is converted to ozone—so there is an almost-instantaneous change in the NO₂

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concentration at twilight as the NO converts to NO₂ (in the evening) or is created by photolysis (in the morning). At night, NO₂ is converted first to NO₃:



and then *via* a three-body reaction to the N₂O₅ reservoir:



This causes a build-up of N₂O₅ during the night followed by a slow release during the following day through photolysis. The diurnal variation of NO₂ therefore comprises a maximum immediately after sunset, followed by a slow decrease throughout the night and a sharp drop to a minimum at sunrise. Thereafter, as N₂O₅ is photolysed NO₂ builds up, finally returning to its maximum as NO is converted to NO₂ at sunset.

As well as the diurnal variation there is a seasonal variation in stratospheric NO₂ at midlatitudes, due to the combined effects of photochemistry and atmospheric transport. During autumn and winter, NO₂ is converted to the long-term reservoir forms HNO₃ and ClNO₃, either through gas-phase reactions (*e.g.* NO₂ + OH + M → HNO₃ + M) or hydrolysis of N₂O₅ on aerosol particles. A minimum in NO₂ occurs in winter, sometimes exacerbated, particularly in the polar vortex, by rapid conversion of N₂O₅ to HNO₃ on polar stratospheric clouds. In spring and summer the reservoir species are photolysed or destroyed by OH, re-generating NO₂ which therefore reaches a maximum around mid-summer. Although these broad features in the NO₂ distribution are satisfactorily explained by photochemical models, it seems that calculations underestimate the amount of NO₂,⁷ especially below 25 km.⁸ This could be due to an incomplete understanding of NO₂ chemistry on aerosol surfaces or uncertainty in gas-phase rate coefficients.⁹

Monitoring of stratospheric NO₂ from the ground or space can be performed by absorption spectroscopy in the visible: an absorption band around 450 nm introduces measurable optical depth to an extraterrestrial light source if the atmospheric path is long. Such conditions apply to solar or lunar spectra measured at the ground near twilight and to solar or stellar occultation measurements from satellites. The first reported measurements of stratospheric NO₂ by this technique were those of Noxon¹⁰ who used a scanning spectrophotometer to make measurements for several years in the Colorado mountains. His measurements clearly showed both the diurnal and seasonal variations of stratospheric NO₂ concentration, and also revealed the so-called 'Noxon cliff'^{11,12}—a sharp decrease in NO₂ vertical columns at around 50°N in winter due to conversion of NO_x to the reservoir species N₂O₅ and HNO₃ in the polar night.

The introduction of multi-diode arrays in the 1980s permitted a considerable advance in the exploitation of the DOAS technique, by enabling spectra to be recorded simultaneously over a wide wavelength interval, without the problem of intensity variations which affect scanning spectrometers. With this technique, structure in the absorption spectrum of a molecule, rather than the absolute amount, is used to measure

the path total.^{13,14} The technique requires the absorption species of interest to have a detailed structure within a fairly narrow wavelength range, within about 10 nm. For stratospheric NO₂, it involves dividing twilight spectra (when the NO₂ optical depth is greatest) by a reference spectrum measured with high solar elevation, then filtering the resulting ratio spectrum to leave high-frequency features resulting from various important atmospheric absorbers, including ozone and NO₂. A particularly notable application of the technique has been in measurements taken at high latitudes in late winter and spring, when the chemistry of the lower stratosphere is perturbed by polar stratospheric clouds.^{15–18}

Stratospheric NO₂ has been measured by a number of satellite instruments since 1979, *e.g.* LIMS (Limb Infrared Monitor of the Stratosphere¹⁹), SME (Solar Mesosphere Explorer²⁰), SAGE-II (Stratospheric Aerosol and Gas Experiment²¹), ISAMS (Improved Stratospheric and Mesospheric Sounder²²), HALOE (Halogen Occultation experiment²³) and POAM (Polar Ozone and Aerosol Measurement²⁴). The most extensive datasets have been obtained by SAGE-II and HALOE, both of which use the solar occultation technique, the first in the visible (448 and 453 nm) and the second in the infra-red (5.26 and 6.25 μm). Drift in the optical components of SAGE-II has caused considerable complications in deriving the NO₂ product (although the latest version, 6.2, agrees better with HALOE). Such drifts emphasise the need for high-quality ground-based monitoring of NO₂. Both instruments were also affected below about 25 km by volcanic aerosol during the period 1991–93, after the eruption of Mt Pinatubo. Stratospheric NO₂ columns have also been derived from the Global Ozone Monitoring Experiment (GOME) instrument on ERS-2, using the DOAS technique. This instrument has also suffered its share of problems although it has been successfully used to derive global fields of stratospheric NO₂ vertical columns and to delineate the position of the Noxon cliff.²⁵ Nevertheless, space-based NO₂ measurements are not yet sufficiently advanced that they can be used reliably to derive trends and interannual variations in NO₂, so it is very important that high-quality ground-based measurements continue at a variety of locations world-wide.

A SAOZ UV-visible zenith-sky DOAS spectrometer has been measuring both NO₂ and ozone vertical columns at Aberystwyth (52.4°N, 4.2°W) since March 1991. This site lies on the western coast of the UK and normally experiences very low pollution in the prevailing westerly airstream. Occasional episodes of high tropospheric pollution are seen when air flows from the east but the generally clean conditions make this a good site for monitoring stratospheric NO₂ in northern mid-latitudes. The SAOZ was occasionally operated at locations other than Aberystwyth, as follows: Lerwick (60°N, 1°W) 2 Nov 1991–9 May 1992; Aberdeen (57°N, 2°W) 8 Feb–3 May 1994; Camborne (50°N, 5°W) 9–23 Sept 1994; OHP† (44°N, 6°E) 8–21 June 1996.

Here we present the results from March 1991 to September 2005 together with a discussion of the data quality and method of analysis.

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2. Experimental method

2.1. The SAOZ instrument

The SAOZ (Système d'Analyse par Observation Zénithale) spectrometer was developed in the mid-1980s¹⁷ to allow automatic measurements of ozone and nitrogen dioxide at latitudes up to the polar circle.²⁶ It consists of a commercial Jobin-Yvon flat field spectrometer equipped with a concave holographic grating and a detector at ambient temperature comprising a Hamamatsu 512 or 1024 diode array (see below) with a 25 or 50 μm entrance slit, respectively, giving a spectral resolution of the order of 1 nm FWHM in the range 300–600 nm. A spectrometer of this design has been based at Aberystwyth routinely measuring ozone and NO₂ since March 1991.²⁷ The SAOZ observes the zenith sky with a field of view of around 30°, measuring light scattered downwards from a range of altitudes. At twilight (Solar Zenith Angle, SZA \sim 90°) the zenith sky is illuminated mainly by molecular scattering from high altitudes. This light travels a long path through the stratosphere, and by comparison a very short vertical path in the troposphere. Absorption features in the spectra measured at this time are therefore heavily biased towards the stratosphere. This makes zenith-sky spectroscopy ideal for distinguishing stratospheric NO₂ from boundary-layer pollution. The spectrometer is housed in a dust- and water-proof container with a quartz window to enable measurements from the zenith sky. The instrument is controlled by a PC, recording and analysing the spectra in real time. Measurements are performed from sunrise to sunset while the Solar Zenith Angle (SZA) is less than 94°. The exposure time is adjusted automatically between 0.1 s to 60 s in order to optimise the signal, and the spectra are added to memory during a 60 s duty cycle. The dark current is measured each time the duration of exposure changes, and is then subtracted. Averages of ozone and NO₂ morning and evening vertical columns are derived from measurements taken between 87° and 91° SZA.

The original detector in the Aberystwyth SAOZ was a Hamamatsu PCD (photoconductive device) 512 diode-array detector. This was replaced in December 1992 with a Hamamatsu NMOS (negative metal oxide semiconductor) 512 diode-array detector. The reason for this change was that the NMOS detector has a thinner passivation layer, which causes fewer interference effects than the thicker PCD detector. It also has a better quantum efficiency and lower dark current, giving better signal to noise ratio. In May 1998 the SAOZ was upgraded to a 1024 pixel detector with a change in the grating from 200 mm^{-1} to 360 mm^{-1} . The slit width was increased from 25 to 50 μm , corresponding to 0.9 and 1.2 nm FWHM, resulting in an improvement of the sampling ratio from 2.4 to 3.5 pixels over the slit width, reducing the interpolation error (see below).

2.2. Data analysis

The basic principle of the SAOZ data analysis is as follows: each twilight spectrum is compared with a reference spectrum, chosen at low zenith angle, to yield a slant column S —the difference in NO₂ total column between the two light paths. The vertical column total V corresponding to that spectrum

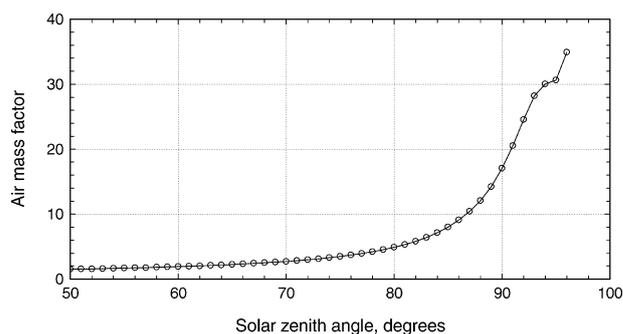


Fig. 1 Air mass factors used in this work.

can then be derived using:

$$V(\chi) = \frac{S(\chi) + R}{\text{AMF}(\chi)} \quad (6)$$

where R is the residual amount of absorber in the reference spectrum and AMF represents the air mass factor—the factor by which the slant column at that particular zenith angle χ exceeds that of a vertical path. This equation is actually the definition of the airmass factor, which is calculated using radiative transfer models and appropriate profiles of ozone and air density.^{28,29} A standard set of AMFs is used in this paper (Fig. 1). This set assumes a constant vertical distribution of atmospheric absorbers and scatterers, and so does not vary with season. Although Sarkissian *et al.*²⁹ quote an uncertainty of 1.1% in the NO₂ AMF, more recent estimates suggest that multiple scattering effects can increase the AMFs by 2–5%.³⁰ For ozone, R may be evaluated by assuming that the ozone concentration remains constant over the day when the reference spectrum is measured.³¹ This method, however, is not suitable for calculating the amount of NO₂ in the reference spectrum since the concentration of NO₂ changes throughout the day.

A Langley plot is a graph of slant column against AMF. From such a plot for a given twilight period the slope gives the vertical column density, and the intercept gives the amount of absorber in the reference spectrum: V and R , respectively in eqn (6), under the assumption that these do not change during the twilight period. This assumption is not valid at dawn since, as mentioned above, rapid changes of NO₂ concentrations occur in the morning due to the photolysis of N₂O₅. In the evening however, N₂O₅ photolysis ceases and there is a period between 80° and 90° SZA when the NO₂ vertical column is effectively constant. A Langley plot during this period can therefore be used to derive $R[\text{NO}_2]$, and is the method used in this work.

The spectra measured by the SAOZ are recorded using real-time programs provided by CNRS, and analysed using WinDOAS, the DOAS software suite developed at IASB.³² The total slant column of NO₂ is derived using the 432–470 nm spectral window, taking into account absorption by ozone, O₄ and H₂O. In brief, the method uses non-linear least-squares fitting of the log-ratio of two atmospheric spectra (measurement and reference) to a set of molecular absorption cross-sections measured in the laboratory at 220 K.³³ The actual algorithm includes many advanced refinements, among which are

capabilities for precise characterisation of both wavelength calibration and spectral resolution of the instrument, and calculation of the ring effect based on Raman scattering modelling. In a special treatment designed for the SAOZ instrument, the slit function is determined for each spectrum and convoluted with the absorption cross-sections as part of the DOAS fitting procedure.

The choice of reference spectrum was found to have a substantial influence on the NO_2 analyses. In previous work deriving ozone from the SAOZ,²⁷ a single reference spectrum was used for periods when the instrument was fixed in one location. For a long-term dataset this has the advantage that any error in the amount of absorber in the reference spectrum (R) does not affect any derived trend in the measurements. However, for this method to work the detector must be rigidly fixed with respect to the slit and diffraction grating—and in the SAOZ it is not. This leads to a changing ‘pixel shift’—the amount by which the measured spectrum must be shifted to fit the reference—which degrades the accuracy of the NO_2 analyses and could introduce spurious ‘trends’. The obvious solution is to use daily reference spectra, but in a location where there is frequent rain and occasional episodes of pollution this leads to loss of good data. The compromise adopted in this work was to use a monthly reference spectrum, and to select that reference spectrum from a day near the middle of the month which was free of pollution and recorded plenty of signal (thus was free of rain). This approach led to the retention of 1% more points in the dataset than with the daily reference spectra. To check that the chosen reference spectrum was a good one, spectra from 80–90° zenith angle on the evening of that day were analysed with respect to the chosen reference spectrum, and the Langley plot of slant column against AMF examined. A correlation coefficient (r) greater than 0.997 and a (negative) intercept within stipulated bounds were required for an acceptable reference spectrum; the inter-

cept of this plot then gave the amount of NO_2 in the reference spectrum, R .

Using monthly reference spectra means that the error in R appears as a random error in any investigation of the long-term trend in the data. The magnitude of this error was estimated by analysing the 1995 dataset with 19 different reference spectra, and comparing the results. This work was carried out in 1999 with CNRS analysis software rather than WinDOAS, giving a standard error of 7% attributable to the choice of reference spectrum; it is unlikely to be substantially different with WinDOAS.

For each twilight period (between 87 and 91°) a weighted average of the NO_2 vertical columns was calculated, using error bars from the WinDOAS spectral fitting. (The number of points per twilight ranged from 3 during the early years to more than 20 in latter years, following improvements in software and upgrades to the computer controlling the SAOZ.) To eliminate bad data from the long-term dataset, the standard deviation of the vertical columns during each twilight was used as a quality indicator. Twilight periods where the standard deviation was greater than $3 \times 10^{14} \text{ cm}^{-2}$ were considered unreliable and removed from the time series. A 3-point median filter run through the afternoon and morning time series separately removed most of the remaining bad data. Fig. 2 shows, for the data measured at Aberystwyth, the points rejected as having excessive standard deviation and those accepted after median filtering: the procedure is seen to be remarkably successful in removing bad data.

In all, of the 5050 days between March 1991 and December 2004, SAOZ NO_2 measurements were obtained on 4300 of them, *i.e.* 85% of the time. The fraction of days rejected by the standard deviation criterion was 9% for the morning twilight series and 12% for the evening twilights. These figures are substantially better for the period of the 1024 pixel detector, with measurements on 95% of all possible days and a rejection

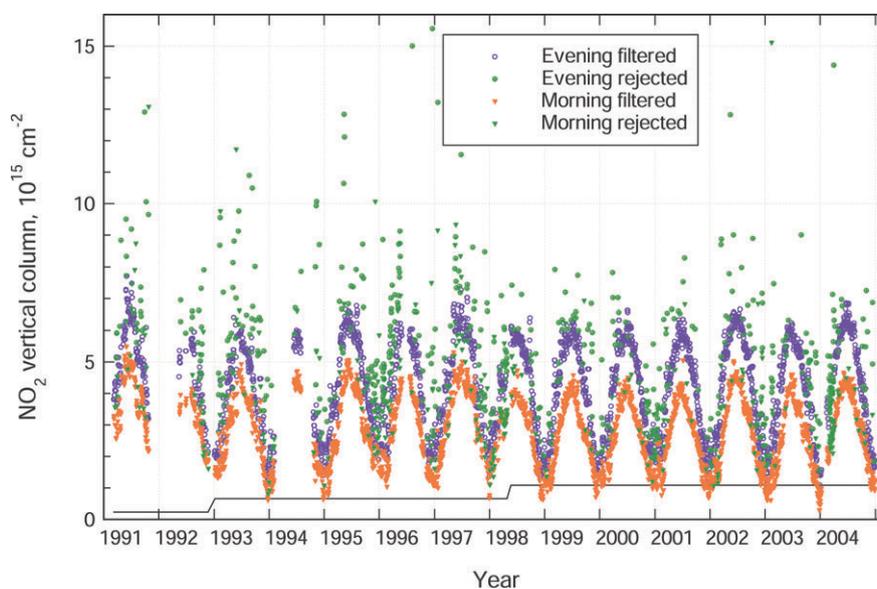


Fig. 2 Removal of bad data points (Aberystwyth data up to end 2004 only). Blue and red symbols refer to data considered reliable, green points to rejected points (standard deviation during twilight $> 3 \times 10^{14} \text{ cm}^{-2}$). A 3-point median filter has been applied to the accepted data. Solid black line indicates changes in detector: the major change from 512 to 1024 pixels occurred in May 1998.

of 6% for morning and 9% for evening twilights. During this period the SAOZ remained in Aberystwyth so data losses due to transportation of the instrument did not occur.

2.3. Intercomparison with other instruments

As described above, the detector used within the SAOZ has been changed twice during its time at Aberystwyth. The first change merely improved the noise performance and had no systematic effect on the measurements, but the introduction of the 1024 pixel detector with the change in grating and slit width was more far-reaching. It is important to understand and quantify any effects these detector changes may have had on the measurements, and to correct for any effects in order to present a homogeneous dataset.

In June 1996 an NDSC (network for the detection of stratospheric change) intercomparison took place at the Observatoire de Haute Provence (OHP) in Southern France (43.9 °N, 5.7°E). Sixteen instruments were involved, including five SAOZs.³⁴ The Aberystwyth SAOZ was present, at that time fitted with the NMOS 512 diode-array detector, as was the OHP SAOZ with an NMOS 1024 diode-array detector (referred to as instrument CNRS2 in Roscoe *et al.*³⁴). The latter is nominally identical to the 1024 pixel SAOZ currently operating at Aberystwyth. The twilight data from this campaign were all re-analysed using the same WINDOAS analysis programs as the Aberystwyth data, using a single reference spectrum from each instrument, to determine any systematic offset between the 512 and 1024 pixel measurements.

Fig. 3 displays the results. There is a clear consistency between the two datasets but also a tendency for the 512 pixel measurements to be slightly higher. The weighted mean offsets between the two data sets for morning and afternoon were $1.3 \pm 0.9 \times 10^{14}$ and $2.5 \pm 1.2 \times 10^{14} \text{ cm}^{-2}$, respectively: consistent with a value of $2 \times 10^{14} \text{ cm}^{-2} \pm 50\%$. In percentage terms this is 3.2% for the morning and 3.9% for the afternoon data—about 3.5% on average, again with an uncertainty of around half this amount. A further uncertainty of around the same amount arises from the residual column (R in eqn (6)) in

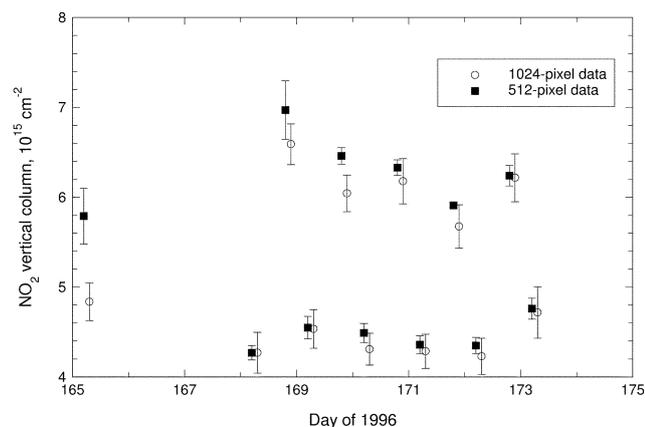


Fig. 3 Comparison of Aberystwyth SAOZ (NMOS 512 diode-array detector) with OHP SAOZ (NMOS 1024 diode-array detector) vertical column NO_2 measurements, when co-located at the 1996 OHP intercomparison. Error bars are 1σ standard errors in the weighted mean for each twilight, derived from the WinDOAS analysis.

each reference spectrum (see discussion of Fig. 7 below). This intercomparison therefore cannot determine accurately any systematic offset between the two detectors, but it does confirm that there is no glaring inconsistency between them. Note the somewhat surprising increase in standard error for the supposedly superior detector. We believe this to be due to the asymmetrical slit function of the 1024 pixel SAOZ, compared with the Gaussian shape of the 512 version.

The OHP intercomparison also provided an indication of the relative accuracy of NO_2 monitoring instruments. In Fig. 12 of Roscoe *et al.*,³⁴ a comparison is presented of the mean relative difference between each of the other instruments and that of NIWA (New Zealand), chosen as the reference in this case. These differences were corrected for the different cross-sections used by each group. In this figure, the Aberystwyth 512 pixel SAOZ measured 16% less than NIWA and the OHP 1024 pixel SAOZ 8% less (a second 1024 pixel SAOZ operated by the NILU group gave the same difference as the OHP SAOZ). In other words, unlike the data in Fig. 3, the 512 pixel SAOZ in Roscoe *et al.*'s paper showed 8% less NO_2 than its 1024 pixel counterpart. This is because the data presented in Roscoe *et al.*³⁴ were analysed using earlier programs with a cruder spectral fitting algorithm and a fixed slit width; the refinements of WinDOAS produces better consistency between the different SAOZ instruments. Roscoe *et al.*³⁴ concluded that there was a 1σ scatter of 6% between the different instruments present at the intercomparison and gave no recommendation on the absolute accuracy of the measurements.

From December 2000 to August 2003 a Brewer spectrophotometer belonging to the UK Met Office was located in Aberystwyth. This instrument measures NO_2 by direct solar observation, rather than zenith sky, and is therefore more sensitive to lower tropospheric pollution. During this period the mean ratio SAOZ/Brewer for individual days was 1.01 (using afternoon Brewer data) with a standard deviation in the ratio of 0.05. While this level of agreement is probably flattering to the two instruments, it does confirm the high quality of the Aberystwyth SAOZ dataset.

We note also here that the NO_2 values derived from the SAOZ are significantly larger than the values derived from GOME²⁵. For 50°N, Wenig *et al.*²⁵ report a maximum NO_2 total column of $3.5 \times 10^{15} \text{ cm}^{-2}$ in summer and a winter minimum of $1 \times 10^{15} \text{ cm}^{-2}$. The solar zenith angle of the GOME data varies with latitude and season so the two data sets cannot be directly compared; nevertheless the daytime NO_2 should be intermediate between the values at dawn and dusk. However, the GOME summer maximum at 10 am is well below that measured by the Aberystwyth SAOZ even at dawn (Fig. 4). Further investigation is required to find the cause of this discrepancy.

3. The Aberystwyth NO_2 time series 1991–2005

Presented in Fig. 4 is the time series of NO_2 measurements from the Aberystwyth SAOZ spanning the period from 1991, when the instrument was installed, to September 2005. The time series also contains measurements from the same

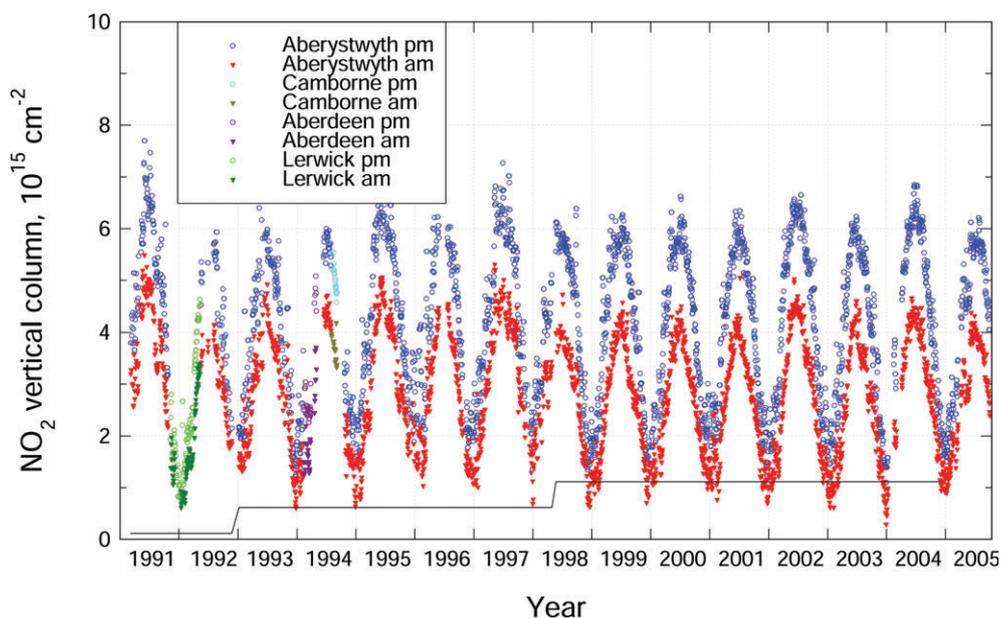


Fig. 4 NO₂ vertical columns measured at Aberystwyth 1991–2005, including measurements made on campaigns at three other locations (Lerwick, 60°N, 1°W; Aberdeen, 57°N, 2°W; Camborne, 50°N, 5°W). Black line is as Fig. 2.

instrument while on campaigns at other locations, and has been cleaned from the effects of pollution as described in Section 2.

Standard errors in the mean of each twilight measurement are shown in Fig. 5. These originate in the spectral fitting procedure performed by WinDOAS, so larger values indicate poorer spectral fits. For the 1024 pixel data (post-1998) the afternoon errors are larger than in the morning, but for most of the 512 pixel record there is little difference between the two. When the errors are expressed as fractions (Fig. 6) this correspondence is reversed: the 1024 pixel fractional errors are the same for both twilight periods whereas the morning 512 data have relatively larger errors.

Clearly, there is a strong seasonal variation in the fractional errors—caused by the seasonal variation in NO₂ itself. For most of the year errors are < 3%, but in the depth of winter the errors increase to > 10%. It is more illuminating therefore to examine the absolute errors. These show a distinct variation over the period of measurement with a reduction as expected when the NMOS-512 detector was installed and a general consistency during the 1024 pixel period. During 1994–1996 errors from the 512 pixel detector were smaller than during the 1024 period, and also very consistent. By contrast, when the SAOZ returned from the OHP intercomparison in July 1996 there was a sharp increase in the errors, which subsided somewhat in 1997 but returned in early 1998. During this

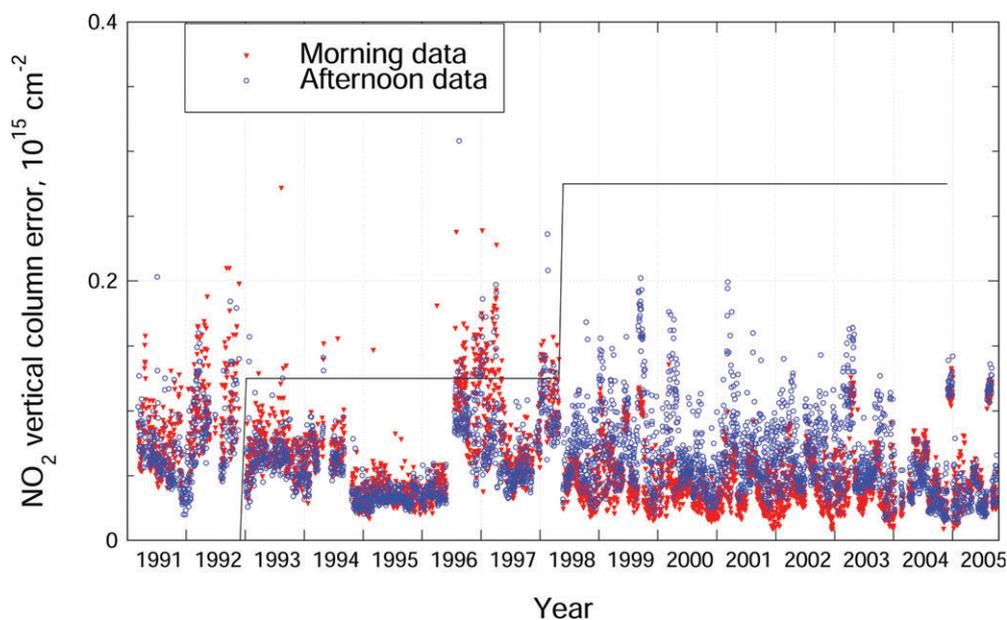


Fig. 5 Standard errors in the mean value for each twilight. Black line is as Fig. 2.

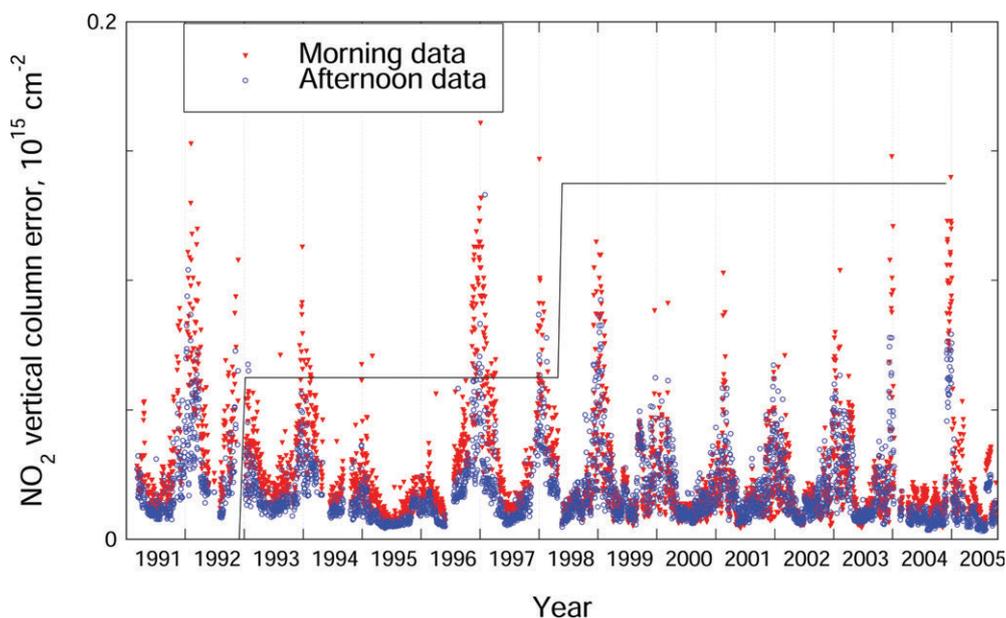


Fig. 6 As Fig. 5 but expressed as a fraction of the average column.

period problems were experienced with the instrument—analyses with a single reference spectrum revealed marked changes in pixel shift over time suggesting a mechanical instability in the detector, despite the SAOZ not being moved until the upgrade in 1998. (These shifts are the reason a monthly reference spectrum was used in the analyses presented in this paper.) The sudden improvement in errors in April 1997 was the result of refocussing the instrument. Nevertheless, the quality of the data between July 1996 and April 1998 is not as good as for the rest of the time series.

In order to focus more on interannual and long-term changes in the NO₂ column, we have fitted to the Aberystwyth data from 1994 onwards an annual and semiannual sine wave:

$$\text{NO}_2(d) = a_0 - a_1 \cos\left(\frac{d + \text{off}_1}{365.25} 2\pi\right) - a_2 \cos\left(\frac{d + \text{off}_2}{365.25} 4\pi\right) \quad (7)$$

using the coefficients in Table 1. The 512 pixel data have been increased by $2 \times 10^{14} \text{ cm}^{-2}$, following the results of the OHP intercomparison; although the uncertainty in this is large the value itself is small and does not have a major impact on the time series. The evening twilight results are shown in Fig. 7, after filtering with an 11 point median filter to reduce the scatter, and again with a 100 day Gaussian kernel to produce a

Table 1 Coefficients of annual and semiannual oscillation fitted to NO₂ time series

	Morning	Evening
Mean value ^a	2.68	4.08
Amplitude of first harmonic ^a	1.50	2.08
Offset of first harmonic, days	0	2
Amplitude of second harmonic ^a	-0.1	0.12
Offset of second harmonic, days	-45	88

^a $\times 10^{15} \text{ cm}^{-2}$.

smooth curve. (Morning twilights showed similar variations but with more scatter.) There is a clear tendency in Fig. 7 for monthly data to cluster, emphasising that the uncertainty in determining R (eqn (6)) is a significant source of error in this technique. From examination of Fig. 7 this error (1σ value) can be estimated as $\sim \pm 3 \times 10^{14} \text{ cm}^{-2}$.

The most obvious feature in Fig. 7 is the sharp relative reduction in NO₂ in late 1991, caused by the eruption of Mount Pinatubo (15.1°N, 120.4°E) in June of that year. Aerosol from this eruption spread around the globe, reaching Europe within 3 months, with the quantity of aerosol reaching a maximum in early 1992.³⁵ Most of the reduction caused by the volcano is due to a real change in the NO₂ column, with a small component (no more than a few percent²⁶) due to a decrease in the air mass factor caused by aerosol scattering from high altitudes. Data for Lerwick and Aberdeen are included in Fig. 7 for illustration only: both stations are affected by the polar vortex in winter and the substantial decrease in observed NO₂ is largely due to the change in location. We cannot therefore infer from this dataset what the NO₂ reduction due to Mt. Pinatubo was at Lerwick or Aberystwyth in the winter of 1991–2. However, it is clear that at Lerwick the diurnal variation in NO₂ columns was absent—in contrast to the rest of the dataset. This feature of the Pinatubo aerosol cloud was pointed out by Goutail *et al.* (1994).²⁶

Occasionally, in winter, the polar vortex extends southward over the UK. As expected on such occasions a reduction in the NO₂ column is observed by the SAOZ, of around $0.7 \times 10^{15} \text{ cm}^{-2}$. Overall in winter there is a statistically significant anticorrelation of NO₂ with potential vorticity at 475 K but the correlation coefficient is only 0.16 so dynamical variability explains only a small part of the variance in NO₂.

From the summer of 1992, when the SAOZ returned to Aberystwyth, to early 1995 the NO₂ columns increase by around $4 \times 10^{14} \text{ cm}^{-2}$, or 10%; note that the 1995 values

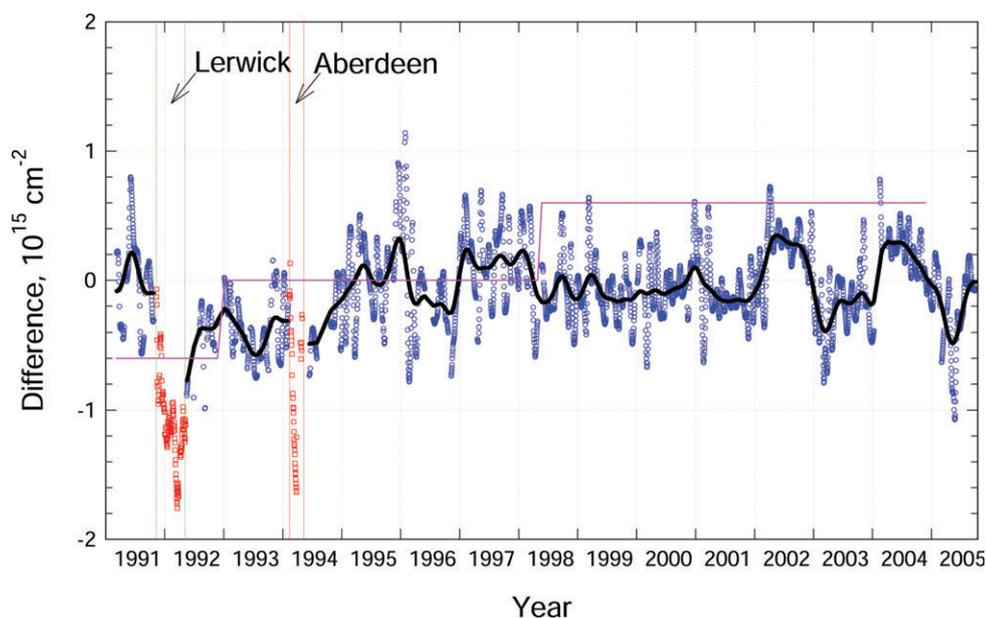


Fig. 7 Blue points: differences between measured NO_2 total columns and statistical model incorporating annual and semiannual variations, evening twilights only, 1991–2005. An 11-point median filter has been applied to the data, and values prior to the detector upgrade in 1998 reduced by $0.2 \times 10^{15} \text{ cm}^{-2}$. Note the clustering of points caused by the use of monthly reference spectra; the scatter of these clusters indicates the uncertainty in the residual column determination. Thick black line is a smoothed (100 day Gaussian filter) version of the blue points; thin magenta line denotes changes of detector. Periods when the SAOZ was in Lerwick and Aberdeen marked with red squares.

are very similar to the pre-Pinatubo spring and summer of 1991. There is a step in the data of around $2 \times 10^{14} \text{ cm}^{-2}$ when the new detector was fitted in May 1998. It is unlikely that this step is real and it would be possible to reduce the 512 pixel series by this amount to remove it; the step is within the uncertainty of the offset derived from the OHP intercomparison. However, we prefer to leave the data set as it stands to make the point that we cannot derive a long-term trend in NO_2 across the whole dataset without making an arbitrary assumption about the change in detector (see the last section of this paper for a discussion of trends).

No such problems have plagued the data in recent years yet there are interesting interannual variations in NO_2 . From 1998 to 2001 there is little departure from the model, consistent with the data from New Zealand,² where the NO_2 annual cycle is consistent for 1996–99. In 2002–05, by contrast, a distinct wave-like variation appears in the columns with an amplitude (peak–peak) of $7 \times 10^{14} \text{ cm}^{-2}$ and an approximately biennial period. In percentage terms this is large—the peak in the summer of 2002 and 2004 corresponds to +7% of the measured values, but the minimum in winter 2003 and mid-2005 is nearer to –10%. (The 512 pixel data show a similar variation from 1995–97 but because of the problems with the instrument this may not be real.)

4. Conclusions

We have presented in this paper fourteen years' measurements of stratospheric NO_2 total vertical columns from the Aberystwyth SAOZ zenith-sky visible spectrometer. The instrument spent most of its time at Aberystwyth with occasional excursions to other locations, notably Lerwick in winter 1991–2 and Aberdeen in the early months of 1994. Data have been analysed

with the WinDOAS analysis program developed at IASB, with low-temperature high-resolution NO_2 cross-sections and fitting a slit function to each spectrum. From March 1991 to April 1998 the SAOZ used a Hamamatsu 512 pixel diode-array detector, which was upgraded to 1024 pixels in May 1998.

The choice of reference spectrum is crucial for the accuracy of the WinDOAS analysis. Aberystwyth is a coastal location, experiencing frequent rain and cloud, and it was found that a reference spectrum taken in clear conditions (or at least not raining) was necessary to derive NO_2 columns with minimal standard error. The use of a single reference spectrum for periods when the SAOZ was physically undisturbed had been found to work well for ozone²⁷ but was not good enough for NO_2 because small pixel shifts between reference and measured spectra degraded the analysis, particularly for the 512 pixel data. (Pixel shifts result from thermal expansion of the optical components over a diurnal and annual timescale, and from mechanical disturbance to the instrument.) Use of daily reference spectra led to the occurrence of poor measurements due to the effects of rain and thick cloud. The method used here was to identify a reference spectrum from a clear day near the middle of each month, and to use this to analyse that month's data. As well as producing a cleaner dataset, this has the effect of converting the uncertainty in the residual column amount R (eqn (6)) to a random error in a long time series. R itself was derived from a Langley plot of slant column *versus* air mass factor between zenith angles 80° and 90° on the day the reference spectrum was measured. It was found that the standard deviation of the vertical columns measured during each twilight period provided a sufficiently robust criterion to remove bad or polluted measurements: if the standard deviation exceeded $3 \times 10^{14} \text{ cm}^{-2}$ that twilight was discarded from the dataset.

There is a very distinct diurnal and annual variation in NO₂ total columns, which are well-known features of odd nitrogen chemistry in the stratosphere. To focus more on interannual and long-term variations in NO₂, a seasonal variation comprising an annual and semi-annual component was fitted to the morning and evening twilight separately (Table 1) from 1994 to the present. This statistical model yielded average NO₂ columns of $4.08 \times 10^{15} \text{ cm}^{-2}$ and $2.68 \times 10^{15} \text{ cm}^{-2}$ for the evening and morning twilights, respectively, with a corresponding annual amplitude of $\pm 2.08 \times 10^{15} \text{ cm}^{-2}$ and $\pm 1.50 \times 10^{15} \text{ cm}^{-2}$.

Since 1998 the instrument has been stable, and the data can be investigated for trends. A linear regression to the departures from the model from 1998 to 2004 (blue points in Fig. 7) yields a trend of $6.0 \pm 0.5\%$ per decade, which is consistent with the results of Liley *et al.* (2000)² and Rinsland *et al.* (2003).⁴ However, it is clear that the time series is not statistically stationary, for during the last three years an interannual variation in NO₂ has developed with an amplitude of $\sim \pm 8\%$, in contrast to the very steady measurements of 1998–2002. Determination of trends over the whole observation period is hampered by the change in detector: a linear regression to the data in Fig. 7 for March–August 1991, Jan 1995–May 1996 and May 1998–December 2004 (*i.e.* omitting data during the Pinatubo period and when the instrument was not performing reliably) in fact yields a trend of $-1.0\% \pm 0.6\%$ per decade. However, if the step which is evident at the change of detector in Fig. 7 is removed from the data (*i.e.* the 512 pixel data are reduced by a further $2 \times 10^{14} \text{ cm}^{-2}$) the deduced trend is $4.4\% \pm 0.3\%$. We therefore conclude that the trends revealed by the Aberystwyth SAOZ agree with those reported elsewhere for the period 1998–2004 and are not inconsistent with them over the whole period of the dataset.

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