S E S 2 0 1 0
Sixth Scientific Conference with International Participation
SPACE, ECOLOGY, SAFETY
2–4 November 2010, Sofia, Bulgaria

TREND ANALYSIS OF THE STRATOSPHERIC NO_2 SLANT COLUMN ABUNDANCE AT STARA ZAGORA

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Key words: *climate change, trace gases, trend analysis*

Abstract: *Since August 1999, daily ground-based spectrometric measurements are carried out during sunrise and sunset at the Stara Zagora (42°N, 25°E) department of the SSTRI-BAS to determine the NO_2 slant column abundance by the help of the GASCOD-BG instrument. Increase or decrease of stratospheric NO_2 density can change ozone concentration, which acts on the radiative balance at the stratosphere and the troposphere. Therefore, the NO_2 trend analysis is very important for the global climate change study. The method described in detail in the paper consists of three stages. In the first one, the daily time series of the NO_2 slant column amounts are analysed and the extreme values, which can result from tropospheric pollutions or be connected with strong lightning processes, are removed. Next, the monthly averages are determined from the remaining daily values. In the second stage, a linear regression model is applied to describe the NO_2 time series components. In the third stage, the significances are tested, taking into account the auto-correlation of NO_2 data.*

Introduction

Nitrogen dioxide (NO_2) is one of the key species of the Earth troposphere and stratosphere. The active nitrogen family (NO_x = NO+NO_2) is an important component of the tropospheric chemistry. Tropospheric NO_x resulting from antropogenic activities and also from natural processes, where the main part of the pollutants as NO_2 are from industrial burning processes (in power plants and also in domestic heating), traffic, biomass burning, soil emissions, and lightning. However, the source strengths have large uncertainties [1]. NO_x is primary emitted in form of NO, which by oxidation forms NO_2. During the day NO_2 is photolytically converted to NO and the photochemical equilibrium is reached within minutes. Tropospheric NO_x is not well-mixed and the NO_x concentrations have very large regional differences. The tropospheric NO_2 is a precursor of ozone in the planetary boundary layer and also influences OH and the oxidation efficiency [2]. Since the pre-industrial times tropospheric NO_2 has increased six times being highest in large urban areas [3] and at the same time ozone has been doubled in the Northern hemisphere [4]. In the tropopause region NO_x can be direct injected by military and civil supersonic aviation [5]. In the stratosphere NO_2 is involved in catalytic cycles of ozone destruction, but also takes part in processes of conversion of reactive chlorine in its reservoir form, mainly in the lower stratosphere. After sunrise, during the day, N_2O_5 is photolysed in NO_3 and NO_2 molecules. During the night NO_2 is converted back into N_2O_5 by triple impacts. This reaction is going on also during the day and causes an increase of NO_2 between sunrise and sunset [6, 7]. NO_2 amounts strongly depend on the stratospheric chemistry controlled by the available solar UV irradiance. In all NO_2 time series strong annual cycles are well observed with the maximum at the summer solstice at all geographic latitudes. In contrast to the tropospheric NO_2 distribution in the stratosphere the NO_2 field has relatively small gradients, particularly in the zonal direction [8].
The relation of NO_2 to the ozone production and ozone destruction underlines its importance for climate models. In particular the quantification of the NO_2 trend is need for the correct determination of the development/prediction of climate for different scenarios. To analyse trend it is necessary to determine factors, which influence the NO_2 amount, to construct an adequate model. The longest NO_2 time series include the time interval of the last 30 years and allow studying the impact of the solar irradiance on NO_2. The correlation between the NO_2 amount, determined at the Lauder station (New Zealand), and the F10.7 radio flux, as a measure of the solar activity, for the time period of 20 years (1980-1999) was poor after correction of the autocorrelation [9]). A quasi-biennial oscillations (QBO) cycle in NO_2 was detected at the equatorial zone [10]. The observed trends of NO_2 at different stations

are varying from - 15% per decade up to 15% per decade [11]. The trends depend on the season and have a strongly regional character. Therefore long time global measurements from ground based stations are needed to determine the global trend. Ground based measurements are also needed to calibrate satellite data [12].

Time series models

General components of a time series X_t are the trend μ_t, seasonal cycles S_t, and a rest component ε_t, irregular short time variations (noise). In the case of an additive model

(1) $$X_t = \mu_t + S_t + \varepsilon_t$$

X_t is formed by the sum of its components. (For multiplicative type of time series, X_t is expressed by the product of its components. Taking the logarithm, the multiplicative model can be transformed in a additive model.) Some authors add to the general components cycles, different than the seasonal ones, with periods greater than one year [13]. In [14] the trend and the cycle component are combined to a smooth component. Mixed additive and multiplicative models are described as well [15]. Usually the trend component is approximated to a linear trend $\mu_t=a+bt$ or to a polynomial of higher order, to an exponential function of *t*, logarithm of *t* or other functions of *t*. Different methods are used to analyze the trend and the seasonal component. In the statistic literature one of the standard methods consists of the stepwise determination of the components. At the first glance the determination of the linear trend as the first step is easy, for example by fitting based on linear regression or smoothing by local averaging. However in the practice it is not so easy. For example it is well known, that a simple sinus oscillation fitted by a linear function gives a linear trend with slope depending on the number of periods included in the time series. De-trending is recommended for time series with trend to avoid spectrum distortion (for example in the program "Statistica"). Therefore the proposed technique [e.g. in 16] to filter the spectrum (without de-trending) in the frequency domain and to calculate the inverse FFT of the filtered time series with the aim of the analysis of the trend in the original series is a risky procedure.
A multitude of methods exists to determine the seasonal component [see e.g. in 17]. In the case of de-trended series the simplest one is to take the average (or median) of all monthly data corresponding to the same month (phase mean). By subtraction of the linear trend, determined for example by smoothing with a filter, which length is greater than the cycle length, this trend can be removed from the original time series. The remaining series consist of the cyclic component and the noise. A second smoothing with a filter of a shorter length removes the noise. Smoothing produces autocorrelation generating quasi periodicities (Slutzky effect). More advanced methods to identify the seasonal component are spline smoothing, Kalman filters [18] determination of Lomb-Scargle Periodogram and the application of wavelet decomposition techniques.
Of course the trend and seasonal components can be determined together based on the OSL. A special method, the Berliner Verfahren, of trend and seasons removal was developed by the German statistic agency (Statistisches Bundesamt) and the Census-11 method was introduced by the American National Bureau of Census [19].
Modern methods are based on stochastic theory, where the deterministic models are replaced by autoregressive models. Very often time series data are combined with cross-section data, as it was mentioned in the above section. The NO_2 amounts are influenced by factors *x* as the solar activity and the QBO, where this factors are time series themselves [11, 20]. Such kind of model can be described as

(2) $$Y_i = \alpha + \beta X_{1,i} + \varepsilon_i, \qquad i = 1....N ,$$

where i are the time points. The factors X can be taken also for certain lags. As by the ordinary regression the linearity is not a very restrictive condition, because instead of the factors *X* can be used their linear transformations.

Data

The NO_2 data used here are obtained by the GASCOD-BG (Gas Analyser Spectrometer Correlating Optical Differences) instrument, developed at the Institute of Atmospheric Sciences and Climate (ISAC) of the Italian National Research Council (CNR) in Bologna [21, 22].
The instrument measures down-welling zenith scattered solar radiation during the sunrise (a.m. data) and sunset (p.m. data) phase. The NO_2 slant column content is retrieved from measurements in the 410–470 nm spectral range, where the absorption features of this gas are well pronounced, applying the DOAS technique. We use the NO_2 slant column amount (sca), interpolated to solar zenith angle of 90° instead of the vertical column amount (vca), to avoid additional errors in the vca calculation. The

GASCOD instrument operates in automatic mode but, due to maintenance procedures or heavy meteorological conditions, the measurement duty cycles are sometimes interrupted and, hence, gaps in the data time series appear, creating non-equidistance of data sampling [23].

Data processing and results

The original NO_2 a.m. and NO_2 p.m. data series are median filtered by a running 7 point filter to eliminate evidently no real results of the NO_2 retrieval procedure. The obtained NO_2 a.m. data are shown in Fig.1. The linear de-trended median filtered data were fitted by a low order (n=10) harmonic progression with a basic period of T=10 years (3652.5 days). This progression was subtracted from the de-trended series and the 2 sigma limits were calculated. It was assumed that values outside these limits are outliers. The most of the outliers are greater than the top 2 sigma limit. In a previous work [24]) it was shown that 30% of these values are connected to strong lightening processes. It is very likely that a great number of positive outliers are related to pollution effects. By both, pollution and lightening, the troposphere content of NO_2 increases at a short time scale. Another part of the outliers can be connected with errors in the NO_2 retrieval procedure. For the determination of the stratospheric NO_2 trend variations of the tropospheric NO_2 part are not of interest. However extreme NO_2 values can bias the trend. Therefore we are not taking into account such values and they were deleted from the original series. The same procedure as the described above one was applied for the NO_2 p.m. data. Using the extreme value removed original data sets the monthly means, the number of measurement days, and the standard deviations for the monthly means were calculated and for future use outputted in matrix forms, easy to use in windows Excel tables. All monthly data were written also in columns. Fig. 2 shows the monthly NO_2 a.m. and NO_2 p.m. data and the previous trends, obtained by OLS linear regression of these data sets using not weighted and sigma square weighted data. The trends of the not weighted data are very strong in particular in the monthly a.m. data. However these results are not directly comparable to the trends found by Gruzdev [11], because the time series have not the same length. The obtained smaller trend in the NO_2 p.m. data is likely generated by a stronger nonlinear trend indicated also by a smaller correlation coefficient. The inspections of the graphics show clearly the expected seasonal cycle. The cycle was estimated calculating average monthly means, average weighted mean, phase means and a simple

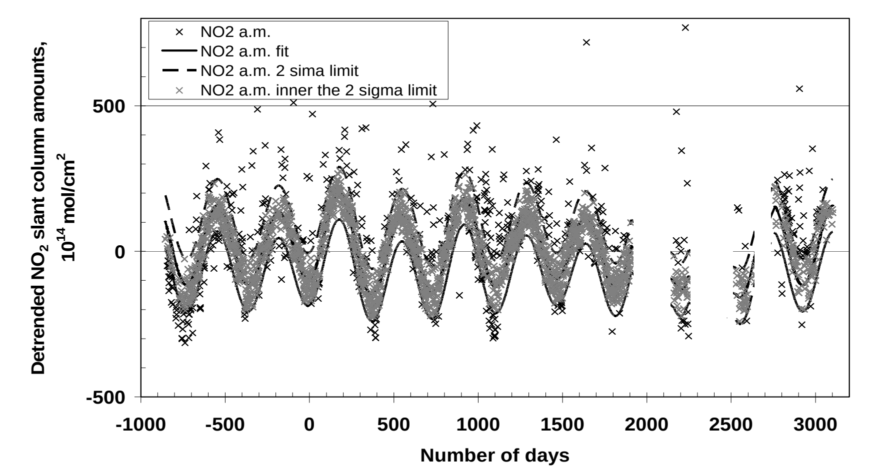

Fig.1. The plot shows the de-trended NO_2 a.m. data, observed at the Stara Zagora Station together with the ±2sigma limits (doted line). Values inside the ± 2sigma limit are shown by grey quadrates. Values outside the limits are presented by black crosses.

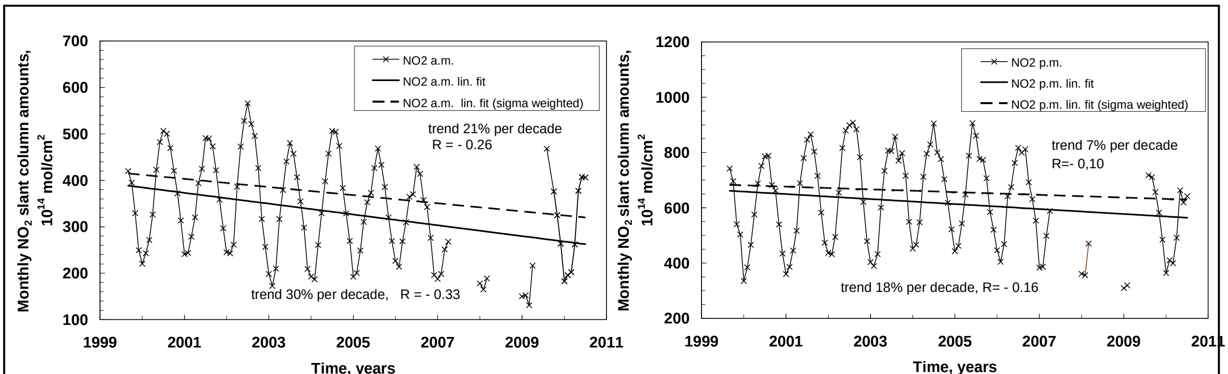

Fig.2. Monthly means of the NO_2 a.m. (left) and the NO_2 p.m. (right) data. The straight lines are the estimated linear trends by simple OLS.

harmonic fit by a series of the first order. The results are graphically presented in Fig.3. The maximum is in the summer months June/July and the minimum - in the winter months December/January, which confirms the expected dominance of the photochemical processes, controlling the stratospheric NO_2 balance and is in accordance with the former findings [11, 25].

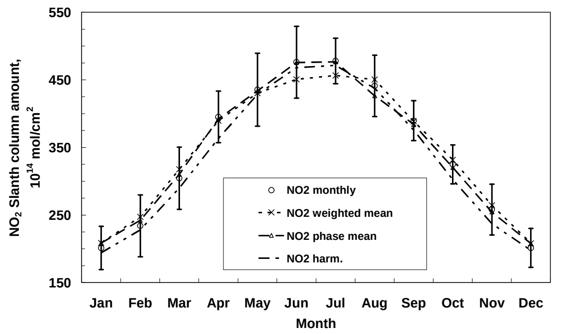

Fig.3. Seasonal component of the NO_2 a.m. series estimated by different methods (see explanation in the text).

All results are very close to each other and are in the 1 sigma limit of the average monthly mean data (presented by error bars in Fig.3). The results show no significant differences in the season figures obtained by the applied methods. Therefore the series was modelled by a simple harmonic mean calculated simultaneously with the linear trend (see Fig. 4). The remaining components (residuals) of the a.m. and p.m. series are shown in Fig. 5. The remaining a.m. and p.m. components have a white noise distribution (not shown here). The autocorrelation properties of this remaining series were analysed using the not interrupted part of the series from the end of 1999 until the beginning of 2007, consisting of 92 data points. The

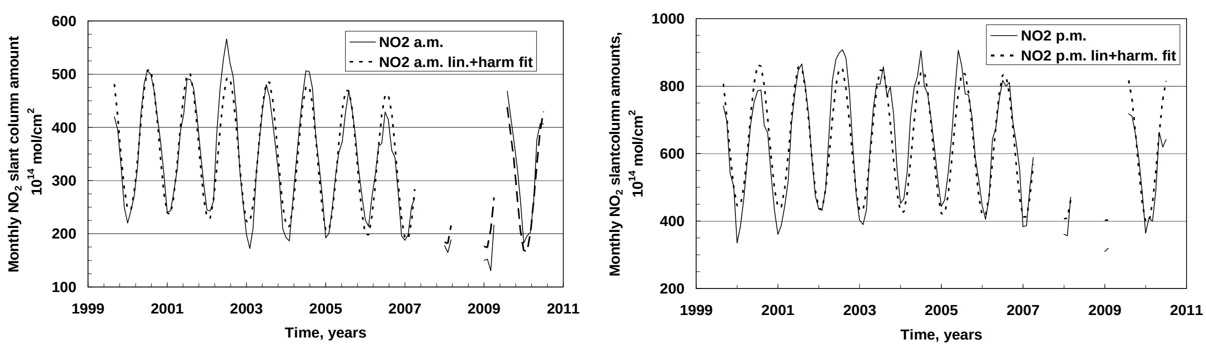

Fig.4. Original NO_2 a.m. (left) and NO_2 p.m. (right) monthly means and the calculated time series model with linear trend and seasonal component consisting of a harmonic series of the first order.

remaining parts are normally distributed, approved by the Kolmogorov-Smirnov, the Shapiro-Wilks W and the Lillefors test. To perform these tests the Statistica 6 program was used. However the residual series are autocorrelated unlike the assumptions of linear regression estimations by OLS. The estimations of the autocorrelations coefficients of the error term are unbiased, but they are not the best linear unbiased estimations (BLUE). The variances of the regression coefficients (in the case of prevailing positive autoregression) are underestimated [17]. The estimated autocorrelation function (EAFC) and the estimated partial autocorrelation function (EPAFC) for the remaining series corresponding to the error terms in Eq.2 were calculated (using Statistica 6 program).The EACF of the NO_2 a.m. and of the NO_2 p.m. series are slowly decreasing with the increasing of the lags up to 9. The NO_2 p.m. EAFC shows a 6 months cycle and a small (not significant) rest of the seasonal cycle. The EPACF of both series shows only one significant coefficient at the lag 1. Both, the course of the EACF and of the EPACF indicate an autocorrelation process of the first order.

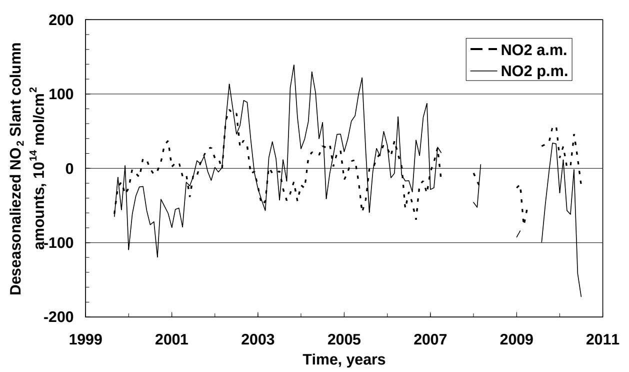

Fig.5. The remaining NO_2 time series components after subtraction of the linear and seasonal components.

(3) $$\varepsilon_i = \rho\varepsilon_{i-1} + u_i ,$$

where ρ is the autocorrelation coefficient at the lag1 and u_i are realizations of a white noise process. The normalized power spectra of the remaining NO_2 a.m. and p.m. series were calculated applying the Fast Fourier transformation (FFT) to answer the question if the remaining series consist of other components than the used here ones. The peaks of the power spectrum were tested for significance by comparison with the normalized power spectrum of a AR(1) (red noise) process [26]:

(4) $$P_k = \frac{1-\rho^2}{1+\rho^2 - 2\rho\cos(2\pi k/N)},$$

where k=0,…,N/2 is the frequency index. Peaks of the NO_2 a.m. and NO_2 p.m. power spectrum are significant, if they are greater than the theoretical background spectrum P_k multiplied with the value of the chi-square distribution of two degrees of freedom and significance level 1-p:

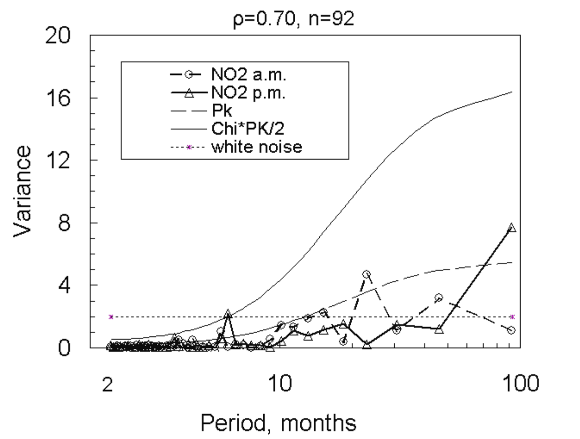

Fig.6. Normalized power spectra of the not interrupted part of NO_2 a.m. and NO_2 p.m. data series in comparison with the power spectrum of a series of an autocorrelated process with autocorrelation of α=0.70 and the FFT of a process with white noise (t_{kr}=1.96).

(5) $$\frac{N|\hat{x}_k|^2}{2\sigma^2} \geq \frac{1}{2}\chi_2^2(p)P_k(\rho),$$

where in the left side of Eq.(5) $N|\hat{x}_k|^2/2$ is the power spectrum of the studied time series x normalized by the squared standard deviation σ^2 [27]. In Fig.6 the Fourier power spectra of the remaining NO_2 a.m. and NO_2 p.m. series are drawn in comparison with the power spectrum of the theoretical AR(1) process with correlation coefficient 0.70, which is approximately the obtained EAFC for the NO_2 a.m. and p.m. series at lag=1. The chi-squared distribution was calculated for a significance level of 0.05. Only the spectrum of the remaining NO_2 p.m. series has a peak at the half year period at the significance limit. It is in accordance with the EAFC. The power spectrum of the a.m. remaining series rises above the significance level of the white noise process for a period near 22 months supposing a QBO effect. However the NO_2 a.m. series has not a peak at this period. The peak is also not significant in relation to the AR(1) background spectrum. Except the mentioned above period of 6 months for the NO_2 p.m. remaining series not significant periods can be detected in the Fourier power spectra. Therefore the NO_2 a.m. and the NO_2 p.m. time series can be approximated with sufficient accuracy by the simple time series model including linear trend and a seasonal component consisting of an annual term for the a.m. series and an annual and a 6 months periods for the p.m. series. The explained variance is 92% for the a.m. series and 90% for the p.m. series. Of course, the 6 months significant peak of the power spectrum doesn't appear when taking into account the half year period for the remaining p.m. series. To apply the Cochrane-Orcutt method [28] for the removal of the autocorrelations of the error terms the missing data were substituted by the forecast values of the time series models. Consequently in the remaining series the missing data are zero. The autocorrelation of the error terms were calculated from the first 92 values of the not interrupted series part. For the a.m. series was obtained $\rho_{a.m.}$ = 0.704 and for the p.m. series $\rho_{p.m.}$=0.697, respectively. After the first iteration of the Cochrane Orcutt method the resulting autocorrelations of the error terms are $\rho_{a.m.}$= 0.03 and $\rho_{p.m.}$= - 0.10 and they both are not significant. Therefore the iteration can be stopped. The obtained slopes are $\beta_{a.m.}$= *0.87* and $\beta_{p.m.}$= 0.78 with the confidence intervals $\Delta\beta_{a.m.}$= ±*0.36* and $\Delta\beta_{p.m.}$= ±*0.71,* where the Student's t value of 1.96 at the significance level of 0.05 was used. The slant column amounts decrease by (104 ± 43) 10^{14} mol/cm^2 during sunrise and by (94 ± 85) 10^{14} mol/cm^2 during sunset in the period of ten years from the end of 1999 till the end 2009, corresponding to linear trends of (27 ± 11) percent per decade and of (14 ± 13) percent per decade related to the values at the end of 1999 for the a.m. and p.m. series, respectively.

Conclusions

Based on the GASCOD-BG NO_2 measurements during twilight it is shown, that the obtained monthly time series can be described by a simple model, containing a linear trend and a seasonal component, which consists of a harmonic annual term for the a.m. series. For the NO_2 p.m. time series an additional harmonic term with the period of six months has to be taken into account to describe better the form of the seasonal component. The explained variances of the model are 92% for the a.m. series and 90% for the p.m. series and are very high. It was demonstrated that the remaining part corresponding to an error term is autocorrelated. By the application of the Cochrane-Orcutt-Method this autocorrelation was removed allowing estimation of the confidence interval based on the Student's *t*-distribution. The obtained in this way linear trends are significant, however they are very uncertain, taking in account, that the time series are interrupted. It was not found a solar or QBO effect influence on the stratospheric NO_2, approving the former findings of Liley [9]. In the future work the results will be compared with series from other stations and satellite measurements.

Acknowledgement

The authors are thankful for the support of this work by the Ministry of Education, Science and Youth under Contract No. DO 02-175/16.12.2008.

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