Formation of nitrogen oxides in the Earth's atmosphere by solar proton flares

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Abstract. The results from the study of daily average values of the background concentrations of nitrogen oxides (NO and NO_2) in the terrestrial atmosphere are presented. The study aim was to reveal some aspects of the relation between the solar flares, as sources of solar energetic protons (SEP-Solar Energetic Protons), and the nitrogen oxides formation in the Earth's atmosphere. For this aim, except the time series of the nitrogen oxides for the period Oct 15, 2004 – Sept 1, 2009, the total daily fluxes of the solar protons for the energy diapasons $E \geq 10\ MeV$ and $E \geq 100\ MeV$, registered by GOES-11 and GOES-13 satellites, were used.The obtained results suggest that the significant peaks in the time series of the nitrogen oxides should be explained with 'volley' effect of NO and NO_2 formations in the middle atmosphere. Such formation processes take place in the time interval from one month to about one year before the peaks registration at the ground-level station of the Rozhen National Astronomical Observatory. In view of the short period with continuous time series, to give a certain answer of the question whether and how the solar protons affect the NO and NO_2 formation it is necessary to prolong the study in future.
Key words: Sun-activity, Sun-flares, Sun-protons, Solar-Terrestrial relations, atmospheric chemistry

1. Introduction

The nitrogen oxides NO, NO_2, NO_x, and their derivate belong to so called 'small components' of the terrestrial atmosphere. In atmospheric chemistry, the term NO_x means the total concentration of NO and NO_2. The nitrogen oxides and volatile organic compounds react in the presence of sunlight to form ozone, which also is associated with human health and ecological effects (U.S. EPA, 1993). By these reasons, the NO_x concentrations in the air are important subjects of ecological monitoring. By the same reasons, in the second half of the last century, the chemical composition of the upper part of the atmosphere (the stratosphere, mesosphere, and lower thermosphere) came into the focus of intensive researches. There are three basic sources of the nitrogen oxides formation in the terrestrial atmosphere. The first two of them are natural (geo-biological and cosmic) sources and the third one is anthropogenic.

The first natural source is presented by two natural processes, which are responsible for the production, deposition, and post-deposition of nitrogen oxides in the Earth's atmosphere. Nitrogen oxide is produced during thunderstorms due to the extreme heat of lightning and is caused by the splitting of nitrogen molecules (Levine et al., 1984). Moreover, the stratospheric NO is mainly produced from the dissociation of nitrogen oxide (NO_2), which is a by-product of the biological nitrogen cycle. This provides a large and relatively constant background source (Jackman et al. 1980).

There are two basic cosmic sources for the nitrogen oxides formation: galactic cosmic rays (GCRs) and the energetic solar activity events. The GCRs come from outside the solar system and they are composed mostly of protons with energies ranging from several 100 MeV far into the EeV range (e.g., Sinnhuber et al., 2012). As the particle energies are so high, they penetrate into the atmosphere at all geographical latitudes, reaching the lower stratosphere or troposphere down to the surface. The mesosphere and lower thermosphere region are not affected by GCRs because the energy of their flux is too low ($\sim 10 - 9\ W/cm^2$) and only secondary particle showers, which provide large fluxes form at lower altitudes. Nevertheless, the GCRs are definitely very important in their contribution to atmospheric ionization. In particular, GCRs are able to penetrate much deeper into the atmosphere than solar ionizing radiation and are the dominant ionization process below about 60 km (e.g. Calisto et al., 2011).

Important solar activity agents for the nitrogen oxides formation are solar ultra-violet (UV), extreme UV, and X-ray irradiances, as well as solar energetic particles (SEPs), such as protons, electrons, and heavier ions (Sinnhuber et al., 2012, for a review). Even though the influence of the SEPs on atmospheric chemistry and dynamics has been shown by several publications to be potentially significant (Calisto, 2011, for a review). The industrial activities, combustion-related technologies, and other human activities are the basic anthropogenic sources of airborne nitrogen oxides (Vitousek et al., 1997; U.S. EPA, 2003).

A solar proton event (SPEs), which lasts for a few days, occurs when protons in the solar plasma are accelerated to very high energies (up to 500 MeV) either close to the Sun during a power solar X-ray (SXR) flares or in interplanetary space by the shocks associated with a coronal mass ejections (CME). If a SXR flare is exceptionally powerful, it can cause a CME. The frequency of occurrence of SXR flares can vary from several per day when the solar activity is in a maximum phase, to less than one in a week during its minimum phases (Gosling, 1993). During unusually strong solar flare events, protons can be produced with sufficient energies (500 MeV and more) to penetrate deeper into the Earth's atmosphere (Jackman et al., 2000, 2008). Therefore, such flares are often called proton flares.

The SPEs lead to polar atmospheric changes through ionization, dissociation, dissociative ionization, and excitation processes. Some of the larger SPEs have caused a significant change in chemical constituents such as hydrogen oxides NO_x (odd hydrogen) and nitrogen oxides NO_x (odd nitrogen), and ozone (Jackman et al., 2009, for a review). From a vital importance for the endothermic reactions, which produce NO_x are SPEs, whose sources are SXR flares of class $\geq M5$ (see, e.g., Jackman and McPeters 2011). Since SPEs affect radiatively active ozone, they have been computed to cause middle atmospheric temperature and other dynamical changes (e.g. Jackman et al., 1995; Krivolutsky et al., 2006; Jackman et al., 2007). Depending on the energy spectra of the solar protons, their largest ionization rate can be found in the mesosphere in the diapason 50-80 km (Calisto, 2011).

The SPE-produced NO_x constituents are relatively short-lived (approximately days) and lead to the destruction of ozone in the upper stratosphere and mesosphere (pressures less than about 2 hPa). Both short- and longer-term (approximately months) catalytic ozone destruction is caused by the SPE-produced NO_x in the lower mesosphere and stratosphere (pressures greater than about 0.5 hPa) via the well-known NO_x ($NO + NO_2$) ozone loss cycle (Jackman et al., 2008):

$$NO + O_3 \rightarrow NO_2 + O_2,$$

followed by

$$NO_2 + O \rightarrow NO + O_2, Net : O + O_3 \rightarrow O_2 + O_2.$$

The net result is 'odd nitrogen', a complex of nitrate radicals designated by the symbol NO_x. Some of the NO_x is transported downward to the troposphere, and then it is precipitated to the surface in 6 weeks.

There were about ten essentially strong SXR flares of class X9 or more in the period 2003-2005. Such SXR flares, which are often called 'mega-flares', are powerful sources of high energy protons ($E \geq 300\ MeV$). The SEPs, including protons with energies above 300 MeV are able to reach the Earth's surface, which lead to increasing of the background radiation, i.e. so called Background Level Enhancement (GLE). There were 68 GLEs in the period from February 1942, when the first GLE was registered, to May 2013. For example, Gopalswamy et al. (2005) reported for the largest GLE of neutrons during solar cycle 23. The GLE occurred on 20 January 2005 and its increase was about 270%.

Many studies have addressed the atmospheric influence of SPEs and the enhancement of the nitrogen oxides concentrations in the stratosphere and mesosphere of the Earth during the period 2003-2005 (e.g. Rinsland et al. 2005; Seppala et al. 2007; Jackman et al. 2007, 2008, 2009, 2011).

The atmospheric dynamical influence of the solar protons that occurred in October-November 2003 (so-called 'Halloween Storms'), the fourth largest period of SPEs measured in the past 40 years, was examined and numerically modeled by Jackman et al. (2007). The authors found that the highly energetic solar protons produced odd nitrogen (NO_x). Moreover, significant short-term ozone decreases (10–70%) followed these NO_x enhancements led to a cooling of most of the lower mesosphere. Their numerical simulations showed the solar proton induced mesospheric temperature and wind perturbations, which diminished over a period of 4–6 weeks after the SPEs. Similar results were obtained in other study (Jackman et al. 2008) related to short- and medium-term atmospheric constituent effects of very large SPEs. The authors showed that polar mesospheric NO_x increase was followed by mesospheric ozone decrease by over 30% during the very large SPEs. In a recent study, Jackman et al. (2009) examined the long-term middle atmospheric influence of very large SPEs, which occurred mainly during very active time period (years 2000–2004). The authors found that the long-term stratospheric ozone effects were caused by the NO_x enhancements. Very large NO_x enhancements lasted for months in the middle and lower stratosphere after a few of the largest SPEs. In a most recent study Jackman et al. (2011) examined large SPEs during 16-21 January 2005 that caused huge fluxes of high-energy SEPs to reach Earth. They found that the NO_x enhancements after such SEPs events reached values, which were tens of times bigger than the statistically mean value of this atmospheric component. The authors also showed that the process of intensive interactions between SEPs and atmosphere spreads at altitudes above 20-25 km.

The maximum of the NO_x formation, and especially of NO_2, is of about 70 km.

Furthermore, it was found that the solar protons with energies between 10 and 300 MeV play the main role in the NO_x formation, while the role of those with energies $\geq 300\ MeV$, i.e. that caused GLE events, is insignificant for this process.

The subject of our study was the relation between the SPEs and the background concentrations of NO, NO_2 and NO_x in the Earth's atmosphere. This study has a few goals, whose achievement will allow revealing some specific aspects of the relation between the SPEs and NOx enhancement in the Earth's atmosphere.

1) Statistical significance and rate of the relation between the solar proton fluxes (i.e. solar proton flares) penetrating in the Earth's atmosphere and the background concentrations of nitrogen oxides registered in a ground-level station.

2) Determination of the time between proton flux action in the middle atmosphere and the nitrogen oxides enhancement in the troposphere, i.e. the delay time between these two events.

3) Estimation of the transfer processes of the nitrogen oxides between the middle atmosphere and the terrestrial surface. It is important to take into account transfer processes, for which the geographical location of NO_x formation is very different from those of the ground-level station, e.g. polar regions, where NO_x formation is most intensive during solar proton flares.

4) Statistical validation of the possibilities for prognoses creation and forecasting of the proton-induced NO_x enhancement in the Earth's atmosphere.

2. Data and methods of analysis

2.1. Data

The daily average values of the background concentrations $[\mu g/m^3]$ of NO, NO_2 and NO_x were registered by the complex background automatic station of the Enterprise for management of the activities by environment protection at the Ministry of Environment and Water. The station is located in the territory of the Rozhen National Astronomical Observatory (Rozhen NAO) at altitude of 1760 m. The station provides nitrogen oxides data since 15 October 2004. By this reason, there are lots of gaps in the time series in the period from 15 October 2004 to 31 August 2009. So, the nitrogen oxides time series from 1 September 2009 to the end of 2012 were used for examination.

The National Oceanic and Atmospheric Administration (NOAA) Geostationary Operational Environmental Satellites (GOES) provided observed proton fluxes since 1994. The data of total daily fluxes [n/day] of the solar energetic protons, registered by GOES-11 and GOES-13 and hosted in Space Weather Center in Boulder, Colorado
(http://www.swpc.noaa.gov/Data/index.html#indices) were also used. The values of the total daily fluxes are considered in two energetic ranges – $E \geq 10\ MeV$ and $E \geq 100\ MeV$.

2.2. Methods of analysis

For examination of the NO, NO_2 and NO_x time series, as well as the statistical significance between nitrogen oxides and solar proton fluxes two methods were used: T-R periodogram analysis and cross-correlation analysis, which are described in detail in Komitov (1986, 1997).

2.2.1. T-R periodogram analysis

The standard T-R periodogram analysis is used for searching for statistically significant cycles of the continuous time series (Komitov, 1986, 1997). This procedure has two work stages.

1. The idea of this method is to approximate the studied time series $F(t)$ by minimized function $\varphi(t)$ of simple periodic type , i.e.

$$F(t) \approx \varphi(t) = A_0 + A\cos(2\pi t/T) + B\cos(2\pi t/T) + ... \qquad (1)$$

where $t = 0$, 1, 2... are the corresponding moments in time step units (for our time - 1 day). A_0 is the mean value of $F(t)$ estimated for the entire time series. For each of the minimized functions $\varphi(t)$ (for a fixed period T) the coefficients A and B are calculated by the mean least square procedure (Komitov, 1997).

T is the period, which is varied in the range $[T_0, T_{max}]$ by step of ΔT. This way, a series of p minimized functions $\varphi(t)$ is obtained, where $p = (T_{max} - T_0)/\Delta T$. The minimal possible value of T_0 is equal to 2 steps of the time series ($\nu = 2$ days). On the other hand, ΔT can be both a whole number and a fractional number in measurement units as that of time series step, i.e. in days.

For each one of the obtained functions $\varphi(t)$ a correlation coefficient R to the time series $F(t)$ is calculated. The local maxima of R point to the possible existence of cycles with duration equal to the corresponding periods T. The error of R is also calculated by the formula $SR = (1 - R^2)/\sqrt{N}$, where N is the length (number of values) of the time series. Since, R depends on T, the series of $R(T)$ values obtained by the afore-mentioned procedure is labeled a 'T-R correlogram' (Komitov, 1997). The T-R correlogram contains local maxima around that values of T, which correspond to the potential cycles present in the examined time series. The cycle amplitude (power) can be calculated by the formula

$$a(T) = \sqrt{A(T)^2 + B(T)^2} \qquad (2)$$

2. For estimation of the statistical significance of the found cycles, two criteria based on the ratio R/SR are used. A cycle is considered with more than 95% confidence, if $R/SR \geq 1.96$. In addition, using a Monte-Carlo time series modeling, an essentially stronger criterion has been derived. It is necessary that $R/SR \geq 4.54/N^2 + 3.46$. For the long series, especially when N tends to infinity, R/SR tends quickly to 3.46. The last criterion arises from the fact that there are many cases of cyclic oscillations in pseudo-random number series, for which R/SR is between the two critical levels. In these cases, accepting the cycle could be based on additional expert criteria.

2.2.2. Cross-correlation analysis

An essential feature of the proton-induced formation of the atmospheric nitrogen oxides is the delay of the 'volley' nitrogen oxides enhancements at the terrestrial surface with respect to their formation by solar proton fluxes in the middle atmosphere. The delay time is from one to three months, i.e. from the short- and medium-term NO_x formation and transfer according to Jackman et al. (2008). For examination of such time-shifted relation between the SPEs and NO_x enhancements, a cross-correlation analysis was used.

We analyze the variation of the coefficients of liner correlation Rc between daily average SEPs fluxes and ground-level concentrations of the nitrogen oxides (NO, NO_2, NO_x) registered in the station at NAO – Rozhen. The aim is to reveal a significant time-shifted relation between SEPs and NO_x events in the diapason from 0 to 500 days. Each of the calculated Rc values was obtained at a shifting step of 1 day. Thus, for the relation between SEPs and concentration of each of the examined nitrogen oxides components a series of 501 Rc values was obtained. Statistical significance of Rc, i.e. the ratio between Rc and its error SRc, was validated by 'sigma-test'(see Section 2.2.1).

3. Results

3.1. Solar energetic particles and ground-level concentrations of nitrogen oxides in the period 2004 - 2012

In Fig. 1, 2, and 3 the top panels present the NO, NO_2, and NO_x concentrations in $\mu g/m^3$, middle panels – solar proton flux with energy $\geq 100\ MeV$, and bottom panels – those with energy $\geq 10\ MeV$. The S1 blue line indicates the threshold level, above which the proton flux already has parameters typical for a radiation storm. Such high energy proton fluxes represent a potential risk for the space and the air technologies. The red circles mark the times of GLEs.

The comparison of the behavior of the NO, NO_2, and NO_x concentrations and the solar proton events presented in the middle and bottom panels of Fig. 1, 2, and 3 suggests two components of the SEPs flux behavior.

1. The proton flux series contain a quiet component that is characterized with low values and very slow and gradual increase from October 2004 to September 2008, whereupon the variation tendency changes to gradual decrease to December 2012.

2. The proton flux series contain consecution of strong and weak flux peaks. The difference between strong and weak flux values vary in the range of several orders. The strong peaks are closely related to the solar proton flares. In fact, the proton flares cause the 'volley' enhancement of nitrogen oxides in the stratosphere and mesosphere.

As can be seen in Fig. 1-3, there are two periods of solar proton flares: one between 15 October 2004 and 31 December 2006 and another, which corresponds to the increase phase onset of the new solar cycle 24 (September 2009). The most powerful SPEs during first period are related with flares on 16 and 20 January, 14 May, and 11 September 2005, as well as the very powerful flares on 7 and 13 December 2006. There are 3 GLEs during this period occurring on 16 and 20 January 2005 and 13 December 2006.

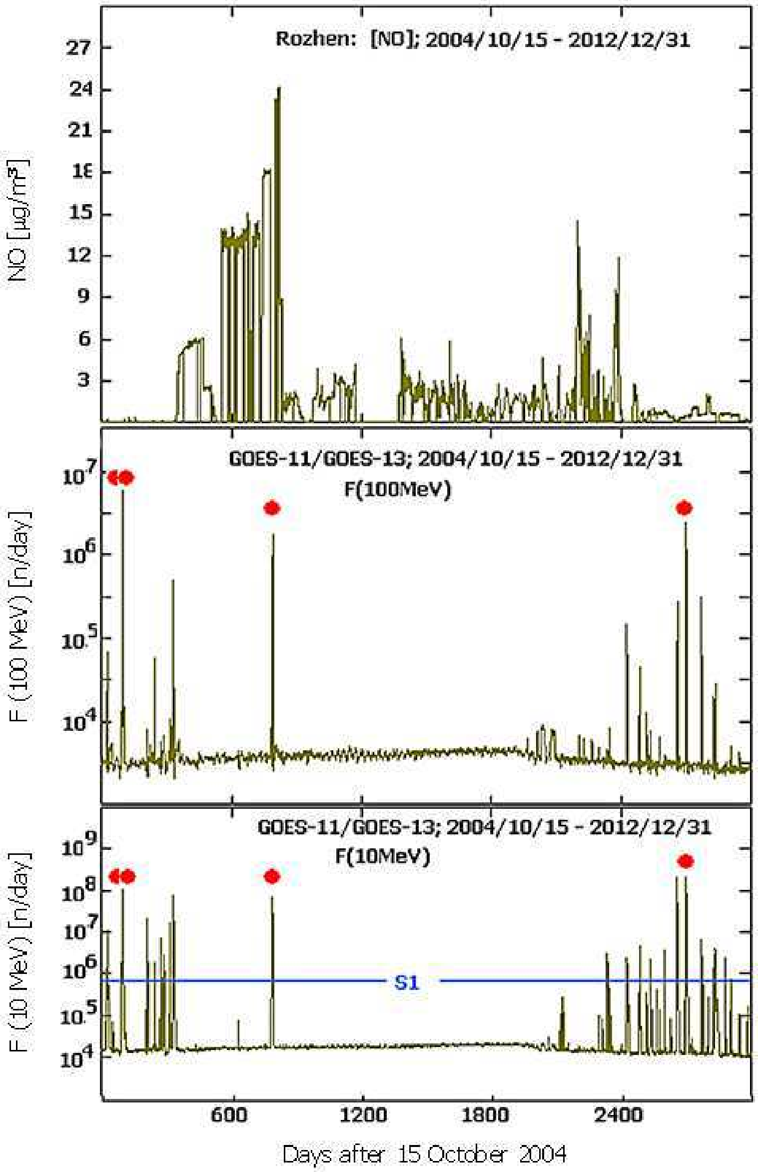

Fig. 1. Daily average values of NO concentration and daily total flux (F) of the high energy protons - $F \geq 100\ MeV$ (middle panel) and low energy protons - $F \geq 10\ MeV$ (bottom panel).

During the second period, related to the solar activity increase, there are more numerous, but less powerful proton flares. Two, the most powerful of them coincide by time with the maximum of the solar cycle 24. They occur on 23 January and 7 May 2012. The second event was followed by GLE.

The top panels of Fig. 1-3 show a period of very high nitrogen oxides concentrations. The period starts in the beginning of October 2005, i.e. $\sim$ 350 day from the beginning of the examined period (15 October 2004). The highest maximum of nitrogen oxides concentrations is in the middle of January 2007 (820 day) and then they rapidly fall. There is a less expressed enhancement of the concentrations in July 2007, which is distinctive for NO_2, less distinctive for NO_x, and in NO series it is absent. After the summer of 2007, the nitrogen oxides concentrations fall down to 1-2 $\mu g/m^3$ and later they faintly increase but remain very low in comparison with the previous period. On the other hand, the presence of many data gaps during second half of 2007 and first months of 2008 makes the conclusion for the low level of nitrogen oxides during a period above 150 days uncertain.

In the beginning of October 2010, the NO and NO_x concentrations suddenly enhance and remain high during 20 days. Such enhancement in the NO and NO_x series is observed 7 months later. Only the second peak in the NO_2 series, is observed.

There is not a presence of annual (seasonal) cycle in the NO, NO_2, and NO_x series in their early parts, until September 2009. Because of many data gaps in the early parts of the series, the effective quantitative analysis for them is inapplicable.

An important question in our analysis of the two types of data series is the search for statistically significant cycles in their behaviors. In the first part of data (15 October 2004 - 31 August 2009) the time series have many data gaps and only visual indications for some cycles could be found. In the second data part (1 September 2009 - 31 December 2012) the time series are continuous and a quantitative analysis is applied for them, e.g. T-R periodogram and cross-correlation analysis.

3.2. Nitrogen oxides concentrations and solar proton flares during ascending phase of solar cycle 24 (2009-2012)

Since in the late part of the nitrogen oxides time series, beginning from 1 September 2009 there were few small data gaps, we made this series continuous by data interpolations in the gaps. So, we were able to use appropriate statistical technics for effective analysis of the nitrogen oxides and solar protons data.

By T-R periodogram analysis we searched for statistical significant cycles in the time series of NO, NO_2, NO_x, and solar proton fluxes, including annual, i.e. seasonal cycles in these data. The results from the T-R periodogram analysis of the nitrogen oxides data are presented in Fig. 4. Its top, middle, and bottom panels present the correlograms of NO, NO_2, and NO_x, respectively. There are no significant quasi-annual cycles, i.e. with period T 360-370 days, in the series of nitrogen oxides. This conclusion, together with those made in Section 3.1, suggest that there are no annual

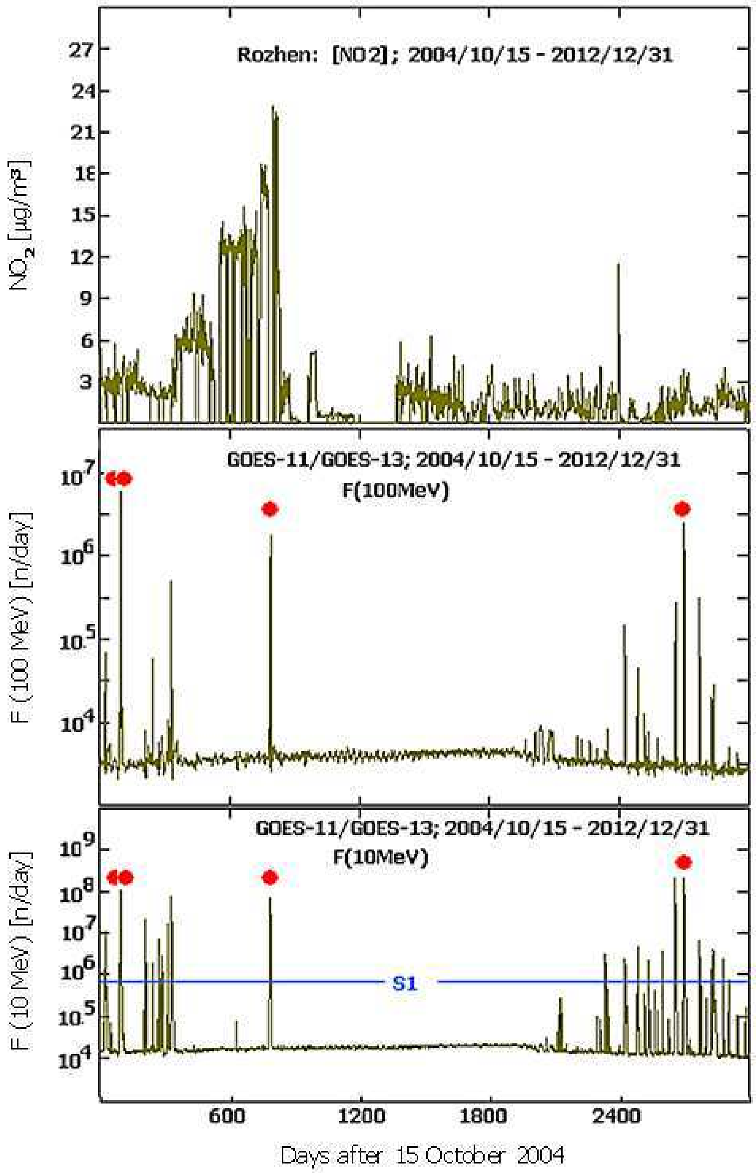

Fig. 2. Daily average values of NO_2 concentration and daily total flux of the high energy protons - $F \geq 100$ MeV (middle panel) and low energy protons - $F \geq 10$ MeV (bottom panel).

variations of nitrogen oxides concentrations during the whole examined period (2004-2012). The presence of a significant semi-annual cycle ($\sim$ 180 days) was found in the time series of NO, NO_2, and NO_x. Besides, a sig-

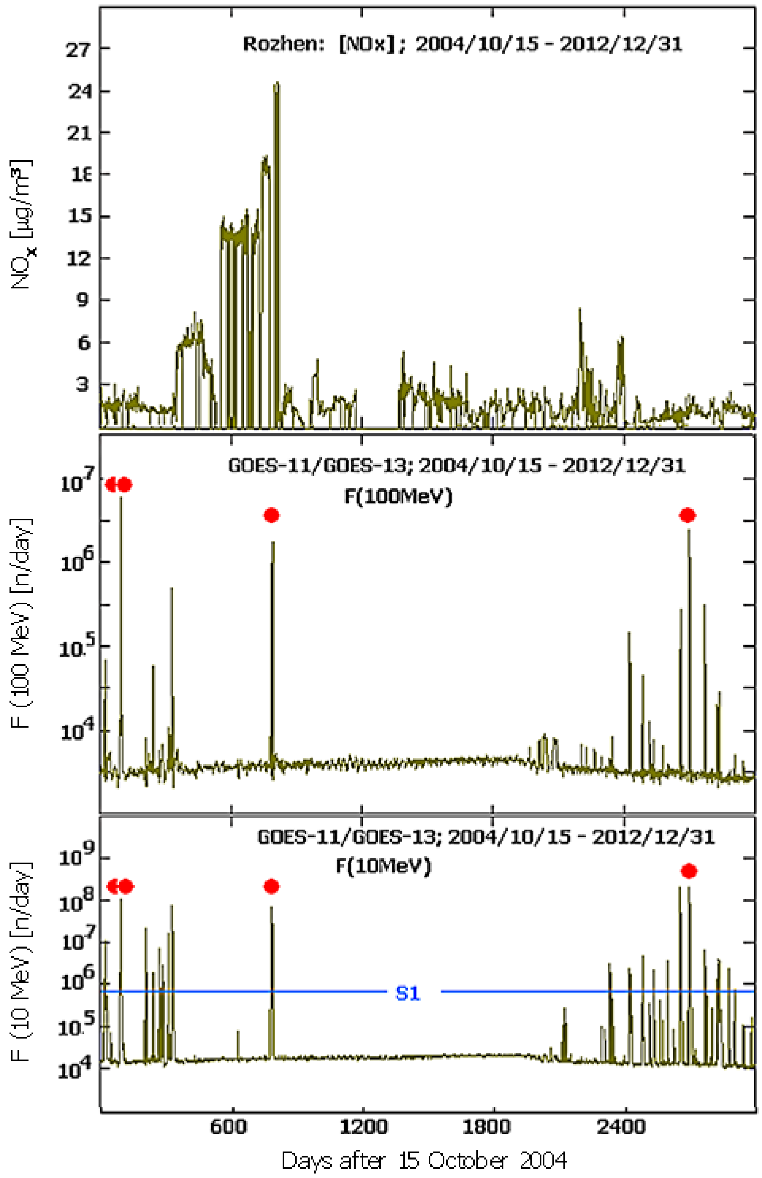

Fig. 3. Daily average values of NO_x concentration and daily total flux of the high energy protons - $F \geq 100\ MeV$ (middle panel) and low energy protons - $F \geq 10\ MeV$ (bottom panel).

nificant variation with duration of about 9-10 months (270-290 days) is well indicated in the NO and NO_2 correlograms in Fig. 4. Moreover, the

NO_2 correlogram shows a well-expressed 540-day cycle, which is resonant multiple of a 9-month cycle.

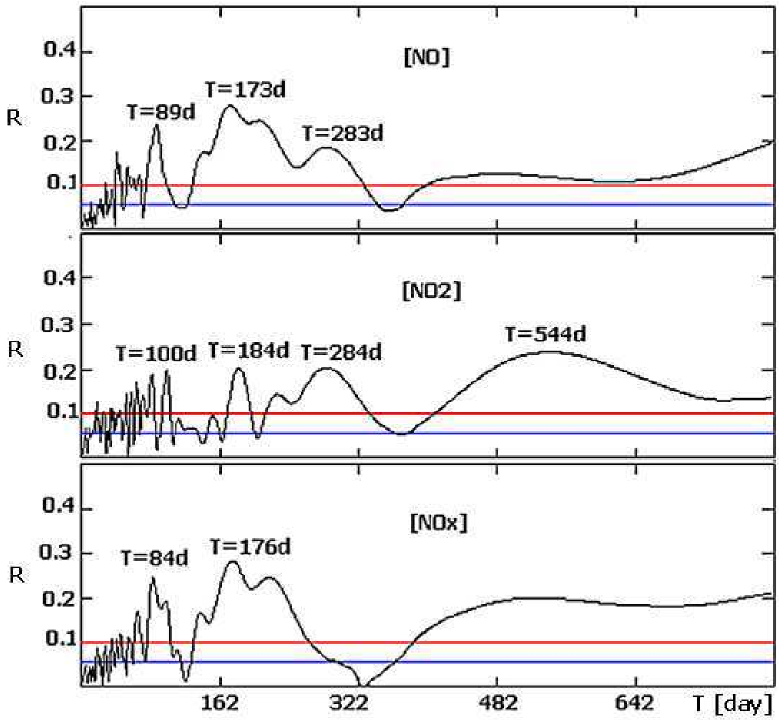

Fig. 4. T-R correlagrams of the NO, NO_2, and NO_x time series for the period 1 September 2009 - 31 December 2012.

The results from T-R periodogram analysis of the time series of the high energy proton fluxes are presented in Fig. 5. The correlograms of the proton fluxes for two energy diapasons $\geq 10\ MeV$ and $\geq 100\ MeV$ are given in the top and the bottom panels of Fig. 5, respectively. The correlograms show two significant quasi-annual cycles: one with a period T=182 days for 10 MeV protons and another with a period T=204 days for 100 MeV protons. The cycle in the series of protons with energy above 10 MeV is statistically more significant, because of their bigger frequency of occurrence than those of the protons with energy above 100 MeV. The presence of semi-annual cycles in the solar protons data is a serious argument that the solar protons cause the cycle with similar duration in the variation of the nitrogen oxides concentrations in the period 2009-2012 rather than the seasonal meteorological changes. The origin of the semi-annual cycle (~ 180 days) in the SPEs data is still uncertain. Most probably, it is related to the occurrence frequencies and power of the solar flares during the ascending phase of solar cycle 24.

The correlograms in Fig. 5 show a 57-58 days cycle in both solar proton series ($\geq 10\ MeV$ and $\geq 100\ MeV$). It is important to note that this cycle is multiple of two 27-day Bartels cycles. The doubled Bartels cycle is typical feature in the behavior of the most solar and geophysical activity indexes during the ascending phases of the 11-year solar cycles.

3.3. Cross-correlation analysis results

The presence of a 182-day cycle in both nitrogen oxides and solar proton fluxes time series suggests the statistically significant cross-correlation dependence between solar proton fluxes and nitrogen oxides concentrations. The cross-correlation analysis was used to reveal some specific features referring to the phase shifting between NO, NO_2, and NO_x time series and those of the SEPs.

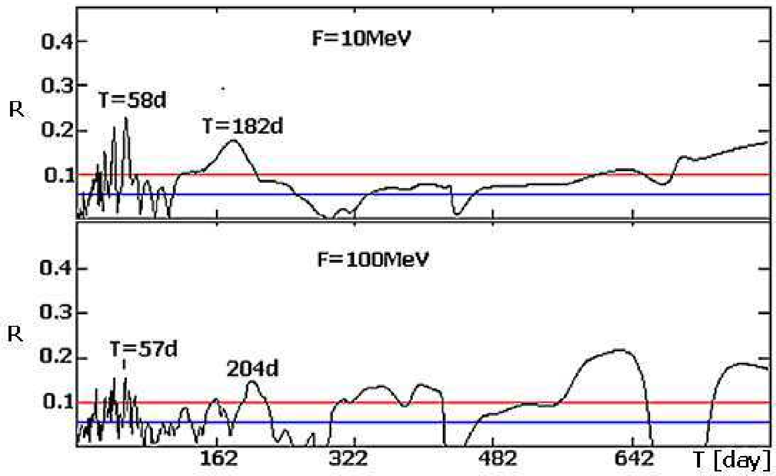

Fig. 5. T-R correlagrams of the daily total fluxes time series of the low energy protons $F \geq 10\ MeV$ (top) and high energy protons $F \geq 100\ MeV$ (bottom) for the period 1 September 2009 - 31 December 2012.

The results of the cross-correlation analysis are presented in Fig. 6 and 7. The phase-shifted relations between the time series of nitrogen oxides (NO, NO_2, and NO_x) concentrations and proton flux $\geq 10\ MeV$ are shown in Fig. 6. The X-axes present the phase-shift between both types of values in days. The values of the correlation coefficients Rc are presented along the Y-axes. The series of the nitrogen oxides concentrations at the terrestrial surface are retarding in phase with respect to those of the proton flux values.The horizontal axes in the three panels of Fig. 6, corresponding to $Rc = 0$ are enclosed by two red lines, which present the critical threshold Rc values calculated for 95% confidential probability. The red lines specify if each of the Rc coefficients is statistically significant according to the criterion $Rc/SRc \leq 1.96$. As can be seen in Fig. 6, there are statistical significant positive Rc peaks at phase-shifting $(t - t_0)$ of about 260-280 days ($\sim 8 - 9$ months), 305-320 days (10 months), and 430-460 days ($\sim$ 15 months). In NO_2 series, a faint peak at $t - t_0 = 32$ days is outlined.

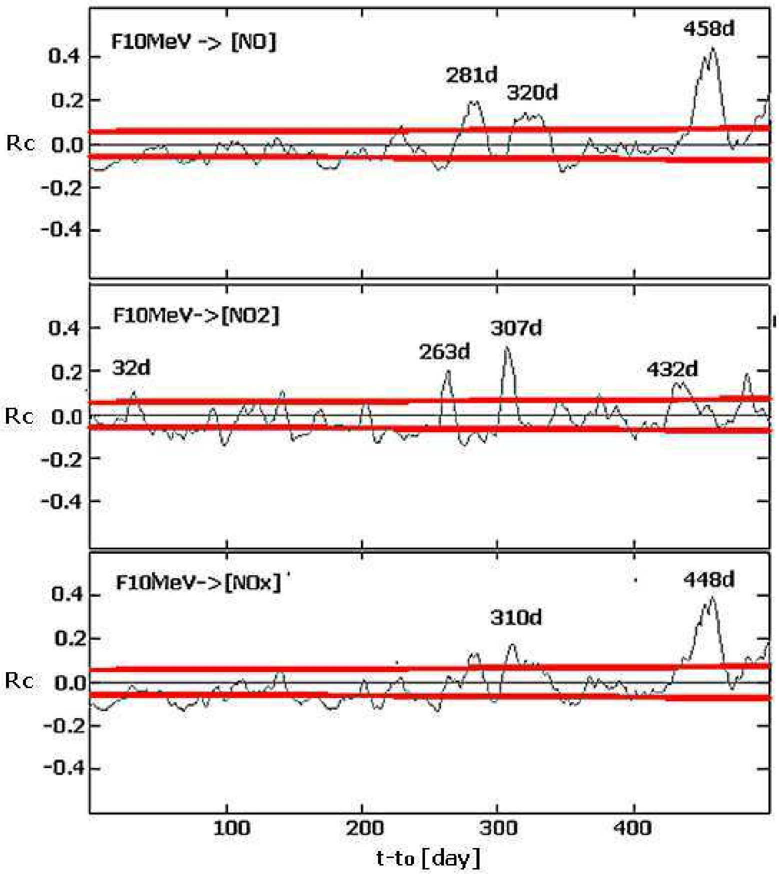

Fig. 6. Cross-correlation coefficients Rc between NO, NO_2, and NO_x concentrations and low energy proton flux $F \geq 10\ MeV$ for the period 1 September 2009 - 31 December 2012.

The result of the cross-correlation analysis between nitrogen oxides and more energetic proton flux ($\geq 100\ MeV$) are presented in Fig. 7. There are well expressed Rc peaks at $t - t_0$ 9, 10, and 15 months in the series of NO

and NO_x. In NO_2 series, Rc peak is observed at $t - t_0 = 30$ days. Similar Rc peak is visible in NO_x series at $t - t_0 = 28$ days.

The NO_2 cross-correlogram shows an interesting feature. There are only two peaks at bigger phase-shift and one of them is very strong. The strong peak corresponds to $t - t_0 = 306$ days (~ 10 months). It has a coefficient of correlation $Rc = 0.48$ and ratio $Rc/SRc = 18$, i.e. the peak has very high significance. Another peak corresponds to $t - t_0 = 263$ days, i.e. almost 9 months. The increase of Rc from low to high values and the following Rc decrease take place during the phase-shifting interval of 2-3 weeks. This fact suggests a 'volley' NO_2 enhancement at the ground surface, whose basic phase arises 9-10 months after the appearance of the assumed agent, e.g. the solar proton flares. The existence of two and more peaks in the cross-correlograms is most probably due to different locations of the proton-induced nitrogen oxides formations in the Earth's atmosphere. For example, the nitrogen oxides can be formed at different atmospheric altitudes in the same geographical region, as well as in different geographical zones. After nitrogen oxides formation, they are transferred to the ground-level stations by atmospheric processes, such as diffusion, convection, and winds.

The results from the cross-correlation analysis are in good agreement with the second conclusion in Section 3.1 about phase-delay of the relation between nitrogen oxides concentrations and SPEs between 2004 and 2009.

4. Discussion

In the high latitude zone of the Earth and especially around the polar regions (auroral zones), the 'volley' production of nitrogen oxides under the influence of solar proton flares is more effective than at low latitudes. Despite of the term 'volley', the formation of nitrogen oxides in the atmosphere is a process, which lasts days, weeks, and more. Such duration is determined by the nature of the proton flares occurrence. The solar proton flares often occur as a sequence of several and more flares during days and weeks. The sources of such flare sequences are a large complex active region or a complex of activity, i.e. several magnetic interrelated active regions. In this respect, a good example was given by Jackman et al. (2011) for very strong solar flares on 16 and 23 January 2005. The enhancements of the solar proton fluxes from these flares at geostationary orbits and corresponding ionization processes in the atmosphere from two eruptive events were strongly overlapped. Hence, independently from the atmospheric chemistry and transfer, the effect of such eruptive flares not always fade rapidly .

The results, obtained in this work, suggest that most probably, the nitrogen oxides peaks registered at NAO-Rozhen station are due to 'volley' production of nitrogen oxides, which is induced by solar proton flares. However, the atmospheric sources of such events are very far from the registration station. Most likely, the formation processes take place in the high-latitude zone of the Northern hemisphere, at northern magnetic latitudes $\geq 50^\circ$. Taking into account that the angle between magnetic and rotational axes of the Earth is 11°, the region of nitrogen oxides formation mainly spreads above Northern America, northern part of Atlantic Ocean, and the mean part of the Arctic Ocean.

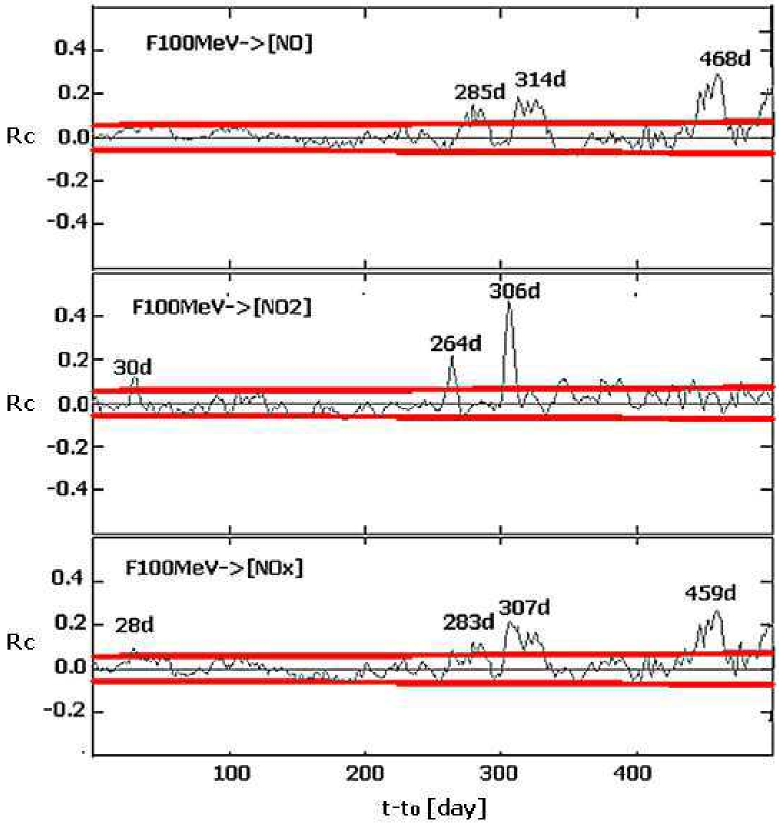

Fig. 7. Cross-correlation coefficients Rc between NO, NO_2, and NO_x concentrations and high energy proton flux $F \geq 100\ MeV$ for the period 1 September 2009 - 31 December 2012.

The transfer of the 'volley' formed nitrogen oxides from high to low latitudes is slow. The rate of the nitrogen oxides concentrations registered at NAO - Rozhen station depends not only on the power and duration of the 'volley' processes at the high latitudes. The atmospheric circulation, which strongly depends on the seasons, is also very important. Noting the role of the atmospheric circulation, some of the faintly expressed peaks of nitrogen oxides, related to the strong flares could be explained. Our analysis shows that the faint nitrogen oxides peaks are related to solar flares that occurred during warm period of the year, when north-south meridional transfer weakens.

A small part of the proton induced nitrogen oxides is probably formed at middle latitudes. It can be assumed that they have a smaller transfer distance to the terrestrial surface, i.e. smaller phase-shifting between their formation processes and registrations. The weak peak in some Rc series obtained for shifting step of 30 days is probably due to a regional source in the middle atmosphere, which is located in the close vicinity of the NAO - Rozhen geographical position.

Conclusion

The obtained results suggest that the significant peaks in the time series of the nitric oxides can be explained with 'volley' production of the NO and NO_2 in the middle atmosphere by solar energetic protons. The significant peaks (cycles) found in data series of two types of events, as well as the delays of the peaks of the nitrogen oxides with respect to those of solar protons are presented in the following points.

1. For the period 2004-2009, i.e. during the minimum between solar cycles 23 and 24, a conformity between the behaviors of two types of events was found – the high values of NO, NO_2, and NO_x concentrations were registered in periods of strong proton flares. The relation between the two events is strongly shifted by time – the nitrogen oxides concentrations were registered 7-10 months later with respect to the SEPs fluxes peaks. There is a second, more expressed tendency of delay of the nitrogen oxides in relation to SEPs fluxes of about one month.

2. For the period 2009-2012, i.e. during the increasing phase of cycle 24, statistically significant semi-annual cycles were found in the series of low energetic ($\geq 10\ MeV$) protons (182 days) and high energetic ($\geq 100\ MeV$) protons (204 days). Significant variations with duration of 9-10 months are outlined in the NO and NO_2 time series. A strongly significant cycle of about 18 months is also found in the NO_2 series.

3. The variations of the NO, NO_2, and NO_x concentrations, registered at NAO-Rozhen station, is retarding in phase with respect to the proton induced endothermic reactions responsible for the nitrogen oxides formation in the middle atmosphere. Several delay times were found for the nitrogen oxides ground level registrations: NO - long-term delay times of 9, 10, and 15 months; NO_2 - one short-term delay time of 30 days and two long-term ones of 9 and 10 months; NO_x – one short-term delay time of 28 days and long-term ones of 9, 10, and 15 months. The variety of different delay times of nitrogen oxides registrations are caused by the combined action of their formation altitude, formation geographical position, and the type of the transfer atmospheric processes.

The time series of the nitric oxides cover only the increasing phase part of solar cycle 24. Therefore, to give a more certain answer to the question how the solar proton flares affect the NO and NO_2 formation, it is necessary to continue the study during next several years, up to the end of the present 24th solar cycle (2018-2019). Such a study could be the base for developing of prognostic models and forecasting of the enhancement of NO and NO_2 concentrations in the troposphere.

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