Increasing in Tropospheric Nitrogen Dioxide over the North-South Transect of Northeast Asia during 1996-2010

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Abstract. Measurements of the global distribution of the tropospheric NO2 column densities have become available with the GOME (Global Ozone Monitoring Experiment) and SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric Chartography) instruments. The spatial and temporal characters of NO2 over the North-South Transect of Northeast Asia (NSTNA) was analyzed using monthly averaged tropospheric NO2 column densities from GOME and SCIAMACHY measurements taken from April 1996 to December 2010. In addition to NO2 (1996-2010) column densities data, land-cover data and characters of NO2 concentration over different ecosystem have been analyzed over the NSTNA. The results indicated that the tropospheric NO2 column densities over the region show distinct regional and seasonal variation characteristics for between 1996 and 2009. The highest concentration was in winter and lowest in autumn. The data also presents zonal distribution and decreasing from northern to southern. Under the influence of the urbanization process, the highest NO2 column densities appeared at cities and metropolitan areas which are located in the north plain of China and the southern areas of the NSTNA. Moreover the lowest column densities appeared at the northern areas of the NSTNA. The tropospheric NO2 column densities have shown significant differences over other ecosystems. In addition, the higher NO2 column density was found over forest and grass land while lower values over lake, tundra and semi-desert. There are different characteristics in five land use types along with the NO2 column densities increasing year by year. The highest values appeared in winter over the forest, grass, lake and tundra while in summer over the semi-desert.

1. Introduction
Nitrogen dioxide (NO2) is one of relatively stable nitrogen oxides in atmosphere. It plays a key role in the photo-chemically which induced catalytic production of ozone [1], and results in summer smog, acid rain and has increased levels of tropospheric ozone [1,2]. NOx has significant natural sources (e.g. lighting and soil emissions) [3] and anthropogenic (e.g. biomass burning, fossil fuel combustion)
sources [1, 3-4]. With the expanding economy, emissions from fossil fuel combustion and biomass burning resulted in the significantly increasing NO2 and air pollution [2].

There is a significant influence in tropospheric NO2 concentration because of the human activity and land cover change. As a result of the sources distribution and the relatively short chemical lifetime, the tropospheric NO2 columns observed from space are dominated by the NO2 amount in the boundary layer. The NO2 columns retrieved from satellite can be used to estimate the currently NO2 emissions [5]. Urban region, as an intensity area of human activity, contains many sources of NO2 emission such as automobiles, fossil fuel combustion and power plant. The increasing emission of automobile has a significant influence on the amount of tropospheric NO2 densities [6]. However, the main sources of tropospheric NO2 columns over forest and grass land where there is little human activity are the atmospheric diffusion and natural emissions [7]. Emissions from soil of cropland come from the plenty of N fertilizer and biomass burning in these areas which have enhanced the concentration of tropospheric NO2.

The tropospheric NO2 increasing in anthropogenic emissions would come back to the terrestrial and marine ecosystems through the way of dry and wet deposition. As an important nutrition and acid source of ecosystems, the sharply change of NO2 concentration becomes consequence for the productivity and stability of terrestrial and marine ecosystems [8]. The ecosystems which are short of nutrition would increase the primary productivity, biomass and the fund of soil organic carbon with the deposition of nitrogen. However, it is harmful for the nitrification ecosystems with the deposition of nitrogen. It also can hasten the nitrogen loss of terrestrial ecosystems and eutrophication in water bodies [9-10]. Thus, it has significant meaning to study the tropospheric NO2 characteristic of different ecosystems.

In recent years using the satellite data, the column densities, vertical profiles at times and emission inventories of the tropospheric NO2 characteristic have been researched. Tropospheric NO2 columns retrieved from GOME satellite measurements have been used to analyze the spatial and temporal patterns of NOx columns. Boersma study error of the system analysis for tropospheric NO2 retrieval from satellite [11]. The quality of SCIAMACHY NO2 data retrieved by KNMI/BIRA has previously been validated by Heue K. P. Gloudemans A. M [12-13]. Tropospheric NO2 columns retrieved from SCIAMACHY have been used to provide top-down estimates of surface NOx emissions via inverse modelling, to examine specific sources, to infer NOx lifetimes, and to estimate surface NO2 concentrations. These analyses, however, are affected by large discrepancies among contemporary tropospheric NO2 retrievals [11-14, 15]. Tropospheric NO2 columns retrieved from SCIAMACHY satellite measurements have been used to evaluate chemical transport models [14], to examine spatial and temporal patterns of NOx emissions. It is important for confidence in the accuracy and reliability of these analyses to assess the quality data which retrieval from GOME and SCIAMACHY satellite measurement in the large scale regions over all seasons. Jagele (2004) [15] studied the NOx seasonal changes in spatial and temporal distribution from biomass burning using GOME satellite data. Boersma (2005) [16] studied NO2 in the troposphere spatial and temporal distribution resulting from lightning using GOME data and model simulation. Andreas Richter (2005) [17] studied the global trends of tropospheric NO2 using GOME and SCIAMACHY data from 1996 to 2004, the results showed that the regions of eastern China and Hong Kong had significant growth. Vander (2006) [18] using satellite data from 1996 to 2005 also found that the concentration of NO2 of some industrial development in eastern China region has significantly increased. Uno (2007) [19] compared the tropospheric NO2 results of GOME data used in 1996-2003 and the CTM simulation. Han (2009) [20] using three-dimensional chemical transport model analyze the NO2 emissions in East Asia and chemical transport mechanism, and compared the result with the GOME data.

Due to the different emission sources, tropospheric NO2 has significantly different characteristics over different regional environment and surface vegetation [21]. Using the fifteen years of available GOME and SCIAMACHY data (GOME: 1996-2002; SCIAMACHY: 2003-2010), the spatial and temporal trends of tropospheric NO2 column densities in NSTNA have been taken to investigate in general. In this study, we also analyzed the variation of tropospheric NO2 columns over different land
covers of NSTNA which derived from the eco-regions and analyzed the sources of tropospheric NO2 emissions.

2. Materials and Methods

2.1 GOME and SCIAMACHY tropospheric NO2 columns

The tropospheric NO2 column densities involved in this paper were level 2 products of version 1.10 of KNMI (Royal Dutch Meteorological Institute, the Netherlands), and were downloaded from the website of the tropospheric Emission Monitoring Internet Service (TEMIS), which is part of the Data User Program (DUP) of the European Space Agency (ESA) (http://www.temis.nl/airpollution/NO2.html). The tropospheric NO2 column data were retrieved by GOME (Global Ozone Monitoring Experiment) [8, 9] and SCIAMACHY (Scanning Imaging Absorption spectrometer for Atmospheric Chartography) [10]. The ground scene of GOME typically has a footprint of 320×40 km2. With an across-track swath of 960 km, global coverage at the equator is achieved within three days [22]. SCIAMACHY has a resolution of 30×60 km2. The total across-track footprint provides global coverage once in every six days at the equator and more frequently at higher latitudes [23]. The algorithm and retrieval error of the NO2 column densities from GOME and SCIAMACHY have been studied by many researchers: for details, see Boersma et al [11, 16], Richter and Burrows [10] and Martin et al [9].

Using the Arcgis soft, we transform the original NO2 column densities data which are HDF format to point data which are SHP format. Then these point data were interpolated into raster format data, which spatial resolution are 0.08333 degree. The purposes of interpolation are to fill the area where data were missing and to analysis the regional transformation of the tropospheric NO2 columns. At last, we clipped the NO2 columns using the North South Transect of Northeast Asia (NSTNA), and obtain the monthly average NO2 data of NSTNA during 1996-2010a.

2.2 Validations of tropospheric NO2 columns from satellite

In contrast to in ShangDianZi (SDZ) site data from pollution monitoring networks, which measure the NO2 concentration near the surface. The remote sensing data from GOME and SCIAMACHY, after correction for vertical sensitivity, yield the column amount integrated over the troposphere. Excepting the emissions of aircraft and lightning, the amount of nitrogen dioxide (NO2) in troposphere are located close to the surface NO2 concentrations. As a result of this NOx source distribution and the relatively short chemical lifetime of NO2. The tropospheric NO2 columns observed from space are dominated by the NO2 amount in the boundary layer. We compared the monthly surface NO2 concentration of SDZ in Beijing and tropospheric NO2 Columns from January 2007 to April 2009 (figure 1). With the scatter plots of the surface NO2 and the tropospheric columns, the regression analysis parameters are given in the figure 1, and it shows better correlation coefficient (R² = 0.79). Therefore the NO2 columns retrieved from GOME and SCIAMACHY can be used to analyze the spatial and temporal distribution characterization of tropospheric NO2 at NSTNA.

2.3 Classifications of the tropospheric NO2 columns

In order to analyze the effects of terrestrial ecosystem by NO2 column concentration change, the NO2 column concentration is divided into seven grades (table 1). There is little reference for classifying the tropospheric NO2 column. So we classified the NO2 column mainly based on Air Pollution Index (API) in this paper. We can get daily API of SDZ from the website http://www.sepa.gov.cn/quality/air.php. According to the formulas of table 1, we could calculate the concentration of NO2 corresponding to different grades API. Then the seven grades of tropospheric NO2 could be classified using the regression equation (section 2.2). The grade level of Tropospheric NO2 columns and air pollution of each level are shown in table 1.
Figure 1. The analysis of relationship between the column densities of tropospheric NO$_2$ and the concentration of NO$_2$ near surface.

Table 1. Scale of column densities of NO$_2$ in seven grades

| Grades | NO$_2$ columns (Unit $10^{15}$mol/cm$^2$) | Air Pollution Level implications |
|--------|-------------------------------------|----------------------------------|
| NO$_2$-I | $\leq 3.74$ | Excellent |
| NO$_2$-II | 5.41 | Good |
| NO$_2$-III | 12.10 | Slightly Polluted |
| NO$_2$-IV | 24.02 | Lightly Polluted |
| NO$_2$-V | 31.75 | Moderately Polluted |
| NO$_2$-VI | 39.69 | Heavily Polluted |
| NO$_2$-VII | $\geq 39.69$ | severley Polluted |

2.4 Study area

The defined study area (figure 2), the North South Transect of Northeast Asia (NSTNA), ranges from 32°N to 78°N and 105°E to 118°E. The transect centres on the Lake Baikal, extending southward to north china area and northward to polar region. It contains the eastern part of Inner Mongolia, metropolitan of Bohai rim, eastern part of Mongolia and middle part of Siberian which include the lake Baikal. It also has the different land cover types such as Beijing-Tianjin metropolis which is located in south of this transect, farming-pastoral zone and the original nature which are less disturbed by human. It is the typical transitional zone that has the spatial distribute from the regions of strong human activity to ones of natural process. The major global change gradient is temperature ranging from 15°C in the south to -15°C in the north for average annual temperature with vegetation along the transect varying gradually from broad leaf forests, agricultural fields, desert steppes to boreal forest, conifer-deciduous broad leaf mixed forests, conifer forests and steppe and tundra. In addition, considered with differences of precipitation, ecosystem and land use intensity, the NSTNA also represents a combined hydrothermal gradient in northeast Asia.
2.5 Land covers of NSTNA
There are two maps (figure 3) of land cover change of NSTNA to analysis the distribution of NO$_2$ column in different land cover. The UMD data (figure 3 A), for indicating the land cover of 1996-2000, was classified into 14 types through NDVI which synthesized 10 days of AVHRR data during 1992-1993 using data mining decision tree. The overall accuracy of this data is 66.9% and the spatial resolution is 1 km. The EUROPE300 data (figure 3 B), for indicating the land cover of 2001-2010, was classified into 23 types through ENVISAT/MERIS data during 2004-2006. The overall accuracy of this data is 73% and the spatial resolution is 300 m. According to Chinese national land resources classification system, we take combination the original 14 categories into six land cover types: water bodies, forest, grass land, cropland, urban area and unused land. The result was shown in figure 3.

3. Results and Discussion

3.1 The spatial distribution of tropospheric NO$_2$ column densities in NSTNA
Using the fourteen years available GOME and SCIAMACHY data (GOME: 1996-2002; SCIAMACHY: 2003-2009), the spatial and temporal trends of tropospheric NO$_2$ column densities in NSTNA have been taken to investigate in general. To illustrate the spatial distribution of NO$_2$, the averages of the tropospheric NO$_2$ column densities derived from SCAMACHY measurements from January to December 2008 is shown in figure 4 A. The results indicate that the highest tropospheric NO$_2$ column densities appeared at the south area of NSTNA, from the plain of north china to the metropolitan regions which are located in Beijing and Tianjin. There is a great contrast between the north (46°-77°N, 105.3°-118°E) and south (31.5°-46°N, 105.3°-118°E) regions of transect. The average tropospheric NO$_2$ columns value is $2.6 \times 10^{15}$ mol/cm$^2$ in fourteen years in south regions, more than five times of the value $0.5 \times 10^{15}$ mol/cm$^2$ in north regions.

The gradient obtained from a linear regression of the annual averages of tropospheric NO$_2$ column densities from 1996 to 2010 is shown in figure 4 B. Reductions of NO$_2$ is observed in NSTNA, while large increase are evident in south regions of NSTNA. However, two exceptions are obvious from the graph: NO$_2$ columns in metropolitan area which contain Beijing-Tianjin cities and Alashan plateau regions, increased strongly while the value decreased in the middle part of NSTNA. There are also some indications of increasing NO$_2$ in the plain regions of north china. Clearly, assuming a linear trend is a simplification, but the overall pattern should be correct. These observations are broadly consistent with a trend of large increases in southeast of NSTNA from 1996 to 2009. But near the northern Polar Regions, the troposphere NO$_2$ increased at the range of $1.0 \times 10^{15}$ mol/cm$^2$.

As a result of the intensive increasing population and urban expending, increasing the amount of automobiles and the rapidly growing economy powered by the generation of energy from fossil fuels, large increases have been predicted for NOx emissions in northern plain of China. Using the MOZART-2 model, Richer et al. researched that a 60% increase in anthropogenic NOx emissions results in a 50% increase of the NO$_2$ column in winter and 57% in summer in China [10]. So to a first approximation, changes in NOx emissions at NSTNA are expected to contribute to the tropospheric NO$_2$ columns.

![Figure 4. Distribution and average annual changes of the tropospheric NO$_2$ column average densities from 1996a to 2010a in NSTNA (Unit: $10^{13}$mol/cm$^2$). A: the spatial distribution of NO$_2$ column densities; B: average annual changes of tropospheric NO$_2$ from 1996 to 2010.](image)

In order to quantitatively describe the characteristic of monthly mean NO$_2$ columns, we use the sine curve model to simulation the changes of tropospheric NO$_2$ column densities [23]:
\[ Y_t = A + BX_t + C \sin\left(\frac{2\pi}{D} X_t + E\right) \]  

Here: \( A + BX_t \) represents the linear trend of tropospheric NO\(_2\) columns from April 1996 to December 2010. \( C \sin\left(\frac{2\pi}{D} X_t + E\right) \) represents the seasonal characteristic; \( X_t \) is months. \( Y_t \) means the tropospheric NO\(_2\) columns in \( X_t \) month. \( A, B, C, D, E \) are model parameter, \( B \) is the variety of average monthly value, \( C \) is the amplitude of seasonal sine curve, and \( D \) is the cycle of sine curve. The average monthly value of NO\(_2\) columns were fitting using formula (1) and the result was shown in figure 5.

Some researches indicated that the sine model have better fitting result in regions where the human activities are less, the seasonal characteristic of tropospheric NO\(_2\) columns is obvious in these areas where natural emission is the main source of tropospheric NO\(_2\) [24]. However, there is poorer fitting result in the anthropogenic emissions in these regions because of the unobvious seasonal variety of tropospheric NO\(_2\) [25]. The tropospheric NO\(_2\) of NSTNA mainly comes from the natural emissions, though there is also part of anthropogenic emissions. But the accuracy of fitting is better, and \( R^2 = 0.513 \).

Figure 5 showed that the increasing trend was not distinct in spring, summer and autumn while increasing sharply in winter of 2006 and 2008. As result of the rapidly growing economic powered by the generation of energy from fossil fuels, large increases have been predicted for NO\(_x\) emissions in south region of NSTNA.

3.2 The variation of tropospheric NO\(_2\) column densities over different land covers of NSTNA

Due to the different regional environment and emission sources, tropospheric NO\(_2\) has significantly different characteristics over different land covers [26]. In this study, we analyzed the variation of tropospheric NO\(_2\) columns over different land covers of NSTNA which derived from the eco-regions.

3.2.1 The seasonal variation of tropospheric NO\(_2\) column densities over different land covers of NSTNA.

There are the similarity seasonal trends of NO\(_2\) columns over four land covers except the semi-desert according to figure 6. The highest value appeared in winter and spring and lowest in summer and autumn. But there is an inverse trend over semi-desert that the highest value appeared in summer and lowest in winter. The main reason of these different seasonal characteristics is the different sources between the anthropogenic emissions of forest, grass, lake and tundra and the natural emissions of semi-desert.
3.2.2 The dynamic changes of variation between NO2 grades and land covers.

During 1996-2010, there are significant variation of NO2 grades in different land covers showed in figure 7. There are same characters of NO2 grades over water bodies, forest and unused land which NO2-Ⅰ is the dominant type with over 99% area per each land cover from 1996 to 2010. Though NO2-Ⅰ is still occupied the main position in grass land, the NO2-Ⅲ and NO2-Ⅳ are increased year by year. Different variation of NO2 grades over cropland and constituted land also showed in figure 7.

The severest NO2 pollution appeared over cropland. The NO2-Ⅰ, NO2-Ⅴ and NO2-Ⅵ represent heavily polluted and show a fast increasing trend over cropland, and these grades are accounted for each area of 20%, 16% and 3%. The NO2-Ⅰ grade is main character over constituted land. However, the NO2-Ⅲ and NO2-Ⅳ grades showed rapidly growth during 2005-2010a.
4. Conclusions

Using the fourteen years available GOME and SCIAMACHY data (GOME: 1996-2002; SCIAMACHY: 2003-2009), the spatial and temporal trends of tropospheric NO$_2$ column densities in NSTNA have been taken to investigate in general. In this study, we analyzed the validation of tropospheric NO$_2$ columns over different land covers of NSTNA which derived from the eco-regions.

(1) NO$_2$ columns in metropolitan area which contain Beijing-Tianjin cities and Alashan plateau regions, increased strongly while the value decreased in the middle part of NSTNA. These observations are broadly consistent with a trend of large increases over southeast of NSTNA from 1996 to 2009. But near the northern Polar Regions, the tropospheric NO$_2$ increased at the range of $1.0 \times 10^{15}\text{mol/cm}^2$.

(2) Seasonal variation and significant increase by year are observed, most notably in the winter values. The highest value of NO$_2$ columns appeared in winter and lowest value in autumn during the period of 1996-2010a except 2007a.

(3) According to the NO$_2$ columns over different land covers, the highest value appeared in the forest and grass land while the lowest value appeared in lake, tundra and semi-desert. Thus, the rapid increases NO$_2$ observed by GOME and SCIAMACHY during 15 years demonstrate that the human activity has significantly increased air pollution over NSTNA. Detailed inventory studies are needed to confirm the conclusions drawn from the satellite observations and to explain the different characteristic emissions of tropospheric NO$_2$ over different land covers.

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