

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)**SciVerse ScienceDirect**

Procedia Environmental Sciences 13 (2012) 1045 – 1056

**Procedia**

Environmental Sciences

The 18th Biennial Conference of International Society for Ecological Modeling

## Evaluation of long-term tropospheric NO<sub>2</sub> columns and the effect of different ecosystem in Yangtze River Delta

M.M. Cheng<sup>a</sup>, H. Jiang<sup>a, b\*</sup>, Z. Guo<sup>c</sup><sup>a</sup> International Institute for Earth System Science, Nanjing University, Nanjing, 210093, China<sup>b</sup> International Research Centre of Spatial Ecology and Ecosystem Ecology, Zhejiang A & F University, Lin'an, 311300, china<sup>c</sup> Colleges of resources science & technology, Beijing normal university, Beijing, 100875, china

### Abstract

The spatial and temporal characters of tropospheric NO<sub>2</sub> column over Yangtze River Delta (YZD) are analyzed using monthly averaged tropospheric NO<sub>2</sub> column densities from GOME (1996-2002) and SCIAMACHY (2003-2010) measurements. In addition, with the NO<sub>2</sub> column densities data and the land cover maps of YZD, the characters of NO<sub>2</sub> concentration over different ecosystem have been analyzed. The results indicated that the tropospheric NO<sub>2</sub> column densities in YZD increased distinctly from 1996 to 2010 and it showed distinct regional and seasonal variation characteristics. It has the highest concentration in winter while lowest in summer. It also presents zonal distribution and decreasing along the Yangtze River from eastern to western. Under the influence of the urbanization process, the highest NO<sub>2</sub> column densities appeared at cities and metropolis which are located in the Shanghai, Nanjing as well as Hangzhou. Moreover the lowest column densities appeared at the forest areas which are in the south and west of Zhejiang province. The sharp increasing of appeared in water bodies, followed urban area and water bodies. The lowest increasing of NO<sub>2</sub> column appeared in grassland. Furthermore, we inferred the ground-level NO<sub>2</sub> concentration from the GOME and SCIAMACHY data in this paper. We compared with the dry plus of N deposition which inferred from the remote sensing data and the mass concentration of N dry deposition from the control experiments, they performed significant correlation ( $P < 0.001$ ), and have the high R value ( $R^2 = 0.86$ ).

© 2011 Published by Elsevier B.V. Selection and/or peer-review under responsibility of School of Environment, Beijing Normal University. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

*Keywords:* Tropospheric NO<sub>2</sub> column densities; temporal and spatial dynamics; Land cover; Yangtze River Delta; N deposition

### 1. Introduction

Nitrogen dioxide (NO<sub>2</sub>) is one of relatively stable nitrogen oxides in atmosphere. Nitrogen oxides are play 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 globally[1, 2]. NO<sub>x</sub> has significant natural sources (e.g. lightning 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 reduce the NO<sub>x</sub> [2] and has significantly increased air pollution.

There is a significant influence to tropospheric NO<sub>2</sub> concentration because of the human activity and land cover change near ground. As a result of NO<sub>x</sub> source distribution and the relatively short NO<sub>2</sub> chemical lifetime, the tropospheric NO<sub>2</sub> columns observed from space are dominated by the NO<sub>2</sub> amount in the boundary layer. The NO<sub>2</sub>

\* Corresponding author. Tel.: 0086-25-83595969; fax: 0086-25-83595969.

E-mail address: [hongjiang1.china@gmail.com](mailto:hongjiang1.china@gmail.com).

columns retrieved from space can be used to prefer the currently estimates of  $\text{NO}_x$  emissions [5]. Urban areas as an intensity human activity contain many sources which emissions from automobiles, fossil fuel combustion and power plant and so on. The increasing emission of automobile has a significant influence in air pollution [2]. However, tropospheric  $\text{NO}_2$  columns are the main come from the atmospheric diffusion and natural emissions over forest and grass land where there is little human activity[1]. Emissions from soil of cropland because of the plenty of N fertilizer and biomass burning in these areas have enhanced the concentration of tropospheric  $\text{NO}_2$ .

The tropospheric  $\text{NO}_2$  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 for ecosystems, the sharply change of  $\text{NO}_2$  concentration has been of consequence for the productivity and stability of terrestrial and marine ecosystems[6, 7]. 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[8]. Thus, it has significant meaning to study the characteristic of tropospheric  $\text{NO}_2$  over different land covers.

In recent years using the satellite data, the column densities, vertical profiles at times and emission inventories are researched. Tropospheric  $\text{NO}_2$  columns retrieved from GOME satellite measurements have been used to analyze the spatial and temporal patterns of  $\text{NO}_x$  columns[9, 10]. Boersma K, et al. study Error of the system analysis for tropospheric  $\text{NO}_2$  retrieval from satellite[11]. The quality of SCIAMACHY  $\text{NO}_2$  data retrieved by KNMI/BIRA has previously been validated by Heue KP et al. and Gloudemans A, et al.[12, 13]. Tropospheric  $\text{NO}_2$  columns retrieved from SCIAMACHY have been used to provide top-down estimates of surface  $\text{NO}_x$  emissions via inverse modeling, to examine specific sources, to infer  $\text{NO}_x$  lifetimes, and to estimate surface  $\text{NO}_2$  concentrations. These analyses, however, are affected by large discrepancies among contemporary tropospheric  $\text{NO}_2$  retrievals [11-13]. Tropospheric  $\text{NO}_2$  columns retrieved from SCIAMACHY satellite measurements have been used to evaluate chemical transport models[14], to examine spatial and temporal patterns of  $\text{NO}_x$  emissions. It is important for confidence in the accuracy and reliability of these analyses to assess the quality data which retrieval from GOEM and SCIAMACHY satellite measurement in the large scale regions over all seasons. Jagele,L studied the  $\text{NO}_x$  seasonal changes in spatial and temporal distribution from biomass burning using GOME satellite data[15]. Boersma, K studied  $\text{NO}_2$  in the troposphere spatial and temporal distribution resulting from lightning using GOME data and model simulation[16]. Richter, A studied the global trends of tropospheric  $\text{NO}_2$  using GOME and SCIAMACHY data from 1996 to 2004, the results showed that the regions of eastern China and Hong Kong had significant growth[5]. Vanders, GJM Using data from 1996 to 2005 also found that the concentration of  $\text{NO}_2$  of some industrial development in eastern China region has significantly increased[17]. Uno, I compared the tropospheric  $\text{NO}_2$  results of GOME data used in 1996-2003 and the CTM simulation[18]. Han, K Using three-dimensional chemical transport model analyze the  $\text{NO}_2$  emissions in East Asia and chemical transport mechanism, and compared the result with the GOME data[19].

Due to the different emission sources, tropospheric  $\text{NO}_2$  has significantly different characteristics over different regional environment and surface vegetation[19]. Using the fourteen years of available GOME and SCIAMACHY data (GOME: 1996-2002; SCIAMACHY: 2003-2010), the spatial and temporal trends of tropospheric  $\text{NO}_2$  column densities in YZD regions have been taken to investigate in general. In this study, we also analyzed the validation of tropospheric  $\text{NO}_2$  columns over different land covers of YZD which derived from the product of UMD and EUROPE300 and analyzed the ecological effect of tropospheric  $\text{NO}_2$  deposition over different ecosystems.

## 2. Materials and methods

### 2.1 GOME and SCIAMACHY Tropospheric $\text{NO}_2$ Columns

The tropospheric  $\text{NO}_2$  column densities involved in this paper were level 2 products of version 1.10 of KNMI(Royal Dutch Meteorological Institute, the Netherlands), and were download 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  $\text{NO}_2$  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  $320 \times 40 \text{ km}^2$ . With an across-track swath of 960 km, global coverage at the equator is achieved within three days[5]. SCIAMACHY have a resolution of  $30 \times 60 \text{ km}^2$ . The total across-track footprint provides global coverage once in every six days at the equator and more frequently at higher latitudes[11]. The algorithm and retrieval error of the  $\text{NO}_2$

column densities from GOME and SCIAMACHY have been studied by many researchers: for details, see Boersma, K[11, 16], Richter, A and Richter, A[10] and Martin, RV[9].

Using the tools of matrix calculation, we translate the original NO<sub>2</sub> column densities data which are HDF format into 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 NO<sub>2</sub> columns. At last, we clipped the NO<sub>2</sub> columns using the Yangtze River Delta region (YZD), and obtain the monthly average NO<sub>2</sub> data of YZD during 1996-2009a.

## 2.2 Validations of tropospheric NO<sub>2</sub> columns from satellite

Blond pointed that NO<sub>2</sub> surface measurements performed in urban areas cannot be used for the validation of the SCIAMACHY NO<sub>2</sub> tropospheric columns with a relatively low spatial resolution. They also show that for rural areas, there is a direct relationship between the measured NO<sub>2</sub> surface concentrations and SCIAMACHY total columns[20]. As a result, we chose the Lin'an air pollution background station (LAS, WMO station) which located in south-western rural area of Hangzhou city in Zhejiang Province. As one of three regional background stations in China (Lin'an, Shangdianzi and Waliguan), LAS is also the only monitoring atmosphere site and present key role in researching the air pollution of YZD. LAS has been monitoring the background atmosphere condition of YZD from July, 2005. In our study, the measured data of LAS has been covered from august of 2005 to June of 2009.

In contrast to in LAS data which measure the NO<sub>2</sub> concentration near the ground, the remote sensing data from GOME and SCIAMACHY, after correction for vertical sensitivity, yield the column amount integrated over the troposphere. With the exception of aircraft and lightning, the sources of nitrogen oxides are located close to the surface. As a result of this NO<sub>x</sub> source distribution and the relatively short NO<sub>2</sub> chemical lifetime, the tropospheric NO<sub>2</sub> columns observed from space are dominated by the NO<sub>2</sub> amount in the boundary layer. We compared the monthly surface NO<sub>2</sub> concentration of SDZ in Beijing and tropospheric NO<sub>2</sub> Columns from January 2007 to April 2009. The NO<sub>2</sub> concentration of LA is the surface average value of the site data during 30 days, while tropospheric NO<sub>2</sub> columns from GOME and SCIAMACHY are the average value of time point, and it is the information of total troposphere column. The tropospheric NO<sub>2</sub> columns have been from the near ground NO<sub>x</sub> emissions. Though there are different spatial and temporal scales of the data from measurement and remote sensing, they have been certain comparability[4].

The comparison indicated that there is finer similarity between satellite measurements and ground based observations (Fig. 1) during January 2007 to April 2009.

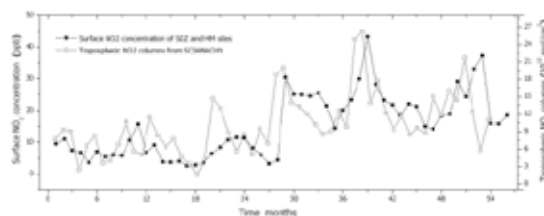


Fig. 1 The comparison between tropospheric NO<sub>2</sub> columns and the near ground NO<sub>2</sub>

We analyzed the correlation between tropospheric NO<sub>2</sub> columns and near ground concentration on the LA site in Zhejiang province from January 2007 to April 2009 (Fig. 2). With the scatter plots of the surface NO<sub>2</sub> and the tropospheric columns, the regression analysis parameters are given in the figure 2, and it shows better correlation coefficient ( $R^2 = 0.86$ , and  $P < 0.001$ ). Therefore the NO<sub>2</sub> columns retrieved from GOME and SCIAMACHY can be used to analyze the spatial and temporal distribution characterization of tropospheric NO<sub>2</sub> at YZD.

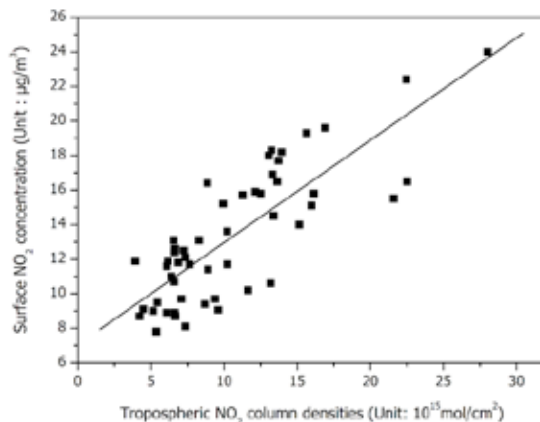


Fig. 2 The analysis of relationship between the column densities of tropospheric  $\text{NO}_2$  and the concentration of surface  $\text{NO}_2$

### 2.3 $\text{NO}_2$ dry deposition Retrievals

Dry deposition refers to the deposition rate of nitrogen as a gas or aerosol in a dry atmosphere, a process that depends on the surface and aerodynamic resistances. It is not only one of the main processes to remove pollutants of atmosphere, but also the efficient way to take the nutrients nitrogen into ecological system from the atmosphere. So the study of dry deposition has been of great significance on the environment and ecology. Dry deposition can thus be estimated if the atmospheric concentrations, the roughness and the wind speed are known. However, deposition of larger aerosols may also occur by sedimentation and impaction. At first, researchers can obtain the dry deposition velocity based on the field or laboratory measurement. Then they developed many models to simulate the deposition process [21, 22], and got the spatial and temporal distribution of  $\text{Nr}$  deposition in certain precision. But due to the lack of reliable regional ground gas concentration and sedimentation velocity data, models simulation also has contained a great deal of limitations. The ratio of dry to total deposition varies markedly over different ecosystem, but is usually between 1:1.7 and 1:2[23], equal or more than wet deposition of  $\text{Nr}$ .

Remote sensing can monitor the concentration of nitrogen oxides distribution over the global in a long time since 1995 [9]. And it provided a new method to study tropospheric  $\text{NO}_2$  distribution and chemical changes based on these satellite data. The dry deposition flux was calculated as the product of the sedimentation velocity and the surface  $\text{NO}_2$  concentration [24] in this study:

$$F(N_d) = V_i(N) \times C_i(N) \quad (1)$$

Here,

$F(N_d)$  dry deposition flux of  $\text{NO}_2$ ;

$V_i(N)$  sedimentation velocity of  $\text{NO}_2$  over the  $i$  ecosystem;

$C_i(N)$  surface  $\text{NO}_2$  concentration over the  $i$  ecosystem.

The dry deposition velocity of  $\text{NO}_2$  were used in this study resulted from zhang, Y[24], which combined the site-specific gradient meteorological data and a big-leaf model to simulate the distribution of dry deposition velocities for the main types of land use present in China. The surface  $\text{NO}_2$  concentrations are retrieval from tropospheric  $\text{NO}_2$  column of GOME and SCIAMACHY.

#### 2.3.1 Inferring surface $\text{NO}_2$ concentration from GOME and SCIAMACHY

We estimate ground-level  $\text{NO}_2$  concentrations from GOME and SCIAMACHY for calculating the  $\text{NO}_2$  dry deposition flux. We follow the approach of empirical formula between ground-level  $\text{NO}_2$  and tropospheric  $\text{NO}_2$  vertical columns in LAS (2.2).

The ground-level  $\text{NO}_2$  is inferred from the equation as follow:

$$Y = 0.591 \times 10^{-15} \times X + 7.041 \quad (2)$$

The  $Y$  denotes the ground-level  $\text{NO}_2$  concentrations. The symbol  $X$  represents the vertical densities  $\text{NO}_2$  of troposphere. Equation (2) implicitly assumes that the tropospheric  $\text{NO}_2$  column is dominated by the emission of the ground. This assumption didn't consider the effect of atmospheric transmission.

### 2.3.2 The reference data of $N$ Dry depositions

In order to verify the flux of the dry deposition using empirical formula, we collected the real  $\text{NO}_2$  dry deposition flux through consulting the published literature [25-31] and the results are shown in table 1.

Table 1  $\text{NO}_2$  dry deposition flux in different sites

Sites	Lat (N, degree)	Lon (E, degree)	Time (a)	dry deposition (Unit: $\text{kg}/\text{hm}^2 \cdot \text{a}$ )	References
Nanjing (Jiangsu)	32.18	118.71	2005	43.83	Deng, 2009[25]
CEF (Beijing)	39.95	116.30	2007	53.3	Shen, 2009[26]
QZ (Hebei)	36.87	115.02	2007	57.4	Shen, 2009[26]
Longyan(Fujian)	25.10	117.03	2004	3.89	Chen, 2006[27]
Zhangzhou(Fujian)	24.51	117.65	2004	5.64	Chen, 2006[27]
Xiamen Univ. (Fujian)	24.44	118.10	2004	4.99	Chen, 2006[27]
Forest of Yintan(Jiangxi)	28.25	116.92	2004	6.58	Fan, 2007[28]
Cropland of Guanzhong(Shanxi)	35.33	109.96	1996	16.3	Li, 1999[29]
Yangling(Shanxi)	34.27	108.08	2006	1.5	Wang, 2008[30]
Luochuan(Shanxi)	35.76	109.43	2006	1.2	Wang, 2008[30]
Caijiatang of shaoshan (Hunan)	27.87	112.91	2001	28.9	Xiang, 2006[31]

### 2. 4 Land cover change maps

There are two maps of land cover change in YZD to analysis the distribution of  $\text{NO}_2$  column in different land cover. The UMD data, for indicating the land cover of 1996-2000, was classified into 14 types land covers 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, for indicating the land cover of 2001-2010, was classified into 23 types land covers through ENVISAT/MERIS data during 2004-2006. The method of this product is three steps: first, they divided the globe land into 22 ecological climate zones; then, the globe map was classified using multiple iterative clustering methods; at last, they chose the 3,000 sites to validate the result of classification. 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 is as shown in Figure 3.

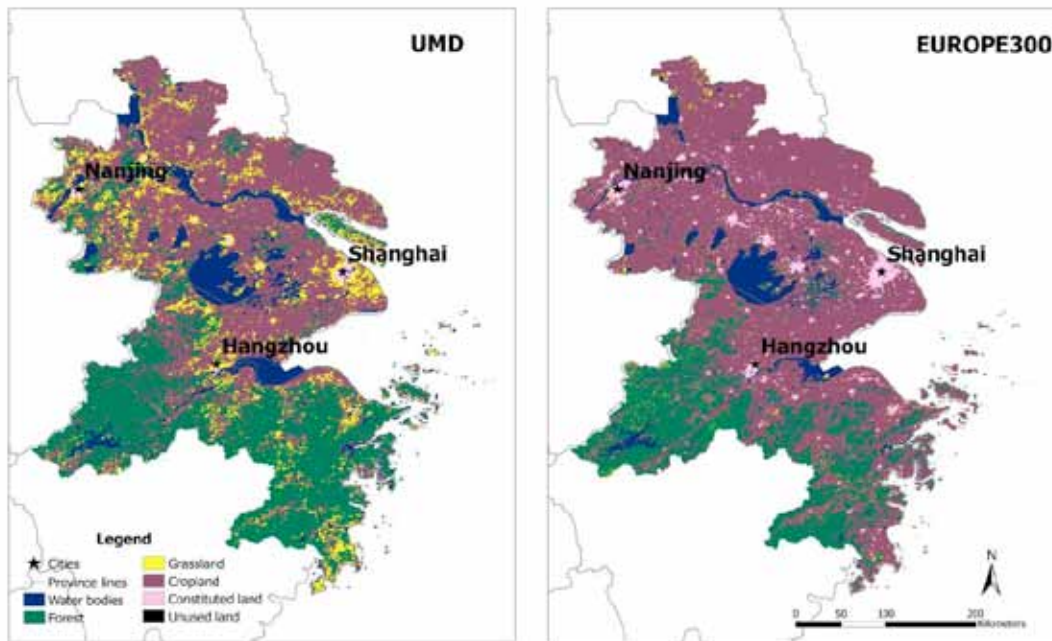


Fig. 3 Land cover maps of YZD during 1996-2010. The left one is derived from the UMD product for indicating the land cover of 1996-2000 in YZD region; the right one is derived from the EUROPE 300 products of 2006 for indicating the land cover of 2001-2010 in YZD region.

### 3. Results and discussion

#### 3.1 General distribution of $\text{NO}_2$ column densities over the YZD

Using the fifteen years of available GOME and SCIAMACHY data (GOME: 1996-2002; SCIAMACHY: 2003-2010), the spatial and temporal trends of tropospheric  $\text{NO}_2$  column densities in YZD have been taken to investigate in general.

To illustrate the spatial distribution of  $\text{NO}_2$ , the averages of the tropospheric  $\text{NO}_2$  column densities derived using SCAMACHY measurements from January to December 2008 are shown in Figure 4 A for the ZD. The result indicate that the highest tropospheric  $\text{NO}_2$  column densities are widespread across the Yangtze River, from Shanghai to the metropolitan regions which are located in south of Jiangsu province. While there is also higher  $\text{NO}_2$  concentration appeared in Hangzhou bay which have the biggest metropolitan area in Zhejiang province.

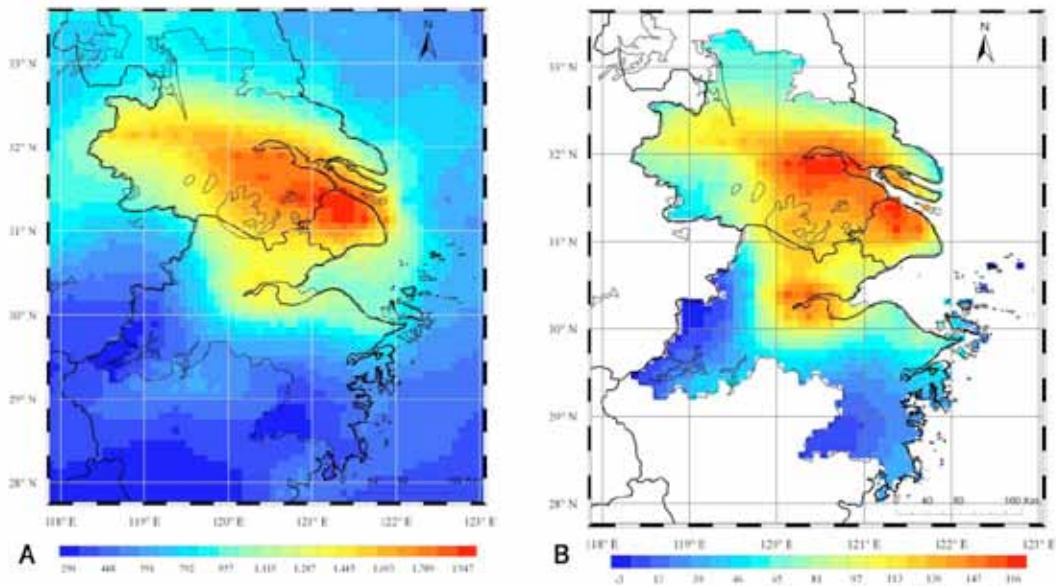


Fig. 4 Spatial variation of tropospheric  $\text{NO}_2$  over YZD region. A is the tropospheric  $\text{NO}_2$  vertical columns derived from SCIAMACHY and averaged between January and December 2008 for YZD; B is the average annual changes in tropospheric  $\text{NO}_2$  as observed by GOME and SCIAMACHY from 1996 to 2010. The gradient obtained from a linear regression of the annual averages of tropospheric  $\text{NO}_2$  column densities, retrieved from 1996 to 2010 is shown. Reductions in  $\text{NO}_2$  are observed over the YZD, while large increase are evident over Shanghai, Nanjing and Hangzhou regions.

Using the fifteen years of available GOME and SCIAMACHY data, the other approach has been taken to investigate possible trends. In a spatial view, a straight line has been fitted to the annual averages of tropospheric  $\text{NO}_2$  from 1996 to 2010. The resulting slopes are shown in Figure 4 B. In most regions of the YZD region, the  $\text{NO}_2$  columns have changed significantly over these 15 years. However, two exceptions are obvious from the graph:  $\text{NO}_2$  columns in metropolitan area which contain Shanghai, Nanjing and Hangzhou cities, increased strongly while they decreased in West and South-Eastern of Zhejiang province. There are also some indications of increasing  $\text{NO}_2$  in the Hangzhou-Jiaxing-Huzhou plain regions and the south of Jiangsu province. 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 over east of China from 1996 to 2004[5].

The biggest surprise is the strong increase in the  $\text{NO}_2$  over the YZD, and this is investigated in more detail in Figure 5, where monthly averages are plotted over the whole region of YZD. Clearly,  $\text{NO}_2$  columns increased throughout the observations, mainly in winter but also in summer. The data also show the large seasonality of the  $\text{NO}_2$  columns which is due to variations in emissions. However there are some different characteristics between the seasonality of satellite data from GOME and from SCIAMACHY. The trend was obviously concluded that it has the highest value in winter and lowest in summer according to the satellite data from GOME. But this character has been showed few distinctly according to SCIAMACHY data.

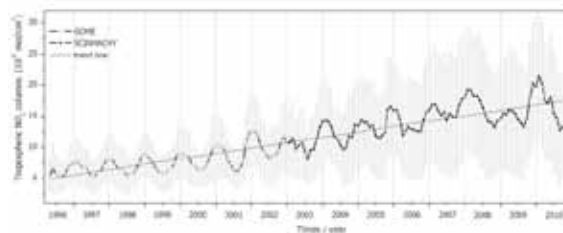


Fig. 5 Time series of satellite observed monthly tropospheric  $\text{NO}_2$  column densities during 1996-2010 over YZD (unit:  $10^{15}$  molecule  $\text{cm}^{-2}$ )



### 3.2 The characterization of tropospheric NO<sub>2</sub> column densities over different ecosystem in YZD

Due to the different regional environment and emission sources, tropospheric NO<sub>2</sub> has significantly different characteristics over different land covers[9]. In this study, we analyzed the variation of tropospheric NO<sub>2</sub> columns over different land covers of YZD which derived from the product of UMD and EUROPE 300.

Figure 6 is the variety trends and the growth rate of NO<sub>2</sub> columns over five land covers. An obvious increasing trend has appeared in all the land covers. According to the NO<sub>2</sub> columns of different land covers, the highest value appeared in the urban area, water bodies and cropland while the lowest value showed over forest and grassland (figure 6 A). The temporal development of the NO<sub>2</sub> column is shown in figure 6 B relative to the value measured in 1996. It is evident from these time series that the changes depicted in figure 6 A are systematic and not dominated by year-to-year variations, in particular over water bodies and forest. There has the fastest increasing amount of NO<sub>2</sub> column over water bodies during 1996-2010, then the urban area, crop land and forest.

The anthropogenic emissions are the main source of tropospheric NO<sub>2</sub> column densities over urban area and crop land. As a contrast, the validation of NO<sub>2</sub> columns is lower value and unobvious annual changes over grass land and forest because of the natural emission of these regions.

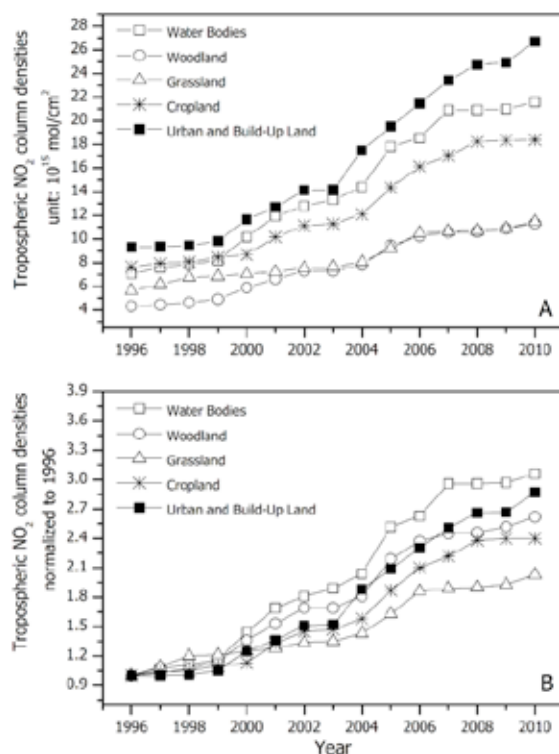


Fig. 6 (A) It is the temporal evolution of tropospheric NO<sub>2</sub> column densities from GOME and SCIAMACHY for different ecosystems in YZD. (B) The mean annual NO<sub>2</sub> column densities normalized to 1996 for the different ecosystems including water bodies, forest, grassland, cropland, and urban area, which are defined in Fig. 3.

The statistical analysis was used to study the characteristic of tropospheric NO<sub>2</sub> column over different land covers during 1996-2010. The result is shown in table 2 and figure 7. At first, amount of the NO<sub>2</sub> column characterized the average densities of NO<sub>2</sub> in troposphere. There is the highest column density of NO<sub>2</sub> in urban area, and then the second is cropland according to table 2. While there are lowest values over water bodies and forest. In addition, the standard variance statistics characterization of NO<sub>2</sub> column indicate the differentiation of NO<sub>2</sub> column densities in spatial. So there is the largest differentiate of NO<sub>2</sub> column in forest (Table 2). And the order of differentiate is grass land, crop land, water bodies and urban area by size. The third, statistical histogram



is reflected the grade distribution of NO<sub>2</sub> column densities. Figure 7 indicated that the NO<sub>2</sub> column has the obviously ‘upper shift’ trend amount the five land covers, especially over urban area and water bodies.

Table 2 Tropospheric NO<sub>2</sub> column densities statistic features over different land coverage

Land coverage	STD	Mean	DMA*
Water bodies	2.90	14.27	3.06
Forest	5.10	7.76	-3.46
Grass land	4.44	8.43	-2.79
Cropland	4.01	12.53	1.32
Urban area	2.74	16.59	5.37

\*DMA: Difference between the Mean values and the Average value of Yangtze region

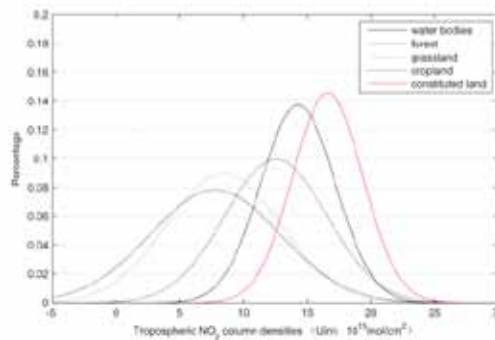


Fig. 7 Tropospheric NO<sub>2</sub> columns statistic curve over different land coverage

To interpret the observed behavior of NO<sub>2</sub> column, the following potential reasons, which might explain an increase of the observed NO<sub>2</sub> columns over different land covers, should be considered. There are a number of population and human activities intensity in urban area and crop land, as a result of a large emission amount in these regions. There are little human activities in forest and grass land, as a result of transmission instead of emission amount of NO<sub>2</sub> column. There is the specific character over water bodies. Although the emission of NO<sub>2</sub> is less the others in water, they are almost located surrounding the human activities indent area such as Taihu Lake in YZD. NO<sub>2</sub> column of Transmission is the main source of water bodies. Then there is plenty of water vapor over there, it can prolong the lifetime of NO<sub>2</sub> in troposphere. As a result there also prefer the high value of NO<sub>2</sub> column over water bodies in YZD region.

### 3.3 Comparison of tropospheric NO<sub>2</sub> column and the flux of NO<sub>2</sub> dry deposition

We compared the tropospheric NO<sub>2</sub> column and the flux of NO<sub>2</sub> dry deposition at this section. The flux of NO<sub>2</sub> dry deposition was collected from the reference literatures which have been published in jurists or magazines. These data have precise coordinates and temporal information. So we elected the tropospheric NO<sub>2</sub> column according to the same coordinates and time, and then carried on the comparison and analysis.

The result is shown as figure 8, and it indicated that there is a significant correlation ( $P < 0.0001$ ,  $R^2 = 0.925$ ) between tropospheric NO<sub>2</sub> and flux of NO<sub>2</sub> dry deposition. However, the discrete phenomena appeared in the high value points because of the lack of flux NO<sub>2</sub> dry deposition data. Overall, it can be used to calculate the NO<sub>2</sub> dry deposition using the satellite data.

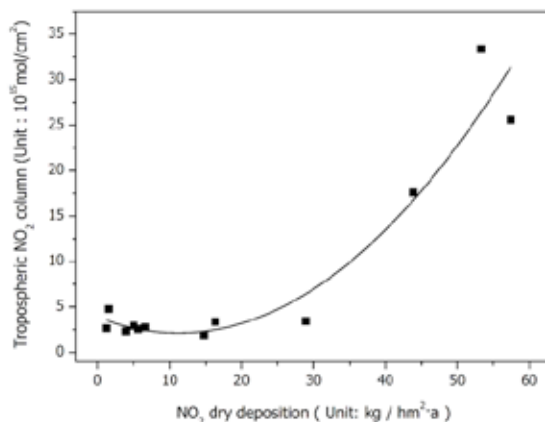


Fig. 8 The analysis of relationship between the column densities of tropospheric  $\text{NO}_2$  and the flux of  $\text{NO}_2$  dry deposition

### 3.4 Flux of $\text{NO}_2$ dry deposition over different land covers in YZD

There are the similarity trends of  $\text{NO}_2$  dry deposition over different land covers. The amounts of  $\text{NO}_2$  dry deposition have increased steadily during 1996 to 2010, which appeared increased significantly in 2005 (Fig.9). However, there also performed distinctly on quantities of  $\text{NO}_2$  dry deposition over per land cover. Through there is the high value of  $\text{NO}_2$  column on water bodies, the amount of  $\text{NO}_2$  dry deposition is smallest among these land covers. It is the highest dry deposition amount of  $\text{NO}_2$  over crop land, then the grass land and forest.

As a result of wet deposition and precipitation are directly related, the nitrogen wet deposition plays a dominated role in the total amount of nitrogen deposition in YZD region. But the dry deposition flux of nitrogen has also the same quantity as the nitrogen wet deposition and cannot be underestimated. Some researches indicated that the dry deposition of nitrogen occupied 20-40 percent of total deposition amount [23]. As a nutrient source of terrestrial ecosystem, atmospheric nitrogen deposition has significant effects on the ecosystem of agriculture, forest and water bodies in YZD region. However, the related conclusions have not been given and this is the next step of our research target.

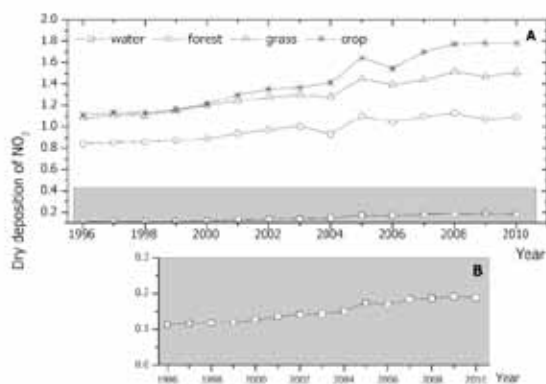


Fig. 9 The trend of the flux  $\text{NO}_2$  dry deposition over different land covers. A is the fluxes of  $\text{NO}_2$  dry deposition over four land covers: forest, water, grass and crop land; B is the flux of  $\text{NO}_2$  dry deposition over water.

## 4. Conclusions

Using the fourteen years of available GOME and SCIAMACHY data (GOME: 1996-2002; SCIAMACHY: 2003-2009), the spatial and temporal trends of tropospheric  $\text{NO}_2$  column densities in YZD region have been taken to investigate in general. In this study, we analyzed the variation of tropospheric  $\text{NO}_2$  columns over different land covers

of YZD which derived from the products of UMD and EUROPE 300. At last, we try to estimate the amount of NO<sub>2</sub> nitrogen dry deposition using satellite data over different land covers.

(1) The result indicate that the highest tropospheric NO<sub>2</sub> column densities are widespread across the Yangtze River, from Shanghai to the metropolitan regions which are located in south of Jiangsu province. In most regions of the YZD region, the NO<sub>2</sub> columns have increased significantly over these 15 years. In spatial, NO<sub>2</sub> columns in metropolitan area which contain Shanghai, Nanjing and Hangzhou cities, increased strongly while they decreased in West and South-Eastern of Zhejiang province. A pronounced seasonal variation and a significant increase from year to year are observed, most notably in the winter values. The highest value of NO<sub>2</sub> columns appeared in winter and lowest value in summer during the period of 1996 to 2010.

(2) NO<sub>2</sub> columns in metropolitan area which contain shanghai, Nanjing and Hangzhou regions, increased strongly while the value decreased in the middle part of YZD. These observations are broadly consistent with a trend of large increases over urban area of YZD from 1996 to 2010.

There are the lowest values of NO<sub>2</sub> column over forest and grass land. It has the same trend of NO<sub>2</sub> column over forest and grass land and distinctly variation on the high value of NO<sub>2</sub> column over urban, water bodies and crop land. There are also different rate of increase over five land covers. It has a maximum growth rate of NO<sub>2</sub> column over water bodies, followed by the urban area, forest and crop land, while a minimum over grass land.

(3) There is the highest column density of NO<sub>2</sub> in urban area, and then the second is cropland. While there are lowest values over water bodies and forest. So there is the largest differentiate of NO<sub>2</sub> column in forest. And the order of differentiate is grass land, crop land, water bodies and urban area by size. The NO<sub>2</sub> column has the obviously ‘upper shift’ trend amount the five land covers, especially over urban area and water bodies.

(4) There are the similarity trends of NO<sub>2</sub> dry deposition over different land covers. The amounts of NO<sub>2</sub> dry deposition have increased steadily during 1996 to 2010, which appeared increased significantly in 2005. Through there is the high value of NO<sub>2</sub> column on water bodies, the amount of NO<sub>2</sub> dry deposition is smallest among these land covers. It is the highest dry deposition amount of NO<sub>2</sub> over crop land, then the grass land and forest.

The characterization of NO<sub>2</sub> column was preliminary analyzed in this paper as well as the amount of NO<sub>2</sub> dry deposition over different land covers. Further work will focus on the sources of NO<sub>2</sub> column over different land covers as well as the ecological effect of NO<sub>2</sub> deposition to terrestrial ecosystem.

## Acknowledgements

This work was Funded by the National Key Project of Basic Research (2010CB428503), and Research Innovation Program for College Graduates of Jiangsu Province (CXZZ11\_0035). The authors thank the anonymous reviewers for their constructive and precious comments on the manuscript.

## References

- [1] Jiang, W.H., Ma, J.Z., Yan, P., Richter, A., Burrows, J.P., and Hendrik, N. Characterization of NO<sub>2</sub> Pollution Changes in Beijing Using GOME Satellite Data. *Journal of Applied Meteorological Science*, 2006. **17**(1): 67-72. (in Chinese)
- [2] Zhang, X.Y., Zhang, P., Zhang, Y., Li, X.J., and Qiu, H. The trend, characterize and source analysis of tropospheric NO<sub>2</sub> in china in 1997-2006. *Science in China (Series D)*, 2007. **37**(10): 1409-16. (in Chinese)
- [3] Fang, S. and Yujing, M. NO<sub>x</sub> fluxes from several typical agricultural fields during summer-autumn in the Yangtze Delta, China. *Atmospheric Environment*, 2009. **43**(16): 2665-71.
- [4] Qi, J.. *Retrieval of nitrogen dioxide total column over China from SCIAMACHY/ENVISAT data*. 2007, Beijing: Chinese Academy of Meteorological Sciences. (in Chinese)
- [5] Richter, A., Burrows, J.P., Nuß, H., Granier, C., and Niemeier, U. Increase in tropospheric nitrogen dioxide over China observed from space. *Nature*, 2005. **437**(7055): 129-32.
- [6] Fang, S.X. and Mu, Y.J. Surface-exchange of NO<sub>x</sub> above a typical wheat land in the Yangtze delta, China. *Acta Scientiae Circumstantiae*, 2006. **26**(12): 1955-63. (in Chinese)
- [7] Zheng, L.X., Liu, X.J., and Zhang, F.S. Atmospheric deposition of organic nitrogen: A review. *Acta Ecologica Sinica*, 2007. **27**(9): 3829-34. (in Chinese)
- [8] Nixon, S.W. Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia*, 1995. **41**: 199-219.
- [9] Martin, R.V., Chance, K., Jacob, D.J., Kurosu, T.P., Spurr, R.J.D., Bucsele, E., Gleason, J.F., Palmer, P.I., Bey, I., and Fiore, A.M. An improved retrieval of tropospheric nitrogen dioxide from GOME. *J. Geophys. Res.*, 2002. **107**(4437): 10.1029.

- [10] Richter, A. and Burrows, J. Tropospheric NO<sub>2</sub> from GOME measurements. *Advances in Space Research*, 2002. **29**(11): 1673-83.
- [11] Boersma, K., Eskes, H., and Brinkma, E. Error analysis for tropospheric NO<sub>2</sub> retrieval from space. *Journal of Geophysical Research*, 2004. **109**(D4): D04311.
- [12] Heue, K.P., Richter, A., Wagner, T., Bruns, M., Burrows, J., Friedeburg, V., Lee, W., Platt, U., Pundt, I., and Wang, P. Validation of SCIAMACHY tropospheric NO<sub>2</sub> columns with AMAXDOAS measurements. *Atmospheric Chemistry and Physics Discussions*, 2004. **4**(6): 7513-40.
- [13] Gloudemans, A., Krol, M., Meirink, J., De Laat, A., Van der Werf, G., Schrijver, H., Van den Broek, M., and Aben, I. Evidence for long-range transport of carbon monoxide in the Southern Hemisphere from SCIAMACHY observations. *Geophysical research letters*, 2006. **33**: L16807/1-L16807/5.
- [14] Velders, G.J.M., Granier, C., Portmann, R.W., Pfeilsticker, K., Wenig, M., Wagner, T., Platt, U., Richter, A., and Burrows, J.P. Global tropospheric NO<sub>2</sub> column distributions Comparing three-dimensional model calculations with GOME measurements. *Journal of Geophysical Research*, 2001. **106**: 12.
- [15] Jaeglé, L., Martin, R., Chance, K., Steinberger, L., Kurosu, T., Jacob, D., Modi, A., Yoboué, V., Sigha-Nkamdjou, L., and Galy-Lacaux, C. Satellite mapping of rain-induced nitric oxide emissions from soils. *J. Geophys. Res.*, 2004. **109**: 1310.
- [16] Boersma, K., Eskes, H., Meijer, E., and Kelder, H. Estimates of lightning NO<sub>x</sub> production from GOME satellite observations. *Atmospheric Chemistry and Physics Discussions*, 2005. **5**(3): 3047-104.
- [17] De Smedt, I. and Kelder, H. Detection of the trend and seasonal variation in tropospheric NO<sub>2</sub> over China. *Journal of Geophysical Research*, 2006. **111**: D12317.
- [18] Uno, I., He, Y., Ohara, T., Yamaji, K., Kurokawa, J.I., Katayama, M., Wang, Z., Noguchi, K., Hayashida, S., and Richter, A. Systematic analysis of interannual and seasonal variations of model-simulated tropospheric NO<sub>2</sub> in Asia and comparison with GOME-satellite data. *Atmospheric Chemistry & Physics*, 2007. **7**: 1671-81.
- [19] Han, K., Song, C., Ahn, H., Park, R., Woo, J., Lee, C., Richter, A., Burrows, J., Kim, J., and Hong, J. Investigation of NO<sub>x</sub> emissions and NO<sub>x</sub>-related chemistry in East Asia using CMAQ-predicted and GOME-derived NO<sub>2</sub> columns. *Atmos. Chem. Phys.*, 2009. **9**(3): 1017-36.
- [20] Reay, D.S., Dentener, F., Smith, P., Grace, J., and Feely, R.A. Global nitrogen deposition and carbon sinks. *Nature Geoscience*, 2008. **1**(7): 430-7.
- [21] Wesely, M. and Hicks, B. A review of the current status of knowledge on dry deposition. *Atmospheric Environment*, 2000. **34**(12-14): 2261-82.
- [22] Smith, R., Fowler, D., Sutton, M., Flechard, C., and Coyle, M. Regional estimation of pollutant gas dry deposition in the UK: model description, sensitivity analyses and outputs. *Atmospheric Environment*, 2000. **34**(22): 3757-77.
- [23] Brook, J.R., Zhang, L., Di-Giovanni, F., and Padro, J. Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America.: Part I: model development. *Atmospheric Environment*, 1999. **33**(30): 5037-51.
- [24] Zhang, Y., Wang, T.J., Hu, Z.Y., and Xu, C.K. Temporal variety and spatial distribution of dry deposition velocities of typical air pollutants over different landuse types. *Clim. Environ. Res.*, 2004. **9**(4): 591-604. (in Chinese)
- [25] Deng, J.J., Wang, T.J., Li, S., Xie, M., and Fan, J.L. Study on atmospheric nitrogen oxidant and deposition flux in suburban of Nanjing. *Scientia meteorologica sinica*, 2009. **29**(1): 25-30. (in Chinese)
- [26] Shen, J., Tang, A., Liu, X., Fangmeier, A., Goulding, K., and Zhang, F. High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain. *Environmental Pollution*, 2009. **157**(11): 3106-13.
- [27] Chen, N., Hong, H., Xiao, J., Zhang, L., and Wang, J. Dry deposition of atmospheric nitrogen to Jiulong River watershed in southeast China. *Acta Ecologica Sinica*, 2006. **26**(8): 2602-7. (in Chinese)
- [28] Sun, B.H., Hu, Z.Y., and Lv, J.L. Dynamic changes of wet nitrogen deposition in a typical hilly agricultural area in Yingtan, Jiangxi. *Journal of Northwest Sci-Tech University of Agriculture and Forestry* 2006. **34**(10): 118-22. (in Chinese)
- [29] Li, S.Q. and Li, S.X. Nitrogen Added to Ecosystems by Wet Deposition in Guanzhong Area in Shaanxi. *Agro-environmental Protection*, 1999. **18**(3): 97-101. (in Chinese)
- [30] Wang, Z.H., Zhang, Y., Liu, X.J., Tong, Y.A., Qiao, L., and Lei, X.Y. Dry and wet nitrogen deposition in agricultural soils in the Loess area. *Acta Ecologica Sinica*, 2008. **28**(7): 3295-301. (in Chinese)
- [31] Xiang, R.J., Chai, L.Y., Zhang, G., Zhang, X.L., and Zeng, M. Input-output dynamics of nitrogen and sulfur in caijiatang forested catchment in Hunan Province. *Acta Scientiae Circumstantiae*, 2006. **26**(8): 1372-8. (in Chinese)