Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

Three Northern Regions Shelter Forest contributed to long-term increasing trend of biogenic isoprene emissions in Northern China

Xiaodong Zhang[1], Tao Huang[1*], Leiming Zhang[2], Yanjie Shen[1], Yuan Zhao[1], Hong Gao[1], Xiaoxuan Mao[1], Chenhui Jia[1], Jianmin Ma[1,3]*

[1]Key Laboratory for Environmental Pollution Prediction and Control, Gansu Province College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, P. R. China
[2]Air Quality Research Division, Environment Canada, Toronto, Ontario, M3H 5T4, Canada
[3]CAS Center for Excellence in Tibetan Plateau Earth Sciences, Beijing 100101, China

Correspondence to: Jianmin Ma, Tao Huang (jianminma@lzu.edu.cn； huangt@lzu.edu.cn)

Abstract. To assess the long-term trends of isoprene emissions in Northern China and the impact of the Three Northern Regions Shelter Forest (TNRSF) on these trends, a database of historical biogenic isoprene emissions from 1982 to 2010 was developed for this region using a biogenic emission model for gases and aerosols. The total amount of the biogenic isoprene emissions during the three decades was 4.4 Tg in Northern China and 1.6 Tg in the TNRSF, with annual emissions ranged from 132,000 to 176,000 ton yr^{-1} and from 45,000 to 70,000 ton yr^{-1}, respectively, in the two regions. Isoprene emission fluxes have increased substantially in many places of the TNRSF over the last three decades due to the growing trees and vegetation coverage, especially in the Central-North China region where the highest emission incline reached to 58% from 1982 to 2010. Biogenic isoprene emissions produced from anthropogenic forests tended to surpass those produced from stead-state natural forests, such as boreal forests in Northeastern China. The estimated isoprene emissions suggest that the TNRSF has altered the

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

long-term emission trend in North China from a decreasing trend during 1982 to 2010 (slope=-0.533, R^2=0.05) to an increasing trend for the same period of time (slope=0.347, R^2=0014), providing strong evidence for the change in the emissions of biogenic volatile organic compounds (BVOCs) induced by the human activities on decadal or longer time scales.

Key words: Volatile organic compounds, human activities, biogenic emissions, ozone formation, statistical trend

1 Introduction

While trees and plants can efficiently remove pollutants from the atmosphere (Nowak et al., 2006，2014; Myles et al., 2012; Camporn, 2013; Fenn et al., 2013; Adon et al., 2013; Zhang et al., 2015), they also emit harmful gases into the air. It has been widely acknowledged that terrestrial ecosystems release large quantities of reactive biogenic volatile organic compounds (BVOCs) into the atmosphere as a significant product of biosynthetic activities of trees and plants (Purves et al., 2004; Zemankova and Brechler, 2010). BVOCs play important roles in tropospheric chemistry, carbon budget, and global climate change (Purves et al., 2004; Nichol and Wong, 2011; Aydin et al., 2014). For example, BVOCs are precursors of surface ozone formation in the presence of nitrogen oxide (NO_x) (Penuelas et al., 2009; Penuelas and Staudt, 2010). It has been shown that VOCs emissions from biogenic sources have far exceeded those from anthropogenic emissions (Guenther et al., 1994, 1995; Aydin et al., 2014).

Among the three dominant VOCs (isoprene, terpenes, oxygenated compounds) contributing to

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

BVOCs emission fluxes, isoprene accounts for 70% of the total BVOCs emissions globally (Guenther et al., 2006; Helmig et al., 2013; Aydin et al., 2014) and about 50% in China (Song et al., 2012, Li et al., 2013). In particular, terrestrial plant foliage is thought to be the major source of atmospheric isoprene which releases over 90% of isoprene from global forests (Lamb et al., 1987; Guenther et al., 2006). Extensive investigations have been conducted over the past several decades to assess BVOCs emissions and their potential influences on tropospheric chemistry and carbon cycle (Lamb et al., 1987; Ceron et al., 2006; Muller et al., 2008; Chang et al., 2009; Pacifico et al., 2009; Zemankova and Brechler, 2010; Guo et al., 2013; Calfapietra et al., 2013). Efforts have been also made to measure and simulate BVOCs emissions in China (Wei et al., 2007; Chen et al., 2009; Song et al., 2012; Li et al., 2013). A recent study by Song et al. (2012) revealed that the annual BVOCs emission in Eastern China was 11.3 $\times 10^6$ t, of which 44.9% was isoprene, followed by monoterpene at 31.5%, and other VOCs at 23.6%. The study also showed high isoprene emissions in boreal forests in Northeastern China, on Qinling – Ta-Pa Mountains in central China, and in Southern China. Li et al. (2013) estimated the 2003 China's total BVOCs emission as 42.5Tg, of which 55% was from isoprene emission.

BVOCs emissions are often thought to be static on decadal or longer time scales because forest coverage from regional to global scales is assumed to be at steady state (Sanderson et al., 2003; Purves et al., 2004). However, there are concerns for the potential impacts of climate change and changes in underlying vegetation coverage on isoprene emissions because leaf level emission intensity depends on

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

biological and meteorological conditions (Turner et al., 1991; Constable et al., 1999; Ashworth et al., 2010; Arneth et al., 2008, 2011). Several modeling studies were conducted to assess the interactions between biogenic isoprene emissions and climate change as well as the human activities (Constable et al., 1999; Sanderson et al., 2003). Using the USDA (the United States Department of Agriculture) Forest Service Inventory Analysis (FIA), Purves et al (2004) estimated decadal changes in BVOCs emissions in the Eastern US between the 1980s and 1990s caused by changes in the extent, structure, and species composition of forests. They attributed these changes to human-induced de-forestation and reforestation. Arneth et al. (2008, 2011) compared the responses of the simulated BVOCs emissions derived using different models to climate and vegetation changes. They found that increasing forest area could add several tens percent to future isoprene emissions. Climate change could also exert influences on isoprene emission via the changes in temperature and CO_2. The latter can benefit forest productivity and leaf growth via fertilization effect. Steiner et al (2002) simulated the effect of human induced land use changes due to urbanization and agriculture on BVOCs emissions. Their results revealed that the increasing anthropogenic emissions of VOCs subject to urbanization overall enhanced total VOCs emissions. Most of the existing studies were carried out using climate models subject to projected climate and land cover change scenarios.

The Three Northern Regions Shelter Forest (TNRSF) program in China, also known as 'the Great Green Wall', began in 1978 and will terminate in 2050 (**Fig. 1**). The program aims to increase China's

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

forest coverage from 5% in the 1970s to 15% by 2050. By the end of the fourth phase in 2010 of this largest afforestation program in the human history, the vegetation coverage over the TNRSF has already reached 12.4% (Wang et al., 2011; Central Government of China, 2012). The program has achieved great successes in mitigating local ecological environment and climate, despite the debates on the effectiveness of the TNRSF in improving the ecological environments in Northern China and negative influences of the program on groundwater storage in arid and semi-arid regions (Pang, 1992; Cheng and Gu, 1992; Parungo et al., 1994; Hu et al., 2001; Zhong et al., 2001; Ding et al., 2005; Liu et al., 2008; Yan et al., 2011; Zheng and Zhu, 2013; Fang et al., 2001; Tan et al., 2007; Zhang et al., 2013). Recently, the TNRSF impact on air quality was also investigated (Zhang et al., 2015), which showed that the increased vegetation coverage in the TNRSF has increased its efficiency in removing air contaminants from the atmosphere as supported by the modeled increased dry deposition velocities and fluxes of sulfur dioxide (SO_2) and NO_x in many places of the region during the past three decades.

Given its unique status in large-scale artificial afforestation in the human history, the TNRSF might provide significant insights into understanding of human induced biogenic VOCs emissions on a long-term scale. In the present study, a framework combining satellite remote sensing data, a biogenic emission model, and uncertainty analysis was first developed to estimate BVOCs emissions in Northern China. Seasonal and annual biogenic isoprene emission inventories were then developed from 1982 to 2010. Finally, the potential influences of the development and expansion of the TNRSF on the long-

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

term trends of the biogenic isoprene emissions were investigated to discern evidence of decadal or longer-term changes in BVOCs emissions from large-scale forest restorations induced by the human activities. The newly generated historical isoprene emissions inventories over Northern China will also be useful for assessing past, current， and future air quality and climate issues.

2 Methodology

2.1 BVOCs emission model

The MEGAN2.1 (Model of Emissions of Gases and Aerosols from Nature version 2.1) (Guenther et al., 2012) which is an updated version of MEGAN2.0 (Guenther et al., 2006) and MEGAN2.02 (Sakulyanontvittaya et al., 2008), was used here to estimate BVOCs emissions in Northern China. This new version includes additional compounds, emission types, and various controlling processes. For BVOCs emissions, MEGAN2.1 is primarily driven by biological and meteorological factors, including vegetation type with which the emission factors of BVOCs are assigned, air and leaf temperatures, light, leaf age and leaf area index (LAI), and soil moisture (Guenther et al., 2006; 2012; Pfister et al., 2008; Arneth et al., 2011). MEGAN2.1 was set up over Northern China with a grid spacing of $0.25^{o} \times 0.25^{o}$ latitude/longitude to produce gridded daily and monthly emission fluxes. Twenty-two land types were used, including an additional crop type which was not specified in MEGAN2.1. These land types in each model grid were identified using the surface roughness lengths estimated from satellite remote sensing data (Zhang et al., 2015). Guenther et al. (2006) reported the differences in MEGAN2.1

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

modeled annual isoprene emissions as a result of changing plant functional type (PFT) (24 %), LAI (29 %), and meteorology (15 %) input data. This suggests that LAI is a crucial variable in the model.

To evaluate the MEGAN2.1 estimated isoprene biogenic emission fluxes, a field campaign was conducted to measure total VOC (TVOC) concentrations at several sites within and outside the TNRSF (Section 2.4). The monitored TVOC concentrations were then converted to TVOC emission fluxes using a box model, developed by Guenther et al (1996) which links biogenic VOC emission and photochemical reaction with OH radicals and ozone. The model was derived from a simplified mixed-layer scalar conservation equation, given by

$$E = z_i L c , \quad (1)$$

where E and c are the emission and concentration in the mixed-layer, z_i is the height of mixed-layer capping inversion, taken as 1000 m following Guenther et al (1996). L is the oxidation rate of VOC subject to OH radical and ozone, defined as $[k_{OH}, OH] + [k_{O3}, O_3]$, where k_{OH} and k_{O3} are reaction rate constants for OH and O_3, respectively. The rate constants and mean concentrations of OH and ozone are presented in Table S1 of Supplementary Materials. Further details are presented in Sections 2.4 and 3.4.

2.2 LAI.

LAI data with $0.25^o \times 0.25^o$ latitude/longitude resolution from 1982 to 2010 were derived from the satellite remote sensing data of the normalized difference vegetation index (NDVI) for the same period. Detailed descriptions of the procedures generating LAI data for the TNRSF region were presented in

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Zhang et al (2015).

2.3 Uncertainty analysis.

Although the BVOCs emissions model was well established for different vegetation types, there were uncertainties in the estimate of BVOCs emission fluxes. Some of these uncertainties are generated from inaccurate emission factors, empirical algorithms, and input data used in the model (Hanna et al., 2005; Guenther et al., 2012). A Monte Carlo technique was used to evaluate uncertainties of modeled isoprene emissions by MEGAN2.1 (Hanna et al., 2005; Guenther et al., 2006, 2012; Situ et al., 2014). In the uncertainty analysis, each input parameter in MEGAN2.1 for isoprene emissions, including LAI, leaf temperature (a function of air temperature), emission factors, several empirical coefficients related to past leaf temperatures, and solar zenith, was treated as a random variable with a normal distribution. The MEGAN2.1 model for BVOCs emissions was run repeatedly 100,000 times at the 95% confidence level based on the coefficients of variation (*CV*, %) of these input parameters. The Monte Carlo simulations showed that the isoprene emissions reached approximately a normal distribution, ranging from 0.05 to 4.38 micro-mole m^{-2} h^{-1} with the variation from 97.1%-157.5%. Details for the uncertainty analysis are presented in Supplementary Materials (Table S2, **Fig. S1**).

The uncertainty analysis using the Monte Carlo technique was also conducted for the box model (Eq. 1). Analogous to the uncertainty analysis for the MEGAN2.1, this box model was also run repeatedly 100,000 times at the 95% confidence level based on the coefficients of variation (*CV*, %) for Z_i, the

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

oxidation rate of isoprene (*L*) by OH and O_3, and the concentrations of OH and O_3. The *CV* for these four parameters were taken from Guenther et al (1996) (Table S3). The results from Monte Carlo simulations showed that the converted isoprene emissions from the measured concentrations using Eq. 1. reached approximately a normal distribution, ranging from 1.2 to 152.9 μg m^{-2} h^{-1} with the variation from 98.3%-116.7% (**Fig. S2**).

2.4 Ambient VOCs concentrations within and outside the TNRSF.

As part of efforts to understand potential uncertainties in the estimation of isoprene emissions from the TNSRF, a field campaign was conducted to measure gas-phase air pollutants, particular matter, and persistent organic pollutants in air, foliage, and soil within and outside the TNRSF in the summer of 2015. The first phase of this field study focused on the Central-North China region of the TNRSF because this region has been paid the highest attention by the TNRSF program due to its proximity to Beijing and Tianjin, the two megacities in Northern China. Eight monitoring sites in this region were selected, with four of these inside and another four outside the forest (**Fig. S3**). All these sites are situated in the northwest and northeast of Beijing where the TNRSF program was operated most successfully. Total VOCs (TVOCs) was measured simultaneously using the GreyWolf TG-502/TG-503 sensors (GreyWolf Sensing Solutions) at each paired sites within and outside the forest but on different days at the selected 4 paired sites. The GreyWolf TG-502/TG-503 instrument uses SEN-B-VOC-PPB PID (photoionization detector) sensor (10.6eV lamp, range: 5 to 20,000 ppb) which responds to the vast

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

majority of VOCs with the response time < 1 min. The environmental conditions for sensor operating range from 0 to 90% RH (relative humidity) and from -15^{o} to 60^{o} C. The GreyWolf TVOC sensor adopts two points calibration approach with low point of 0 ppb and high point at 7500~9000 ppb, respectively. Standard calibration gas is isobutylene. More details of the GreyWolf TG-502/TG-503 TVOC sensor can be found at the GreyWolf website (https://www.wolfsense.com/directsense-tvoc-volatile-organic-compound-meter.html). Typical tree species planted in this region were selected in the field monitoring program. Among them, poplar (*populus*), a broadleaf tree species, dominated the two forest sites in Langfang and northern Zhangbei County. Poplar has been the major tree species planted across the Central-North China region of the TNRSF over the last thirty years. From the late half of the 2000s, due to the death of many poplars in this region, Scots pine (*Pinus sylvestris var*), which is a coniferous tree species, has been recommended and planted in this region. Scots pine is the major tree species at northern Zhangbei County and Xinglong forest sites. As for the comparative monitoring sites outside the forests, the Langfang site is 500 m away from the forest and located in a corn field, the Zhangbei north and south sites are about 1 km and 600 m, respectively, away from the forest and both are located in a grassland, and the Xinglong site is about 400 m away from the forest and located in a corn field. The sampling was operated in early morning from 6:15 – 8:15am, and early afternoon from 2:15 – 4:15 pm with sampling frequency of 1 min. The sampling date was on August 9th, 2015 at the Langfang sites, 10th at the Xinglong sites, 12th at the Zhangbei north sites, and 13th at the Zhangbei

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

south sites. It should be noted that this field measurement program was not aimed to determine the spatial and temporal distributions of isoprene emissions, but instead to examine and verify the release of this reactive biogenic VOC species from the TNRSF.

3 Results

3.1 Isoprene emission inventory in TNRSF

Figure 2 shows the TNRSF domain-averaged annual biogenic isoprene emissions (micro-moles m^{-2} h^{-1}) aggregated from monthly values. In general, emissions in Northern China were slightly lower than those from most regions of the United States (US) and considerably lower than those in the Southeast US, which were also computed using the MEGAN2.1 (Guenther et al., 2012). The magnitudes of isoprene emissions estimated in the present study agree with the China's BVOCs emission inventory established previously, particularly in the natural forests (Song et al., 2012; Li et al., 2013), as elaborated below. A long-term increasing trend up to 2007, although with fluctuations in certain years, was observed (**Fig . 2)** The Central-North region of the TNRSF exhibited the strongest increasing trend with the highest emissions increased by 58% over the 30 years period.

Figure S4 illustrates the MEGAN2.1 simulated isoprene emission fluxes across the TNRSF in 1982, the early stage of the TNRSF construction, and 2010, the end of the fourth phase (2001-2010) of the program, respectively. Compared with the emission fluxes in 1982, higher isoprene emissions in the Central-North China region and lower emission fluxes in the Northeast region and Eastern Inner

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

Mongolia region of the TNSRF were identified in 2010 (**Fig. 1**). The differences in the biogenic isoprene emissions between 1982 and 2010 were calculated as $E_{dif} = E_{2010} - E_{1982}$. The spatial pattern of E_{dif} (**Fig. 3**) is consistent with the emission fluxes in 1982 and 2010, as shown in **Fig. S4a** and **b**. Positive differences of E_{dif} were observed in the mountainous areas of west Xinjiang, Shaanxi, eastern Gansu provinces, and the Central-North China region (**Fig. 3**), suggesting increasing isoprene emissions associated with the expansion of the TNRSF in these regions.

3.2 Isoprene emission trend in the TNRSF and Northern China

Decadal or longer time trends in isoprene emissions over the TNRSF and Northern China can provide some insights into the impact of the large-scale artificial afforestation on BVOCs emissions - the knowledge that is needed to address air quality, climate, and ecosystem issues. **Figure 4** illustrates modeled isoprene emission fluxes (micro-moles m^{-2} hr^{-1}) in 2000 (**Fig. 4a**), after 20 years construction of the TNRSF, and the slopes (trends) of the linear regression relationship between isoprene emission and the time sequence of 1982 through 2010 (**Fig. 4b**) over Northern China, respectively. High isoprene emissions can be found in the regions extending from northeast Qinghai province to Ta-Pa Mountains, the boreal forest in Northeast China, Central-North China, and Tianshan Mountain and Pamirs in Xinjiang province. The spatial pattern of the estimated emissions in Northeastern China is similar to Song et al.'s results from 2008 to 2010 (Song et al., 2012). They showed high isoprene emissions from the boreal forest in Northeastern China and Qinling – Ta Pa Mountains.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

The total annual isoprene emission, summed from annual emissions of applicable model grids, ranged from 45,000 to 70,000 ton yr^{-1} during 1982-2010 for the whole TNRSF (the area encircled by the blue solid line in **Fig. 4**), and from 132,000 to 176,000 ton yr^{-1} for the whole Northern China (**Fig. 4**). This is equivalent to a total emission of 1.6 Tg and 4.4 Tg, respectively, for the two regions during the past three decades from1982 to 2010. It is worth noting that, although the TNRSF accounts for 59% of the total area of the Northern China and 42% of the mainland China (Zhang, et al., 2015), it covers almost all arid and semi-arid regions in Northern China (**Fig. 1**). Vegetation coverage in these regions was still sparse after 30 years construction of the TNRSF, and shrubs, instead of trees, are major plant types in the Western China region of the TNRSF. The isoprene emissions are considerably low in these regions, as shown by **Figs. 4** and **5**. In addition, as shown by **Fig. 4**, the region of Northern China defined in this study extends virtually to 30°N. Although the isoprene emissions in the TNRSF only accounted for 37% of the total emissions in Northern China, the relatively strong increasing trend (**Fig. 2**) in the TNRSF has reversed the negative trend (slope=-0.534, R^2=0.05) of the total annual isoprene emissions to the positive trend (slope=0.347, R^2=0.014) from 1982 to 2010 in Northern China, as shown in **Fig. S5**.

To highlight the contribution of the TNRSF to the increasing isoprene emissions, the trend of the gridded isoprene emissions over the TNRSF was further investigated. As expected, the estimated monthly emission fluxes showed dramatic seasonal variations with the largest values in summer and the lowest values in winter, consistent with the seasonal changes in LAI over the TNRSF (figure not shown).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

Figure 5 presents the gridded trends of the annual biogenic isoprene emissions (Eq. 1) across the TNRSF from 1982 to 2010. Positive trends of the emissions were observed in the mountainous and surrounding areas of the Junggar Basins (north Xinjiang), eastern Qinghai province in the Northwest China region of the TNRSF, the Central-North China region, and western Liaoning province in the Northeast China region of the TNRSF. These provinces and locations are marked in **Fig. 1**. In particular, the largest positive trends can be observed in the areas north of the two megacities - Beijing and Tianjin. These two megacities have been targeted as key cities to be protected by the TNSRF from sandstorms from the north. Extensive tree planting activities have been promoted to the north of these two megacities (Central Government of China, 2012).

Figure 6 shows the isoprene emissions from 1982 to 2010 averaged over the Northwest China, the Central-North China, and the Northeast China regions of the TNRSF, respectively. It can be identified again that the domain averaged isoprene emissions in the Central-North China region of the TNRSF exhibited a clear increasing trend with the slope of 0.0004 ($R = 0.591$). Whereas, there were almost no statistically significant trends of isoprene emissions in the other two regions. The increase of isoprene emissions over the Central-North China region can be attributed to continuous expansion of forest coverage. Compared with the Central-North region of the TNRSF, the forests in the Northeast China region are mixed with natural forests. These natural forests already reached the steady state before the 1980s, so they would not contribute to the increasing trend of biogenic isoprene emissions. The

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Northwest China region of the TNRSF is arid and semi-arid area with low precipitation. Shrubs, instead of trees, were planted in many places of this part of the TNRSF regions, resulting in low biogenic isoprene emissions.

Trends of isoprene emissions were also compared between those within and outside the TNRSF and in natural forests. Three small areas were selected for the comparison, each consisting of 4 grid points, in the Central-North China region of the TNSRF (marked by the red circle in the inner map of **Fig. 1**), a farmland outside the TNSRF (blue circle), and in the boreal forest of Northeast China (the Greater Khingan Mountains, marked by yellow circle in **Fig. 1**), respectively. Trends in annually averaged isoprene emissions from these three small areas are shown in **Fig. 7.** Significant increasing trend is only seen in the area within the TNRSF. The levels of isoprene emissions in the other two small areas were almost uniformly distributed for the last three decades.

3.3 Comparison with the previous emission data

No direct measurements of BVOCs emission data across the TNRSF have been ever reported before. Li et al. (2013) established an emission inventory of BVOCs (isoprene, monoterpene, sequiterpene and other VOCs) over China using MEGAN2.1 model. Their results showed that annually averaged isoprene emission fluxes ranged from 0 to 22 μg m^{-2} h^{-1} in 2003 in northern Xinjiang, Qinghai, Gansu, and Shaanxi provinces in the Northwest China region of the TNRSF, and western Inner Mongolia. The average isoprene emission fluxes estimated in the present study for the same regions and the same year

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

ranged from 0.01 to 18.2 μg m^{-2} h^{-1}, agreeing reasonably well with Li et al's data. Likewise, Li et al's inventory (2013) also showed high isoprene emission flux in the Central-North China region, including the north of Shanxi and Hebei provinces, Beijing, and the natural (boreal) forest area in Northeast China, ranging from 22 to 880 μg m^{-2} h^{-1}, which were comparable with our results of 20.4 to 122.4 μg m^{-2} h^{-1} for the same region. Song et al. (2012) simulated BVOCs emissions in Eastern China from 2008 to 2010. A portion of their model domain in Eastern China superimposed with the Central-North China and the Northeast China region of the TNRSF defined in our study. The annually averaged isoprene emission fluxes from 2008 to 2010 from Song et al's model simulations ranged from 10 to 100 μg m^{-2} h^{-1} in Inner Mongolia region, and 100-1000 g m^{-2} h^{-1} in the north of Shanxi and Hebei provinces, Beijing, and Tianjin, which were higher than our results of 0 to 32.6 μg m^{-2} h^{-1} and 20.4 to 122.4 μg m^{-2} h^{-1}, respectively, in these two regions. Song et al. used MEGAN2.04 model with different emission factors adjusted based on China's principal vegetation species (Song et al., 2012). These likely resulted in different biogenic isoprene emissions.

3.4 Emissions converted from ambient concentrations

Figure 8 illustrates measured afternoon (local time 2-4 pm) TVOC levels in the atmosphere at the 4 paired monitoring sites in the Central-North China region of the TNRSF. Detailed descriptions of these sites and sampling procedures are presented in the Methodology section, **Fig. S3**, and Table S4, respectively. Higher TVOC air concentrations were observed at all forest sites than those sites outside

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

the forests. In particular, the TVOC levels at the southern and northern Zhangbei sites within the TNRSF were 3 to 4 times higher than that measured in the grassland sites outside the TNRSF, suggesting that the forests made significant contributions to the sampled TVOC levels. Using the box model (Eq. 1), emission fluxes were converted from the measured TVOC concentrations at the four forest sites. Taking the TVOC levels as the box model input (Eq. 1), and assuming the isoprene emission to be 50% of the TVOC (Song et al., 2012; Li et al., 2013), we obtained the emission fluxes of 32.3, 44.1, 52.9, and 44.1 μg m^{-2} h^{-1} at the Langfang, Xinglong, Zhangbei (North), and Zhangbei (South) sites, respectively. These values agree nicely with the MEGAN2.1 modeled emission fluxes of 36, 41.5, 49, and 47.6 μg m^{-2} h^{-1} at the same sites. It is noticed that the box model (Eq. 1) does not take into account the effect of wind speed on the emissions. An effort was also made to use a simplified Gaussian model for an area source (Arya, 1999) to convert the measured TVOC concentration to emissions. Under approximately calm wind conditions (<0.5 m s^{-1}) at the sampling sites and the same assumption of isoprene emission as the half of the TVOC emission, the converted fluxes using this model are factors of 2-3 higher than the MEGAN2.1 estimated fluxes. Results are presented in Supplementary Materials. Nevertheless, it should be noted that the TVOCs concentrations were measured at a single site within the selected forests in this field campaign which represent typical tree species in the Central-North China region of the TNRSF. Whereas, the underlying surface of a model grid square (27.83 ×

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

27.83 km^2) is not fully covered by trees but consists of other surface types, such as croplands, bare soils, water surfaces, and towns where considerably lower VOCs were emitted.

It is worthwhile to note that anthropogenic VOC might contribute to the ambient concentrations of TVOCs measured at these selected sampling sites. In addition, the emissions and concentration ratios are not identical for all VOCs due to their different reactivity. A VOC can be emitted in relatively low amounts but make a large contribution to the TVOC if it is considerably less reactive than isoprene. Wang et al (2014) collected ambient concentrations of VOCs at 27 sites across Beijing from July 2009 to January 2012, including urban, suburban, and rural sites. To identify potential sources of isoprene, they estimated the ratio of isoprene to 1,3-butadiene. While the reactivity for these two VOC compounds was similar, their emission sources differ significantly. Vehicular exhaust was found to be the dominant source of 1,3-butadiene in Beijing (Wang et al, 2010) whereas isoprene was largely related to biogenic emissions. Their results showed that the wintertime isoprene/1,3-butadiene was 0.30–0.34 ppbv ppbv^{-1}, characterizing the emission from vehicular exhaust in Beijing (Wang et al. 2010). That is, vehicular exhaust was the dominant source of atmospheric isoprene during the wintertime. In the warm period (May - September), their measured ratios of isoprene/1,3-butadiene ranged from 16 to 43 ppbv ppbv^{-1}, two order of magnitude higher than that in the wintertime, indicating that biogenic emissions dominated the summertime isoprene. Considering that our sampling sites (especially the Langfang and Xinglong sites) are close to Beijing and covered by similar tree species to

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

those planted in the suburban and rural areas of Beijing, the results from Wang et al (2014) might be applicable in our cases because our measurements were also taken in the summertime (August). In particular, our sampling sites are all located in rural areas, far away from traffic, industrial, and residential areas, indicating weak influence of the anthropogenic emissions on the measured TVOC level, half of which has been hypothesized to be isoprene in the present study.

4 Discussions

Overall the estimated biogenic isoprene emission fluxes across the TNRSF illustrated an increasing trend from the 1980s onward (**Fig. 2**). The incline trend was most significant in the Central-North region of the TNRSF where most intensive afforestation has been carried out in Northern China (Zhang and Zhu, 2013), in order to protect the national capital (Beijing) region from dust and sandstorms. The increasing biogenic isoprene emissions can be attributed to the development of the TNRSF. The forest expansion in the TNRSF can be identified by the satellite derived LAI, as seen from **Fig. S6a** and **b**. The linear increasing trend of the LAI across the TNRSF is consistent with the modeled isoprene emission fluxes. The maximum increase (58%) of the isoprene emissions from 1982 to 2010 in the Central-North region of the TNRSF seems to agree well with the model prediction by Arneths et al. (2008, 2011) based on projected land use changes. Their modeling results suggested that increasing forest area could lead to several tens percent change in biogenic isoprene emissions.

As shown above, the significant incline trend of the annual total isoprene emissions in the TNRSF

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

has affected the long-term trend of the emission in Northern China. This implies that the increasing emission trend across the TNRSF could alter the large-scale BVOCs emissions not only in the TNRSF, but also in Northern China. Considering that the TNRSF occupies 59% of the Northern China and 42% of the whole mainland China. Future impacts of the TNRSF on BVOCs emissions may be even stronger with continuous increase of vegetation coverage till the end of the program in 2050.

While BVOCs emissions vary on short time scales, the global BVOCs emissions are often assumed to change little on long-term (e.g., decadal) scale (Purves et al., 2004; Sindelarova et al., 2014) considering the steady state of global forests. Since BVOCs can partition onto or form particles in the atmosphere after oxidation, their emissions could affect aerosol formation, cloud condensation nuclei, and climate (Makkonen et al., 2012, Penuelas and Staudt, 2010). Temporal uniformly distributed BVOCs emissions on decadal or longer time scales might bring uncertainties in the prediction of impacts of climate change on current and emerging environmental issues from regional to global scales. The evidence identified in this study suggested that the human-induced BVOCs emissions via large-scale afforestation exert strong influence on long-term BVOCs emission and should be taken into consideration in projected climate change scenarios, at least on a regional scale, such as in Northern China. As a precursor of secondary organic aerosols and tropospheric ozone, the significant incline of biogenic isoprene emissions also carry significant implications to the air quality in Northern China. Heavy air pollutions in Beijing-Tianjin-Hebei (**Fig. 1**) have been widely known nationally and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

internationally, characterized by year round high levels of fine particular matter ($PM_{2.5}$) and high surface ozone concentrations in summertime. Chinese government has decided to extend the TNRSF as one of the primary measures to reduce and remove air pollutants from Beijing-Tianjin-Hebei area (Chinese Environmental Protection Agency, 2013). As shown in **Figs. 5** and **6**, the TNRSF in the Central-North region covering a large part of Beijing-Tianjin-Hebei area has already gained the most rapid development as compared to the other two northern regions of the TNRSF (**Fig. 1**), leading to marked incline of isoprene emissions. However, it is yet clear if and how the extension of the TNRSF could otherwise improve local air quality. Our previous study suggested that the TNRSF played a moderate role in removing SO_2 and NO_x (Zhang et al., 2015). Under the rapidly increasing NO_x emissions in the past decade due to rapidly increasing number of private vehicles in Beijing-Tianjin-Hebei area, it is necessary to assess the interactions between BVOCs emission from the TNRSF and local air quality in this region.

In addition to its long-term trend, isoprene emission also exhibited short-term interannual fluctuations, as also observed from **Fig. 2**. Factors causing the fluctuations or interannual changes in the emission fluxes depend on meteorological and biological processes. Afforestation and deforestation often took place during the course of the TNRSF construction due to favorable or unfavorable weather and climate conditions for tree growth. For example, 10% - 50% of trees planted since the late 1970s in the Central-North region of the TNRSF were reported dead in 2007 (Zhang et al., 2013; Tan and Li, 2015), causing

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

considerable decline of the forest coverage and isoprene emissions in this region, as shown in **Fig. 2**. The lower isoprene emission in 2010 in the Northeast China region and eastern Inner Mongolia region of the TNRSF as compared with that in 1982 was inconsistent with the increasing trend of the emission. The forest coverage in Northeast China region did not show considerable change between1982 and 2010. On the other hand, lower annual temperatures (e.g., by around 1 ^{o}C) in 2010 than in 1982 were evident over the Northeast China region of the TNRSF (**Fig. S7**), which likely caused lower biogenic emissions in 2010 (Purvis et al., 2004; Arneth et al., 2008, 2011) assuming that the mixed forests in this region already reached a steady state

The comparison between the isoprene emission trends and the emissions in 2000 in Northern China also carries a significant implication for the human induced BVOCs emissions. As shown from **Fig. 4b**, the trend of isoprene emissions from 1982 to 2010 over Northern China showed a rather different spatial pattern from its emissions in 2000 (**Fig. 4a**). No significant trends were observed in the boreal forest in Northeastern China，though a larger amount of isoprene was emitted from the forest in this region in 2000 (**Fig. 4b**). This implies that this natural forest has reached a steady state from which the biogenic isoprene emissions were not altered on the decadal basis.

Although Qinghai – Ta-Pa Mountains exhibited the highest emissions in 2000 (**Fig. 4a**), negative trends of the biogenic isoprene emissions dominated this area, indicating the declining of the emissions over the period of 1982 through 2010. This is consistent with the decreasing vegetation coverage during

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

this period in this region, as shown by the negative trends of the leaf area index (LAI) in Northern China (**Fig. S6**). On the other hand, most positive trends can be identified in the Central-North region and along the foots of Tianshan Mountain in west China (see the areas encircled by the solid blue line in **Fig. 4)**. This manifests that the TNRSF exerts strong influences on biogenic VOCs emissions, particularly on their decadal variation, though the magnitude of emissions might not be higher than that from natural forests in Northern China (**Fig. 4a**). Results further imply that the TNRSF is very likely the major source contributing to the increasing biogenic isoprene emissions over the past 30 years and many years to come in Northern China. Climate change has been thought also to play an important role in the changes in biogenic emission of isoprene on decadal or longer time scale because it can alter temperature and vegetation coverage (Turner et al., 1991; Sanderson et al., 2003). It is unknown if and to what extent the increasing vegetation coverage and temperature over the TNRSF were induced by climate change. Evidence shows that the human induced afforestation contributed mostly to the increased vegetation coverage over the TNRSF and Northern China (Wang et al., 2011), as shown by **Fig. S6a**, and hence to the increased biogenic isoprene emissions.

Among the three small areas within the TNRSF, in the farmland, and in the boreal forest of the Northeastern China (**Fig. 7**), the emission values increased by nearly 5 times from 1982 to 2010 in the area within the TNRSF with the slope of 0.0018 (r = 0.74). On the other hand, no statistically significant increasing trends of biogenic isoprene emissions were found in the farmland and the boreal

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

forest, though the higher emissions were observed in the boreal forest. More interestingly, the biogenic isoprene emissions in the selected small area of the Central-North China region tend to surpass the isoprene emissions in the boreal forest from 2004 onward. This can be partly attributed to rapidly growing forest coverage and higher temperatures in this region as compared to Northeast China. The large area of foliage trees planted in this region also played a role for relatively high and increasing isoprene emissions as compared with the boreal forests in Northeast China where coniferous trees are major tree species which release relatively lower isoprene to the atmosphere as compared to broadleaf trees in the selected area in the Central-North China region of the TNRSF (Guenther et al, 2012).

5 Conclusions

Gridded monthly and annual biogenic isoprene emissions in Northern China were modeled for the period of 1982 to 2010 and were then applied to assess the long-term trends of the biogenic isoprene emissions in the TNRSF in order to discriminate the signals of the human activities in decadal and longer-term trends of BVOCs on large spatial scales. Significant impacts of the TNRSF in Northern China on the BVOCs emissions were identified during the past three decades. Annual isoprene emissions in many places of the TNRSF region, especially in the Central-North China region, exhibited an inclining trend. The maximum increase in the isoprene emission flux (emission minus dry deposition) reached 58% between 1982 and 2010, indicating important roles of the human activities on BVOCs emissions. The comparison of isoprene emission fluxes among the Central-North China region of the

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

TNRSF, farmland, and the boreal forest in Northeast China outside the TNRSF revealed that the biogenic isoprene emissions in some areas of the Central-North China region of the TNRSF produced by man-made forests have surpassed the emissions from the natural forests. This suggests that the TNRSF was a main contributor to the decadal or longer-term changes in BVOCs in Northern China. The impact of the TNRSF on BVOCs emissions is expected to be stronger in the coming years along with continuous development of the TNRSF program till 2050. Since VOCs are major precursor of tropospheric ozone, future studies are needed to investigate how the increased BVOCs in the TNRSF contribute to ozone formation, especially in the case of concurrently increasing NO_x emissions in Northern China.

The Supplement related to this article is available online.

Acknowledgement

This work is supported by the National Natural Science Foundation of China through grants 41371478 and 41371453.

References

Adon, M., Galy-Lacaux, C., Delon, C., Solmon, F., and Tchuente, A. T. K.: Dry deposition of nitrogen compounds (NO2, HNO3, NH3), sulfur dioxide and ozone in west and central African ecosystems using the inferential method, Atmos. Chem. Phys., 13, 11351-11374, 2013.

Arneth, A., Schurgers, G., Hickler, T., and Miller, P. A.: Effects of species composition, land surface cover, CO2 concentration and climate on isoprene emissions from European forests, Plant Biol., 10, 150-162, 2008.

Arneth, A., Schurgers, G., Lathiere, J., Duhl, T. R., Beerling, D. J., Hewitt, C. N., Martin, M., and Guenther, A. B.: Global terrestrial isoprene emission models: sensitivity to variability in climate and vegetation, Atmos. Chem. Phys., 11, 8037-8052, 2011.

Arya, S.P.: A*ir Pollution Meteorology and Dispersion*. Oxford University Press, Inc.; New York, New York, 1999.

Ashworth, K., Wild, O., and Hewitt, C. N.: Sensitivity of isoprene emission estimated using MEGAN to the time resolution of input climate data, Atmos. Chem. Phys., 10, 1193-1201, 2010.

Aydin, Y. M., Yaman, B., Koca, H., Dasdemir, O., Kara, M., Altiok, H., Dumanoglu, Y., Bayram, A., Tolunary, D., Odabasi, M., and Elbir, T.: Biogenic volatile organic compound (BVOC) emissions from forested areas in Turkey: Determination of specific emission rates for thirty-one tree species, Sci. Total Environ., 490, 239-253, 2014.

Calfapietra, C., Fares, S., Manes, F., Morani, A., Sgrigna, G., and Loreto, F.: Role of biogenic volatile organic compounds (BVOC) emitted by urban trees on ozone concentration in cities: A review, Environ. Pollut., 183, 71-80, 2013.

Camporn, S. J.: Ecophysiological Responses of Plants to Air Pollution, DOI: 10.1002/9780470015902.a0003206.pub2, 2013. Available at http://onlinelibrary. wiley. com/doi/ 10.1002/9780470015902.a0003206.pub2.

Central Government of China: Forest cover area from artifcial afforestation in the Three Northern Regions Shelter Forest regions (in Chinese), 2012. Available at http://www.gov.cn/jrzg/2012-08/27/content_2211594.htm .

Chang, K. H., Yu, J. Y., Chen, T. F., and Lin, Y, P.: Estimating Taiwan biogenic VOC emission: Leaf energy balance consideration, Atmos. Environ., 43, 5092-5100, 2009.

Chen, Y., Li, D. W., Shi, Y., and He, X.: Emission rate of biogenic volatile organic compounds from urban trees in Shenyang, China, Journal of Northeast Forestry University, 37, 47-49, 2009 (in Chinese).

Cheng, D., Gu, J.: Influence of the Three Northern Regions Shelter Forest on micro-scale climate. In: Zhu, T. (Ed.), Ecological Benefit and Physical Characteristics of Atmospheric Boundary-layer of the Three Northern Regions Shelter Forest (in Chinese), Meteorological Publisher of China, Beijing, pp. 209-216, 1992.

Chinese Environmental Protection Agency (1992) Action plans for implementing air pollution control strategy. Available at http://www.zhb.gov.cn/gkml/hbb/bwj/ 201309/t20130918_260414.htm, in Chinese.

Constable, J. V. H., Guenther, A. B., Schimel, D. S., and Monson, R. K.: Modelling changes in VOC emissions in response to climate change in the continental United States, Global Change Biol., 5, 791-806, 1999.

Ding, Y., Li, Q., and Dong, W.: A numerical assessment of effect of forest coverage on regional climate in China (in Chinese), J. Meteorol. Res., 63,613-621, 2005.

Fang, J. Y., Chen, A. P., Peng, C. H., Zhao, S. Q., and Ci, L. J.: Changes in forest biomass carbon storage in China between 1949 and 1998, Science, 292, 2320-2322, 2001.

Fenn, M. E., Ross, C. S., Schilling, S. L., Baccus, W. D., Larrabee, M. A., and Lofgren, R. A.:

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

Atmospheric deposition of nitrogen and sulfur and preferential canopy consumption of nitrate in forests of the Pacific Northwest, USA, Forest Ecol. Management, 302, 240-253, 2013.

Fensholt, R., Rasmussen, K., Nielsen, T. T., and Mbow, C.: Evaluation of earth obser-vation based long term vegetation trends—intercomparing NDVI time seriestrend analysis consistency of Sahel from AVHRR GIMMS, Terra MODIS and SPOTVGT data, Remote Sens. Environ., 113, 1886-1898, 2009.

Geron, C., Guenther, A., Greenberg, J., Karl, T., and Rasmussen, R.: Biogenic volatile organic compound emissions fromdesert vegetation of the southwestern US, Atmos. Environ., 40, 1645-1660, 2006.

Guenther, A， Zimmerman, P., Klinger, L., Greenberg, J., Ennis, C., Davis, K., and ait Pollock, W.: Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements, J. Geophys. Res.-Atmos., 101(D1), 1345-1359.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global-model of natural volatile organic-compound emissions, J. Geophys. Res.-Atmos, 100, 73-92, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions ofGases andAerosols from Nature), Atmos. Chem. Phys., 6, 181-210, 2006.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, 2012.

Guo, P. P., Guo, K. J., Ren, Y., Shi, Y., Chang, J., Tani, A., and Ge, Y.: Biogenic volatile organic compound emissions in relation to plant carbon fixation in a subtropical urban-rural complex, Landscape and Urban Planning, 119, 74-84, 2013.

Hanna, S.R., and Strimaitis, D. J.: *Workbook of Test Cases for Vapor Cloud Source Emission and Dispersion Models*. Published by CCPS/AIChE, 1989, 345 East 47th St., New York, NY 10017, 103 pp.

Hanna, S. R., Russell, A. G., Wilkinson, J. G., Vukovich, J., and Hansen, D. A.: Monte Carlo estimation of uncertainties in BEIS3 emission outputs and their effects on uncertainties in chemical transport model predictions, J. Geophys. Res., 110, 372-384, 2005.

Helmig, D., Daly, R. W., Milford, J., and Guenther, A.: Seasonal trends of biogenic terpene emissions. Chemosphere, 93, 35-46, 2013.

Hu, H., Wang, H., Lu, X., and Qiu, Z.: Assessment of influence of shelter forest on climate in arid and semi-arid regions in China, J. Nanjing Forestry University (Natural science), 25, 77-82, 2001 (in Chinese).

Lamb, B., Guenther, A., Gay, D., and Westberg, H.: A national inventory of biogenic hydrocarbon emissions, Atmos. Environ., 21, 1695-1705, 1987.

Li, L. Y., Chen, Y., and Xie, S. D.: Spatio-temporal variation of biogenic volatile organic compounds emissions in China, Environ. Pollut., 182, 157-168, 2013.

Liu, Y. Q., Stanturf, J. A., and Lu, H. Q.: Modeling the potential of the northern China Forest Shelterbelt in improving hydroclimate conditions, J. Amer. Water Resources Assoc., 44, 1176-1192, 2008.

Makkonen, R., Asmi, A., Kerminen, V. M., Boy, M., Arneth, A., Guenther, A., and Kulmala, M.: BVOC-aerosol-climate interactions in the global aerosol-climate model ECHAM5.5-HAM2, Atmos. Chem. Phys., 12, 10077–10096, 2012.

Mao, D., Wang, Z., Luo, L., and Ren, C.: Integrating AVHRR and MODIS data to monitor NDVI changs and their relationships with climatic parameters in Northeast China, Inter. J. of Appl. Earth Obser. Geoinformation, 18, 528-536, 2012.

Muller, J. F., Stavrakou, T., Wallens, S., and Smedt, I. D.: Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model, Atmos. Chem. Phys., 81,329-341, 2008.

Myles, L., Heuer, M. W., Meyers, T. P., and Hoyett, Z. J: A comparison of observed and parameterized SO2 dry deposition over a grassy clearing in Duke Forest, Atmos. Environ., 49, 212-218, 2012.

Nichol, J., and Wong, M. S.: Estimation of ambient BVOC emissions using remote sensing techniques, Atmos. Environ., 45, 2937-2943, 2011.

Nowak, D. J., Crane, D. E., and Stevens, J. C.: Air pollution removal by urban trees and shrubs in the United States, Urban Forestry & Urban Greening, 4, 115-123, 2006.

Nowak, D. J., Hirabayashi, S., Bodine, A., and Greenfield, E.: Tree and forest effects on air quality and human health in the United States, Environ. Pollut., 193, 119-129, 2014.

Pacifico, F., Harrison, S. P., Jones, C. D., and Sitch, S.: Isoprene emissions and climate, Atmos. Environ., 43, 6121-6135, 2009.

Pang, Q.: Construction of the Three Northern Regions Shelter Forest in China, Forestry Publisher of China, Beijing, 1992 (in Chinese).

Parungo, F., Li, Z., Li, X., Yang, D., and Harris, J.: Gobi dust storms and the Great Green Wall, Geophys. Res. Lett., 21, 999-1002, 1994.

Penuelas, J., and Staudt, M.: BVOCs and global change, Trends Plant Sci, 15, 133-144, 2010.

Penuelas, J., Rutishauser, T., and Filella, I.: Phenology feedbacks on climate change, Science, 324, 887-888, 2009.

Pfister, G. G., Emmons, L. K., Hess, P. G., Lamarque, J. F., Orlando, J. J., Walters, S., Guenther, A., Palmer, P. I., and Lawrence, P. J.: Contribution of isoprene to chemical budgets: A model tracer study with the NCAR CTM MOZART-4, J.Geophys.Res.-Atmos., 113, 79-88, 2008.

Purves, D. W., Caspersen, J. P., Moorcroft, P. R., Hurtt, G. C., Pacala, S. W.: Human-induced changes in US biogenic volatile organic compound emissions: evidence from long-term forest inventory data,

Global Change Biol., 10, 1737-1755, 2004.

Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnark, M., Miford, J., and Guenther, A.: Monoterpene and sesquiterpene emission estimates for the United States, Environ. Sci. Technol., 42, 1623-1629, 2008.

Sanderson, M. G., Jones, C. D., Collins, W. J., Johnson, C. E., and Derwent, R. G.: Effect of climate change in isoprene emissions and surface ozone levels, Geophysical Research Letters, 30, 159-171, 2003.

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A. B., Tilmes, S., and Stavrakou, T.: Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years, Atmos. Chem. Phys., 14, 9317–9341, 2014.

Situ, S., Wang, X., Guenther, A., Zhang, Y. L., Wang, X. M., Huang, M. J., Fan, Q., Xiong, Z.: Uncertainties of isoprene emissions in the MEGAN model estimated for a coniferous and broad-leaved mixed forest in Southern China, Atmos. Environ., 98, 105-110, 2014.

Song, Y. Y., Zhang, Y. Y., Wang, Q. G., An, J. L.: Estimation of biogenic VOCs emissions in Eastern China based on remote sensing data, Acta Scientiae Circumstantiae, 32, 2216-2227, 2012 (in Chinese).

Steiner, A., Luo, C., Huang, Y., Chameides, W. L.: Past and present-day biogenic volatile organic compound emissions in East Asia, Atmos. Environ., 36, 4895-4905, 2002.

Stroud, C., Makar, P., Karl, T., Guenther, A., Geron, C., Turnipseed, A., Nemitz, E., Baker, B., Potosnak, M., and Fuentes, J. D.: Role of canopy-scale photochemistry in modifying biogenicatmosphere exchange of reactive terpene species: Results from the CELTIC field study, J. Geophys. Res. 110, D17303, doi:10.1029/2005JD005775, 2005.

Tan, K., Piao, S., Peng, C., and Fang, J.: Satellite-based estimation of biomass carbon stocks for northeast China's forests between 1982 and 1999, Forest Ecol Management, 240, 114-121, 2007.

Tan, M., and Li, X.: Does the Green Great Wall effectively decrease dust storm intensity in China? A study based on NOAA NDVI and weather station data, Land Use Policy, 43, 42-47, 2015.

Turner, D. P., Wones, A. G., Pross, D., and Phillips, D. L.: Climate change and global isoprene emissions, Paper 91-126. 3, Global Climate Change: Papers from the 84th Annual General Meeting of the Air and Waste Management Association, June 16-21, Vancouver, 1991.

Wang, Q., Zhang, B., Dai, S. P., Zou, Y., Ma, Z. H., and Zhang, Y. N.: Dynamic changes in vegetation coverage in the Three Northern Regions Shelter Forest Program based on GIMMS AVHRR NDVI, Resour. Sci., 33, 1613-1620, 2011 (in Chinese).

Wang, B., Shao, M., Lu, S. H., Yuan, B., Zhao, Y.,Wang, M., Zhang, S. Q., and Wu, D.: Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008, Atmos. Chem. Phys., 10, 5911–5923, 2010.

Wang, M，Shao, M，Chen, W，Yuan， B ., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile

organic compounds in Beijing, China， Atmos. Chem. Phys., 14, 5871–5891, 2014

Wei, X. L., Li, Y. S., Lam, K. S., Wang, A. Y., and Wang, T. J.: Impact of biogenic VOC emissions on a tropical cyclone-related ozone episode in the Pearl River Delta region, China, Atmos. Environ., 41, 7851-7864, 2007.

Yan, Q. L., Zhu, J. J., Hu, Z. B., and Sun, O. J.: Environmental impacts of the Shelter Forests in Horqin sandy land, Northeast China, J. Environ. Qual, 40, 815-824, 2011.

ZemanKova, K., and Brechler, J.: Emissions of biogenic VOC from forest ecosystems in central Europe: Estimation and comparison with anthropogenic emission inventory, Environ. Pollut., 158, 462-469, 2010.

Zhang, X., Huang, T., Zhang, L., Gao, H., Shen, Y., and Ma, J.: Trends of deposition fluxes and loadings of sulfur dioxide and nitrogen oxides in the artificial Three Northern Regions Shelter Forest across northern China, Environ. Pollut., 207, 238-247, 2015.

Zhang, Y., Wang, X., and Qin, S.: Carbon stocks and dynamics in the three-north protection forest program, China, Austrian J. of Forest Sci., 130, 25, 2013.

Zheng, X., and Zhu, J.: Estimation of shelter forest area in Three Northern Regions Shelter Forest Program region based on multi-sensor remote sensing data, Chin. J. Appl. Ecol., 24, 2257-2264, 2013.

Zhong, Z., Wang, H., Xiong, W., and Sha, W.: A numerical investigation of association between environment and the Three Northern Regions Shelter Forest: Model evaluation and verification, J. PLA University of Technology, 2, 7-12, 2001 (in Chinese).

The Supplement related to this article is available online

Figures captions

Figure 1. The Three Northern Regions Shelter Forest (TNRSF) in Northern China. The Northwest China region of the TNRSF, defined by grey color, includes Xinjiang, Gansu, the north of Qinghai, Ningxia, West Inner Mongolia, and the north of Shaanxi; The Central-north China region, defined by orange gold color, includes the north of Shanxi and Hebei provinces, Beijing, Tianjin, and Central Inner Mongolia; The Northeast China region, defined by brass color, includes East Inner Mongolia, part of Liaoning, Jilin, and Heilongjiang provinces. Red, blue and yellow circles in the inner figure (right-lower corner of the figure) indicate three small areas in the TNRSF, a farmland, and the boreal forest from which isoprene emission flux are extracted for comparison (see Results and Discussions sections). Two megacities, Beijing and Tianjin in the Central-North China region, are also indicated.

Figure 2. Domain-averaged annual emission flux (micro-moles m^{-2} h^{-1}) of isoprene over the TNRSF from 1982 to 2010. Red dot line indicates linear trend of emission fluxes and shading stands for ± 1 standard deviation of emission fluxes.

Figure 3. Differences of emission flux (E_{2010} - E_{1982}, micro-moles m^{-2} h^{-1}) of isoprene between 1982 and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

2010. The emission fluxes in these two years are shown in Fig. S3a and b of Supporting Information

Figure 4. (a) Gridded annual isoprene biogenic emission (micro-moles m^{-2} h^{-1}) in 2000 over Northern China with spacing $1/4^o \times 1/4^o$ latitude/longitude; (b) slopes of linear regression relationships between annual mean isoprene emission flux (micro-moles m^{-2} h^{-1}) and the time sequence (or linear trend) from 1982 to 2010 across the TNRSF.

Figure 5. Slopes of linear regression relationships between annual mean isoprene emission flux (micro-moles m^{-2} h^{-1}) and the time sequence (or linear trend) from 1982 to 2010 across the TNRSF.

Figure 6. Temporal trend in emission flux of isoprene averaged over three regions of the Northeast, Central-North, and Northwest China region of the TNRSF. Dotted straight lines represent linear trends of isoprene emission fluxes in the Central-North China region.

Figure 7. Annual variation and trend of isoprene emission flux spatially averaged over three small areas in and outside the TNRSF in Central-North China and natural (boreal) forest region as marked in **Fig. 1**. The left-hand-side y-axis scales trend of isoprene emission fluxes in the TNRSF region and boreal forest in Northeast China and right-hand-side y-axis scale emission flux from the farmland outside the TNRSF.

Figure 8. Measured ambient concentrations of TVOC (mg m^{-3}) with frequency of 1 min from 2 – 4 pm local time at 4 paired monitoring sites within and outside the TNRSF. (a) Langfang (August 9 2015), (b) Xinglong (August 10 2015); Zhangbei (North, August 12 2015), (c) Zhangbei (South, 13 August 2015).

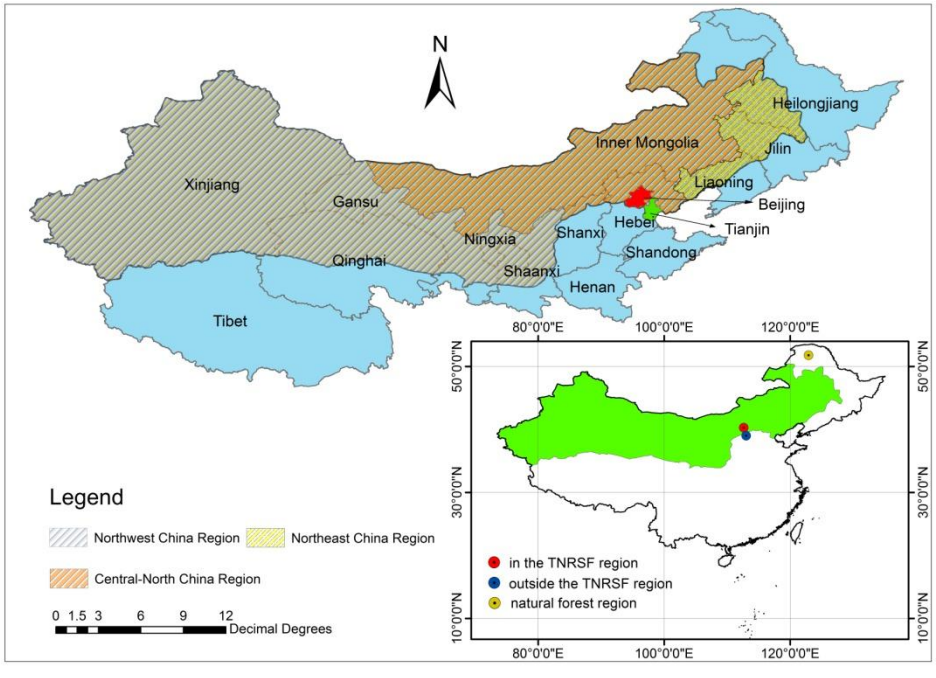

Figure 1

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

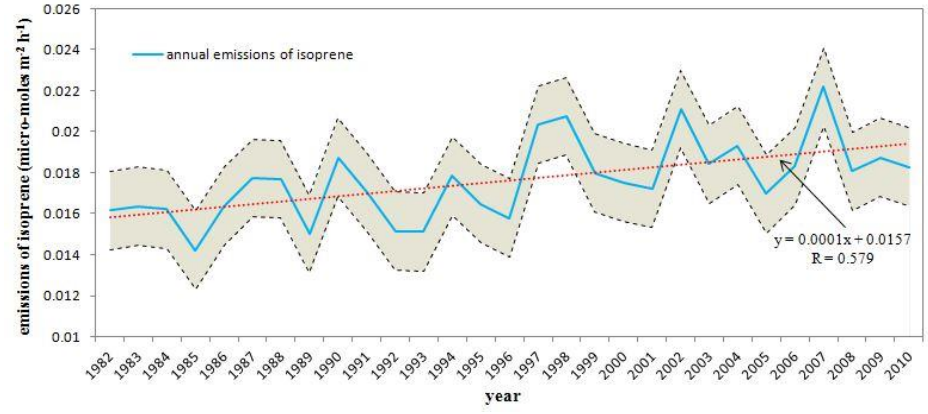

Figure 2

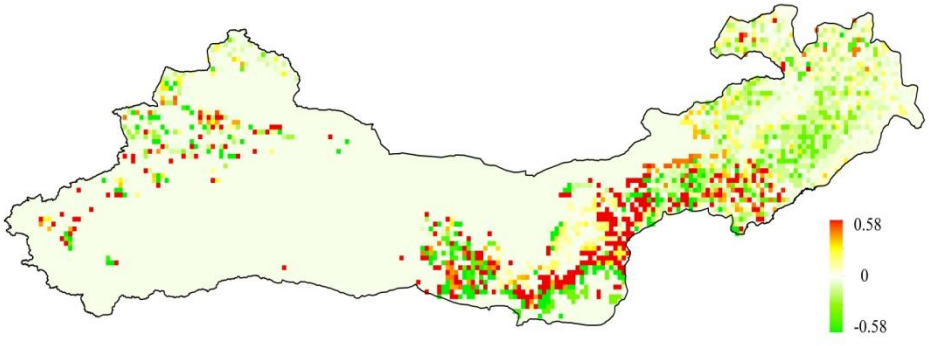

Figure 3

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

Atmospheric Chemistry and Physics Discussions

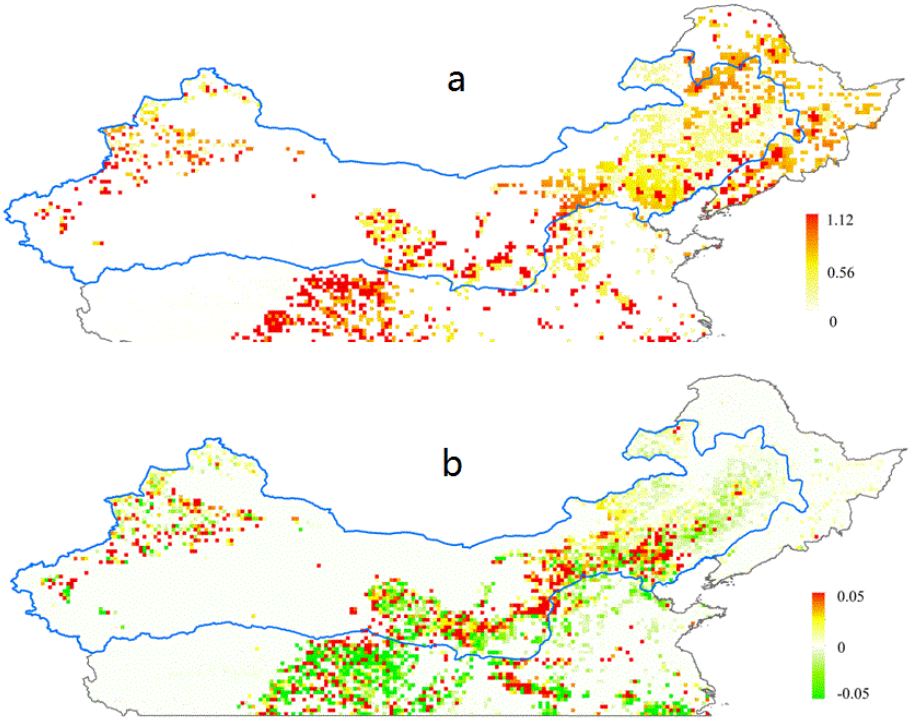

Figure 4

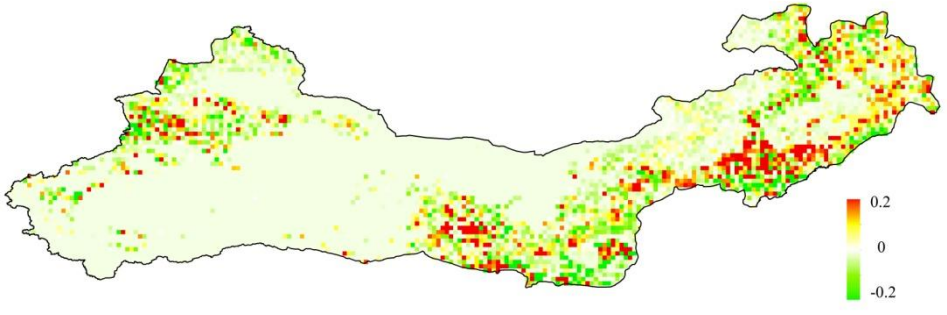

Figure 5

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

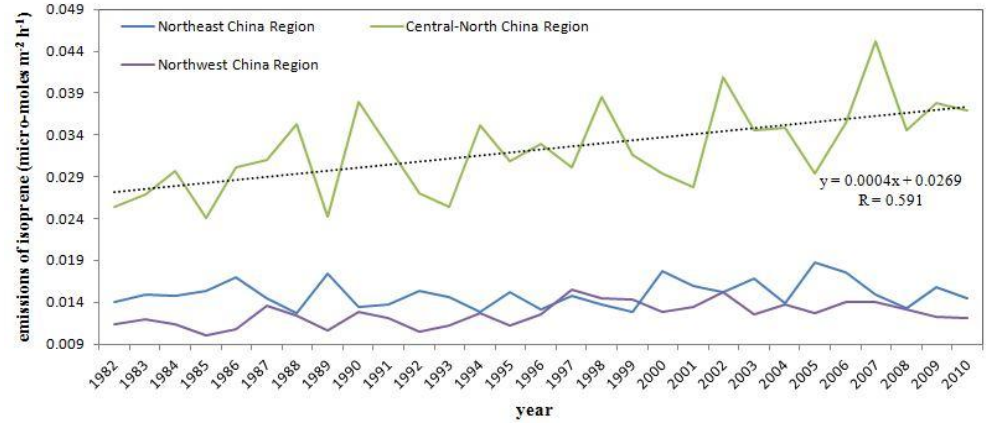

Figure 6

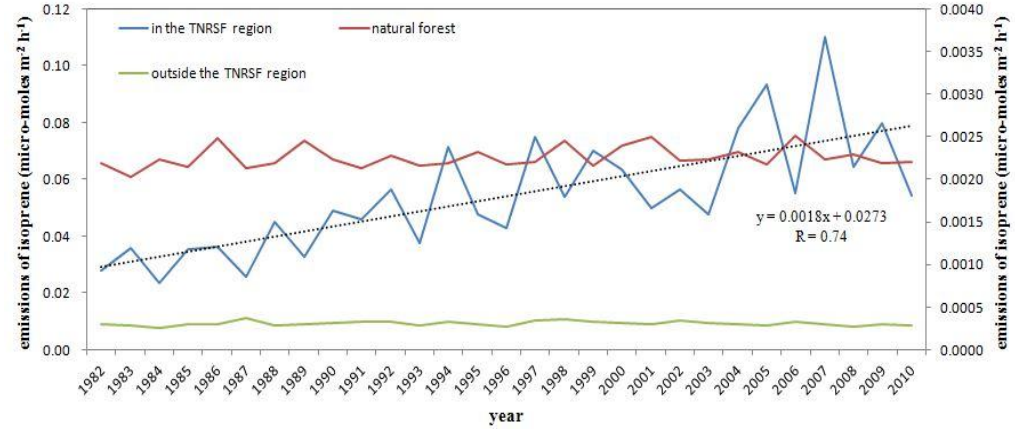

Figure 7

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-944, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 21 January 2016

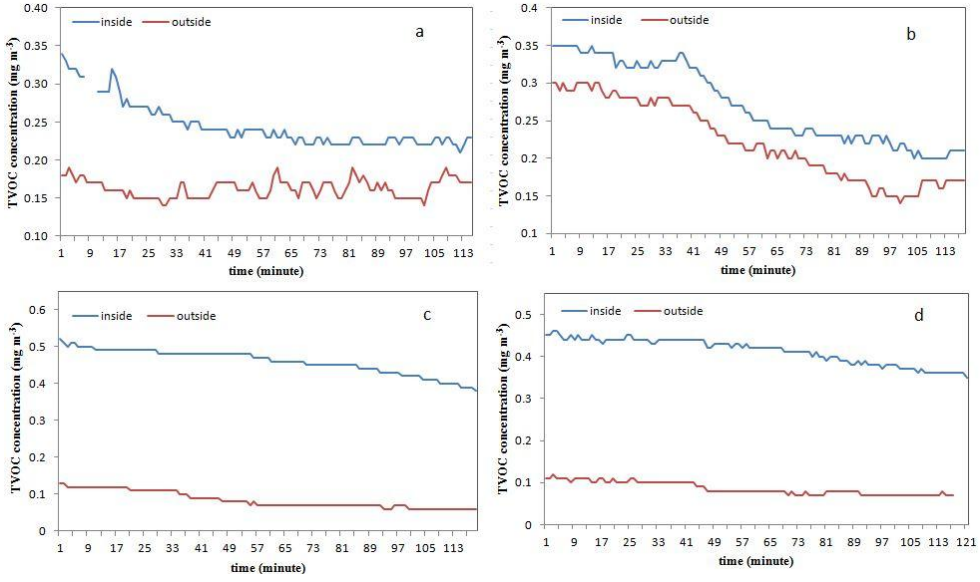

Figure 8