Response to the Editor and Reviewer#3 comments

First of all, we would like to thank the Editor for his constructive comments and suggestions during the course of the revision of this paper, which improve greatly the interpretations and presentation of the manuscript. Following the Editor's suggestion, we have removed those discussions related to the ambient observation of TVOC and inverse modeling using box models. We also deleted the corresponding references, figures, and tables in main text and Supplement. Detailed responses to the Editor and Reviewer#3's comments are presented below.

REVIEWER COMMENT: L43: “they also contribute to air pollution through atmospheric chemistry”

EDITOR SUGGESTION: I suggest changing “they also contribute to” to “they also play a role in”

AUTHOR RESPPONSE: Done, thanks!

REVIEWER COMMENT:L64: “Efforts have been also made to measure and simulate BVOC emissions in China”, my suggestion is more other studies should be introduced and cited here.

EDITOR SUGGESTION: No further revisions are needed.

REVIEWER COMMENT: L96: please introduce the coverage of the Three Northern Regions Shelter Forest (TNRSF) in the text and in the figure 1. Does it cover the Inner Mongolia and Beijing area? According to public references, the TNRSF covers Inner Mongolia and Beijing. Why the authors say differently?

EDITOR SUGGESTION: I assume the “green” area in Figure 1 is the TNRSF but you should make this clear. In that case it appears that Beijing and inner Mongolia are in the TNRSF but again you should clarify this. Also, you should make it clear that there are areas in the TNRSF zone but they are not (yet) forested areas.

AUTHOR RESPPONSE: Yes the TNRSF covers Beijing and Inner Mongolia. In Fig. 1 caption we have listed all provinces and two megacities, Beijing and Tianjin covered by the different regions of the TNRSF. As shown by Figure 1, both Beijing and Inner Mongolia are included in the TNRSF. To clarify this, in the revised paper we add text " **Figure 1** illustrates the TNRSF regions, including 11 provinces and two megacities, Beijing and Tianjin, as highlighted in the figure caption and marked in the figure." (line 98-100). In Fig. 1 caption, we added more details in the coverage of the TNRSF and stated that " many places in this part of the TNRSF, particularly in Gansu, Ningxia, and West Inner Mongolia, are not covered by forest but by shrubs".

REVIEWER COMMENT: L144: PAR was calculated from solar radiation provided by the Big-leaf dry deposition model. Are these PAR values compared with the ground observations at some sites for hourly and daily PAR? What are the calculating errors in TNRSF? Then, what uncertainties would be caused to BVOC emissions?

EDITOR SUGGESTION: No further revisions are needed.

REVIEWER COMMENT: L241: The GreyWolf VOC sensor can only measure TVOC, how authors examine and verify the release of BVOC species from the TNRSF? Based on measurements, the contributions of isoprene to BVOC emissions or to TVOC emissions are vegetation and season dependent, assuming the isoprene emission to be 50% of the TVOC would cause large errors.

EDITOR SUGGESTION: Change “this reactive biogenic VOC species” to “total biogenic VOC species”

AUTHOR RESPONSE: The paragraph with these texts have been deleted in the revised paper.

REVIEWER COMMENT:L263-264:“…suggesting increasing isoprene emissions associated with the expansion of the TNRSF in these regions”. Is it the only factor for isoprene emission increasing? How about the roles of other factors, for example, PAR and temperature?

EDITOR SUGGESTION: This is an important point. At a minimum you should address it by including temperature and PAR trends in the figure.

AUTHOR RESPONSE: We did recognized the important role of temperature in isoprene emission. Since this study focused on long-term trend of isoprene emission, we have mentioned the influence of climate change, characterized by changes in mean temperature, on isoprene emission, e.g., lines 76, 89-91, 390-405, and Fig.S5. In the revised paper, following the Editor and Reviewer#3's comments, we replaced Fig. S7a by Fig. S5a which displays the differences of surface temperatures T_{dif} between 1982 and 2012 across the TNRSF (now Fig. S5a), instead of T_{dif} in the Northeast China region only as presented by Fig. S7 in the previous Supplement of the manuscript. Figure 5b presents 30 years trend of SATs from 1982 to 2010 across the Northeast China region of the TNRSF which was used to explain negative trend of isoprene emissions in this part of the TNRSF (Fig. 4b). Corresponding discussions are presented in Discussion section (Section 4, line 386-405). In Section 3.2, we also added a paragraph " As aforementioned in Introduction, in addition to forest expansion, biogenic isoprene emissions are also associated with climate change via changes in mean temperature (Sanderson et al., 2003) and PAR (Guenther et al., 2006, 2012; Situ et al., 2014). Since the influence of climate change on BVOC is beyond scope of this article, we shall not assess detailed associations between climate change (mean temperature) and isoprene emissions from the TNRSF.

Nevertheless, in Section 4, we shall discuss briefly the potential influence of the changes in annual mean air temperature and PAR on long-term trends of biogenic isoprene emissions in the Northeast China region of the TNRSF."

In new Fig. S6, we presented the linear trends of PAR from 1982-2010. We added a new paragraph (line 406-429) to discuss and interpret the trend of PAR. Results suggested that PAR was unlikely to overwhelm the long-term trend of isoprene emissions.

REVIEWER COMMENT:L587: “Since VOCs are major precursor” should be changed to “Since BVOCs are major precursors”.

EDITOR SUGGESTION: You should make this change

AUTHOR RESPONSE: Done!

Marked up manuscript

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

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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 natural forests, such as boreal forests in Northeastern China. The estimated isoprene emissions suggest that the TNRSF has altered the 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=0.014), 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, 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 play a role in ~~contribute to~~ air pollution through atmospheric chemistry. 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 VOC emissions from biogenic sources have far exceeded those from anthropogenic sources (Guenther et al., 1995; Aydin et al., 2014).

Among the three dominant VOCs (isoprene, monoterpenes, oxygenated compounds) contributing to BVOC emission fluxes, isoprene accounts for 70% of the total BVOC 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 BVOC 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 BVOC 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 BVOC emission in Eastern China was 11.3 $\times 10^6$ t, of which 44.9% was isoprene, followed by monoterpenes 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 China's total BVOC emission as 42.5Tg in 2003, of which 55% was isoprene emission.

BVOC 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 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 BVOC 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 BVOC emissions derived using different models to climate and vegetation changes. They found that increasing forest area could add several tens of 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 BVOC emissions. Their results revealed that the increasing anthropogenic emissions of VOCs subject to urbanization overall enhanced total VOC

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. **Figure 1** illustrates the TNRSF regions, including 11 provinces and two megacities, Beijing and Tianjin, as highlighted in the figure caption and marked in the figure. The program aims to increase China's 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 increased modeled 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 VOC 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 BVOC 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-term trends of the biogenic isoprene emissions were investigated to discern evidence of decadal or longer-term changes in BVOC 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. BVOC 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 BVOC emissions in Northern China. This new version includes additional compounds, emission types, and various controlling processes. For BVOC 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), solar radiation/photosynthetically active

141 radiation (PAR), wind speed, humidity, and soil moisture (Guenther et al., 2006; 2012;
142 Pfister et al., 2008; Arneth et al., 2011). MEGAN2.1 was set up over Northern China
143 with a grid spacing of $0.25^{o} \times 0.25^{o}$ latitude/longitude to produce gridded daily and
144 monthly emission fluxes. Meteorological data used in the MEGAN2.1 employed the
145 6-hourly objectively analyzed data from the 1°×1° latitude/longitude NCEP (National
146 Centers for Environmental Prediction) Final Operational Global Analysis
147 (http://dss.ucar.edu/datasets/ds083.2/). These data were then interpolated into the
148 TNRSF grids on the spatial resolution of 0.25×0.25 latitude/longitude. PAR was
149 calculated from solar radiation provided by the Big-leaf dry deposition model (Zhang
150 et al., 2002). Twenty-two land types were used, including an additional crop type
151 which was not specified in the MEGAN2.1. These land types at each model grid were
152 identified using the surface roughness lengths estimated from satellite remote sensing
153 data (Zhang et al., 2015). Guenther et al. (2012) reported the differences in
154 MEGAN2.1 modeled annual isoprene emissions as a result of changing plant
155 functional type (PFT) (24 %), LAI (29 %), and meteorology (15 %) input data. This
156 suggests that LAI is one of crucial variables in the model.
157 ~~To evaluate the MEGAN2.1 estimated isoprene biogenic emission fluxes, a field~~
158 ~~campaign was conducted to measure total VOC (TVOC) concentrations at several~~
159 ~~sites within and outside the TNRSF (Section 2.4). The monitored TVOC~~
160 ~~concentrations were then converted to TVOC emission fluxes using a box model,~~
161 ~~developed by Guenther et al (1996) which links biogenic VOC emission and~~
162 ~~photochemical reaction with OH radicals and ozone. The model was derived from a~~

~~simplified mixed-layer scalar conservation equation, given by~~

~~$E = z_i Lc$, (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 Zhang et al (2015).

2.3. Uncertainty analysis.

Although the BVOC emissions model was well established for different vegetation types, there were uncertainties in the estimate of BVOC 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). Situ et al showed that, in addition to the emission factors, PAR and temperature also created large uncertainties in the MEGAN model (Situ, et al., 2014). 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), PAR, 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 BVOC 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 5.29 micro-mole m^{-2} h^{-1} with the variation from 97%-211%. Details for the uncertainty analysis are presented in Supplementary Materials (Table S1, **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 measured isoprene concentration (*C*), 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 TNRSF, 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 VOC (TVOC) 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 sampling frequency was set at 1 min. 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 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). It should be noted that the GreyWolf VOC sensor can only measure TVOC, hence the concentration of individual VOC species is not reported here. Typical tree species planted in this region were selected in the field~~

~~monitoring program. Among them, poplars (*Populus spp*), a broadleaf tree species, dominated the two forest sites in Langfang and northern Zhangbei County. Poplars 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*), 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 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. The magnitudes of isoprene

emissions estimated in the present study agree with the China's BVOC 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 emissions in the Central-North region of the TNRSF exhibited the strongest increasing trend with the highest emission increase by 58% over the 30 years period.

Figure S2 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 Mongolia region of the TNRSF were identified in 2010. 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. S2a** 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, suggesting increasing isoprene emissions associated with the expansion of the TNRSF in these regions.

As aforementioned in Introduction, in addition to forest expansion, biogenic isoprene emissions are also associated with climate change via changes in mean temperature (Sanderson et al., 2003) and PAR (Guenther et al., 2006, 2012; Situ et al., 2014). Since the influence of climate change on BVOC is beyond scope of this

273 article, we shall not assess detailed associations between climate change (mean
274 temperature) and isoprene emissions from the TNRSF. Nevertheless, in Section 4, we
275 shall discuss briefly the potential influence of the changes in annual mean air
276 temperature and PAR on long-term trends of biogenic isoprene emissions in the
277 TNRSF.

278 **3.2. Isoprene emission trend in the TNRSF and Northern China**

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

293 The total annual isoprene emission, summed from annual emissions of the model
294 grids that fall within the TNRSF domain, ranged from 45,000 to 70,000 ton yr^{-1}

295 during 1982-2010 for the whole TNRSF (the area encircled by the blue solid line in
296 **Fig. 4**), and from 132,000 to 176,000 ton yr^{-1} for whole Northern China (**Fig. 4**). This
297 is equivalent to a total emission of 1.6 Tg and 4.4 Tg, respectively, for the two regions
298 during the past three decades from1982 to 2010. It is worth noting that, although the
299 TNRSF accounts for 59% of the total area of Northern China and 42% of mainland
300 China (Zhang, et al., 2015), it covers almost all arid and semi-arid regions in Northern
301 China. Vegetation coverage in these regions was still sparse after 30 years
302 construction of the TNRSF, and shrubs, instead of trees, are major plant types in the
303 Northwest China region of the TNRSF. The isoprene emissions are considerably low
304 in these regions, as shown by **Figs. 4** and **5**. In addition, as shown by **Fig. 4**, the
305 region of Northern China defined in this study extends virtually to 30^{o}N. Although the
306 isoprene emissions in the TNRSF only accounted for 37% of the total emissions in
307 Northern China, the relatively strong increasing trend (**Fig. 2**) in the TNRSF
308 (slope=0.881, R^2=0.335) has reversed the negative trend (slope=-0.533, R^2=0.05) of
309 the total annual isoprene emissions in Northern China, which did not take the isoprene
310 emissions in the TNRSF into consideration, to the positive trend (slope=0.347,
311 R^2=0.014) from 1982 to 2010 in Northern China, as shown in **Fig. S3**.
312 To highlight the contribution of the TNRSF to the increasing isoprene emissions,
313 the trend of the gridded isoprene emissions over the TNRSF was further investigated.
314 As expected, the estimated monthly emission fluxes showed dramatic seasonal
315 variations with the largest values in summer and the lowest values in winter,
316 consistent with the seasonal changes in LAI over the TNRSF (figure not shown).

Figure 5 presents the gridded trends of the summer biogenic isoprene emissions across the TNRSF from 1982 to 2010. The summer emission fluxes exhibited similar annual pattern to the annual emissions (**Fig. 4b**) but were greater than the annual emissions, as shown by **Fig. 5**. 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 TNRSF 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^2 = 0.35, p=0.002). Whereas, statistically insignificant and relatively weak trends of isoprene emissions were found in the Northeast China (slope=0.00003, R^2=0.032, p=0.484) and Northwest China (slope=0.00009, R^2=0.27, p=0.012) regions of the TNRSF, respectively. 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

339 the TNRSF, the forests in the Northeast China region are mixed with natural forests.
340 These natural forests already reached the steady state before the 1980s, so they would
341 not contribute to the increasing trend of biogenic isoprene emissions. As shown by
342 **Fig. 4b**, the isoprene emissions in most places of Northeast China show almost no
343 trends. The Northwest China region of the TNRSF is arid and semi-arid area with low
344 precipitation. Shrubs, instead of trees, were planted in many places of this part of the
345 TNRSF regions, resulting in low biogenic isoprene emissions.

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

356 **3.3. Comparison with the previous emission data**

357 No extensive and direct measurements of BVOC emission across the TNRSF have
358 been ever carried out. Several field campaigns were conducted to measure BVOC
359 emissions in Northern China but these monitoring programs were not typically
360 designated for the TNRSF (Klinger et al., 2002; Wang et al., 2003). Li et al. (2013)

established an emission inventory of BVOCs (isoprene, monoterpenes, 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 ranged from 0.01 to 18.2 μg m^{-2} h^{-1}, agreeing reasonably well with Li et al's data. 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}. While the lower limit of their estimated flux agrees well -with our lowest emission flux of 20.4 μg m^{-2} h^{-1}, the upper limit of their emission flux was 880 μg m^{-2} h^{-1}, a factor of 4 higher than our value (122.4 μg m^{-2} h^{-1}) for the same region. Li et al (2013) adopted more locally updated species-specific emission factors and a vegetation classification based on a new vegetation investigation in the late 1990s and early 2000s in China. Their calculation also used hourly and diurnal meteorological (temperature, radiation, winds) data. Our estimated fluxes used the emission factors specified in the MEGAN2.1 (Guenther et al., 2012) and vegetation types classified by the roughness lengths (Zhang et al., 2002, 2015). In addition, our model input daily meteorological data. These different input data to the MEGAN model resulted likely in the difference of the isoprene emission fluxes between Li et al (2013) and our results. Song et al. (2012) simulated BVOC emissions in Eastern China from 2008 to 2010. A portion of

383 their model domain in Eastern China superimposed with the Central-North China and
384 the Northeast China region of the TNRSF defined in our study. The annually averaged
385 isoprene emission fluxes from 2008 to 2010 from Song et al's model simulations
386 ranged from 10 to 100 μg m^{-2} h^{-1} in Inner Mongolia region, and 100-1000 g m^{-2} h^{-1} in
387 the north of Shanxi and Hebei provinces, Beijing, and Tianjin, which were higher than
388 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
389 two regions. Song et al. used MEGAN2.04 model with different emission factors
390 adjusted based on China's principal vegetation species (Song et al., 2012). These
391 could also lead to different biogenic isoprene emissions.

392 ~~**3.4. Emissions converted from ambient concentrations**~~

393 ~~**Figure 8** illustrates measured afternoon (local time 2-4 pm) TVOC levels in the~~
394 ~~atmosphere at the 4 paired monitoring sites in the Central-North China region of the~~
395 ~~TNRSF with sampling frequency of 1 min. Detailed descriptions of these sites and~~
396 ~~sampling procedures are presented in Methodology section, **Fig. S3**, and Table S4,~~
397 ~~respectively. Higher TVOC air concentrations were observed at all forest sites than~~
398 ~~those sites outside the forests. In particular, the TVOC levels at the southern and~~
399 ~~northern Zhangbei sites within the TNRSF were 3 to 4 times higher than that~~
400 ~~measured in the grassland sites outside the TNRSF, suggesting that the forests made~~
401 ~~significant contributions to the sampled TVOC levels. Using the box model (Eq. 1),~~
402 ~~emission fluxes were converted from the measured TVOC concentrations at the four~~
403 ~~forest sites. Taking the TVOC levels as the box model input (Eq. 1), and assuming~~
404 ~~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 (Eq. S1) for an area source (Arya, 1999) to convert the measured TVOC concentrations 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 about a factor of 2 higher than the MEGAN2.1 estimated fluxes. Results are presented in Supplementary Materials. The potential differences between the MEGAN2.1 modeled and converted fluxes from the Gaussian model (Eq. S1 of Supplementary) might be attributed to several causes. Firstly, the TVOC 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 × 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 BVOC emissions might be lower. In addition, in the simplified Gaussian model (Eq. S1, Supplementary) we choose the fetch Δl =3km which is related directly to the magnitude of the converted emission fluxes which was subject to uncertainties. Nevertheless, overall the converted fluxes from the measured TVOC concentrations using the simplified Gaussian model are about the 2-fold of the~~

modeled fluxes, suggesting the reasonable accuracy of the MEGAN model applied in the present investigation.

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), suggesting that the atmospheric isoprene during the wintertime was emitted mostly from vehicular exhaust 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 the summertime isoprene was released from biogenic sources. Considering that our sampling sites (especially the Langfang and Xinglong sites) are close to Beijing and covered by similar tree species to 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 North 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. S4a** 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 Arneth et al. (2008, 2011) based on projected land use changes. Their modeling results suggested that increasing forest area could lead to several tens of percent change in biogenic isoprene emissions.

As shown above, the significant incline trend of the annual total isoprene emissions in the TNRSF 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 BVOC emissions not only in the TNRSF, but also in Northern China considering that the TNRSF occupies 59% of Northern China and 42% of whole mainland China. Future impacts of the TNRSF on BVOC emissions may be even stronger with continuous increase of vegetation coverage till the end of the program in 2050.

While BVOC emissions vary on short time scales, the global BVOC emissions are often assumed to change little on a 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). Identification of the impact of climate change on BVOC emissions is not straightforward if regional or global forests reach a steady state. The evidence identified in this study suggested that the human-induced BVOC emissions via large-scale afforestation exert strong influence on long-term BVOC emission and should be taken into consideration in projected climate change scenarios, at least on a regional scale, such as 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 internationally, characterized by year round high levels of fine particular matter ($PM_{2.5}$) and high surface ozone concentrations in the

493 summertime. Chinese government has decided to extend the TNRSF as one of the
494 primary measures to reduce and remove air pollutants from Beijing-Tianjin-Hebei
495 area (Chinese Environmental Protection Agency, 2013). As shown in **Figs. 5** and **6**,
496 the TNRSF in the Central-North region covering a large part of Beijing-Tianjin-Hebei
497 area has already gained the most rapid development as compared to the other two
498 northern regions of the TNRSF (**Fig. 1**), leading to marked incline of isoprene
499 emissions. However, it is not yet clear if and how the extension of the TNRSF could
500 otherwise improve local air quality. Our previous study suggested that the TNRSF
501 played a moderate role in removing SO_2 and NO_x (Zhang et al., 2015). Under the
502 rapidly increasing NO_x emissions in the past decade due to rapidly increasing number
503 of private vehicles in Beijing-Tianjin-Hebei area, it is necessary to assess the
504 interactions between BVOC emissions from the TNRSF and local air quality in this
505 region.

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

515 isoprene emission in 2010 in the Northeast China region and eastern Inner Mongolia
516 region of the TNRSF as compared with that in 1982 was inconsistent with the
517 increasing trend of the emission. The forest coverage in the Northeast China region
518 did not show considerable change between 1982 and 2010. On the other hand, lower
519 annual temperatures (e.g., by around 1^{o}C) in 2010 than that in 1982 were evident over
520 the Northeast China region of the TNRSF as shown by the differences of annual
521 surface temperatures (SATs, C^{o}) between 1982 and 2010 (T_{dif}=T_{2010} −T_{1982}, **Fig. S5a**),
522 which likely caused lower biogenic emissions in 2010 (Purvis et al., 2004; Arneth et
523 al., 2008, 2011). Negative T_{dif} in the Northeast China region of the TNRSF
524 corresponded nicely to negative E_{dif} (**Fig. 3**), indicating the strong association
525 between SATs and isoprene emissions. In addition, compared with the increasing
526 trend of LAI in the Northeastern China region of the TNRSF (**Fig. S4a**), no
527 statistically significant increasing trends of the isoprene emissions are discerned in
528 this region. **Figure S5b** displays the trend of annual SATs in the Northeast China
529 region of the TNRSF from 1982 to 2010. Overall the SATs exhibited a decreasing
530 trend, caused mostly by declining SATs since the late 1990s. Since temperature plays
531 a key role in canopy BVOC emissions (Guenther et al., 2012; Li et al., 2013), the
532 lack of the incline trend of the isoprene emission fluxes in the Northeast China region
533 of the TNRSF might be attributable to the decreasing SAT from the late 1990s.
534 Another environmental factor that may exert the influence on the trend of
535 isoprene emissions is solar radiation/PAR (Situ et al., 2014). Analogous to the
536 response of the BVOC emissions to temperature, increasing radiation could also

enhance the isoprene emissions, or vice versa, particularly on daily or monthly basis.

To elucidate potential association between the long-term trend of biogenic isoprene emission and PAR, we estimated the trend of the flux of PAR (Guenther et al., 1995) over the TNRSF from 1982 to 2010. Results are shown in **Fig. S6**. Positive trends can be observed in the Northwest China region of the TNRSF (Xinjiang, Gansu) and Inner Mongolia. In contrast to the positive trends of isoprene emissions in the Central-North China region of the TNRSF, PAR fluxes in this region exhibited negative trends. Hu et al (2010) have calculated the long-term changes in PAR in Beijing using a broadband global solar radiation dataset. Their result revealed a significant declining trend of PAR from the late 20th century. They attributed the decrease of PAR to increasing aerosol emissions from large amounts of fossil fuel combustion due to rapid economic development and industrialization in North China, including Beijing-Tianjin-Hebei region, in the past several decades. The increase in anthropogenic aerosol particles can both absorb and scatter solar radiation in the atmosphere, contributing to the decreasing PAR. Within and proximate to North China where most heavy industries in China are located, the Central-North China region is the mostly contaminated area in the TNRSF by particulate matter and other air pollutants. Higher aerosol loading to this region was at least partially responsible for the decrease in the trend of PAR. This turns out that, while PAR contributes significantly to daily and monthly changes as well as spatial distribution in biogenic isoprene emissions in the TNRSF, it is unlikely to overwhelm the long-term trend of isoprene emissions.

559 The comparison between the isoprene emission trends and the emissions in
560 2000 in Northern China also carries a significant implication for the human induced
561 BVOC emissions. As shown from **Fig. 4b**, the trend of isoprene emissions from 1982
562 to 2010 over Northern China showed a rather different spatial pattern from its
563 emissions in 2000 (**Fig. 4a**). No significant trends were observed in the boreal forest
564 in Northeastern China，though a larger amount of isoprene was emitted from the
565 forest in this region in 2000. This implies that this natural forest was likely under a
566 steady state from which the biogenic isoprene emissions were not altered on the
567 decadal basis (Sanderson et al., 2003; Purves et al., 2004).
568 Although Qinghai – Ta-Pa Mountains exhibited the highest emissions in 2000
569 (**Fig. 4a**), negative trends of the biogenic isoprene emissions dominated this area,
570 indicating the declining of the emissions over the period of 1982 through 2010. This
571 is consistent with the decreasing vegetation coverage during this period in this region,
572 as shown by the negative trends of the leaf area index (LAI) in Northern China (**Fig.**
573 **S4**). On the other hand, most positive trends of LAI can be identified in the Central-
574 North region and along the foots of Tianshan Mountain in West China (see the areas
575 encircled by the solid blue line in **Fig. 4)**. This manifests that the TNRSF exerts strong
576 influences on biogenic VOC emissions, particularly on their decadal variation, though
577 the magnitude of emissions might not be higher than that from natural forests in
578 Northeast China (**Fig. 4a**). Results further imply that the TNRSF is very likely the
579 major source contributing to the increasing biogenic isoprene emissions over the past
580 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. S4a**, 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 Northeast 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^2 = 0.55). On the other hand, no statistically significant increasing trends of biogenic isoprene emissions were found in the farmland and the boreal 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 Northeastern 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 Northeastern 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

603 the TNRSF (Guenther et al, 2012).

604 **5. Conclusions**

605 Gridded monthly and annual biogenic isoprene emissions in Northern China were
606 modeled for the period of 1982 to 2010 and were then applied to assess the long-term
607 trends of the biogenic isoprene emissions in the TNRSF in order to discriminate the
608 signals of the human activities in decadal and longer-term trends of BVOCs on large
609 spatial scales. Significant impacts of the TNRSF on the BVOC emissions in Northern
610 China were identified during the past three decades. Annual isoprene emissions in
611 many places of the TNRSF region, especially in the Central-North China region,
612 exhibited an inclining trend. The maximum increase in the isoprene emission flux
613 reached 58% between 1982 and 2010, indicating important roles of the human
614 activities on BVOC emissions. The comparison of isoprene emission fluxes among
615 the Central-North China region of the TNRSF, farmland, and the boreal forest in
616 Northeastern China outside the TNRSF revealed that the biogenic isoprene emissions
617 in some areas of the Central-North China region of the TNRSF produced by man-
618 made forests have surpassed the emissions from the natural forests. This suggests that
619 the TNRSF was a main contributor to the decadal or longer-term changes in BVOCs
620 in Northern China. The impact of the TNRSF on BVOC emissions is expected to be
621 stronger in the coming years along with continuous development of the TNRSF
622 program till 2050. Since BVOCs are major precursor of tropospheric ozone, future
623 studies are needed to investigate how the increased BVOCs in the TNRSF contribute
624 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.

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Figures captions

Figure 1. The Three Northern Regions Shelter Forest (TNRSF) in Northern China, defined also by green color in the inner figure (right-lower corner of Fig. 1) and three regions of the TNRSF. 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, many places in this part of the TNRSF, particularly in Gansu, Ningxia, and West Inner Mongolia, are not covered by forest but by shrubs; 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 2010. The emission fluxes in these two years are shown in Fig. S2~~3~~a 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 Northern China.

Figure 5. Slopes of linear regression relationships between summer 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. Annual variations of emission fluxes of isoprene averaged over three regions of the Northeast, Central-North, and Northwest China region of the TNRSF. Dotted straight line represent linear trend 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).~~

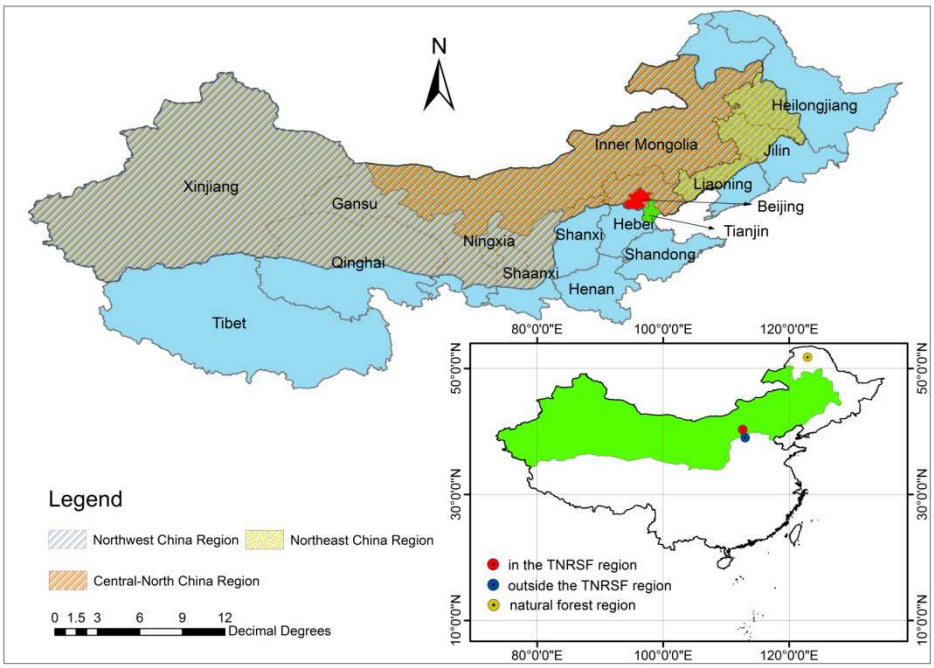

Figure 1

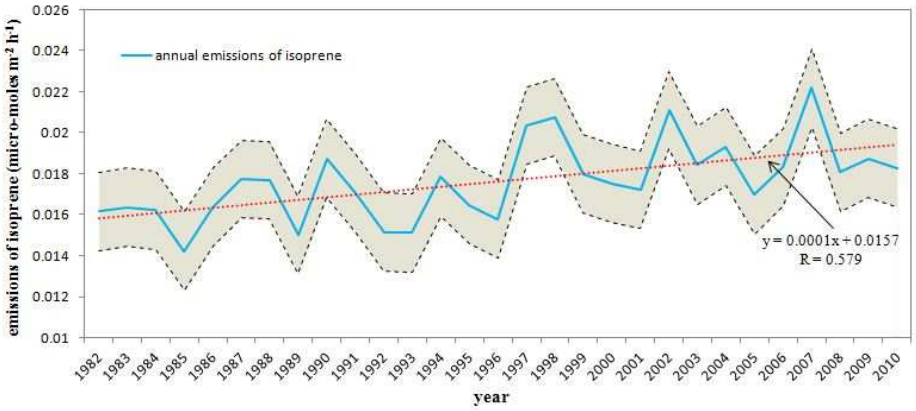

Figure 2

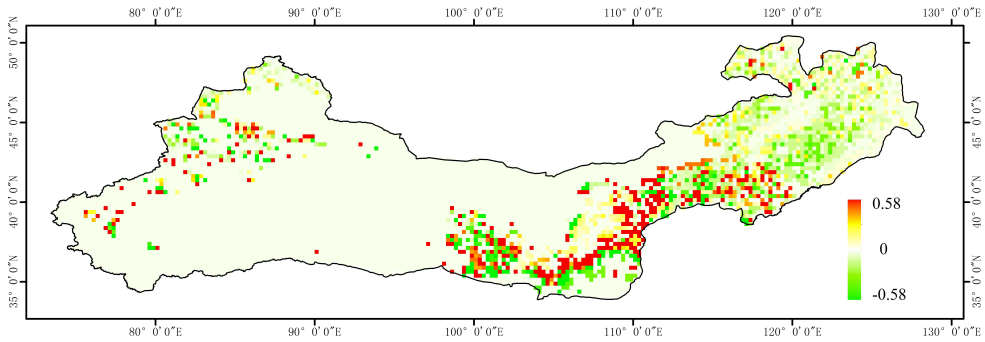

Figure 3

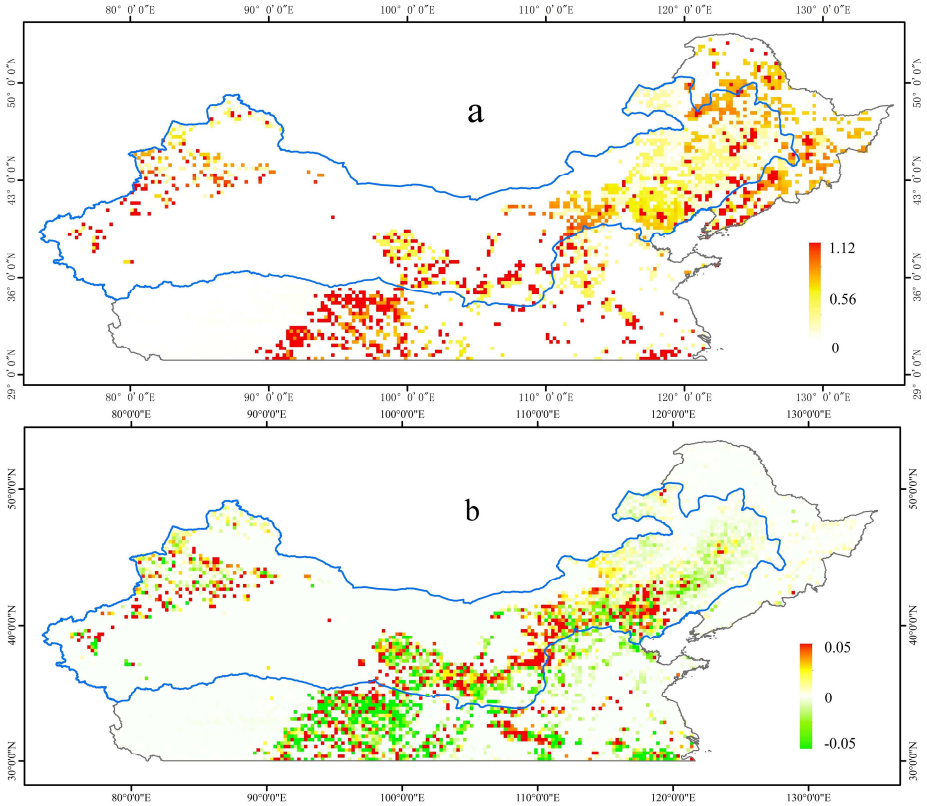

Figure 4

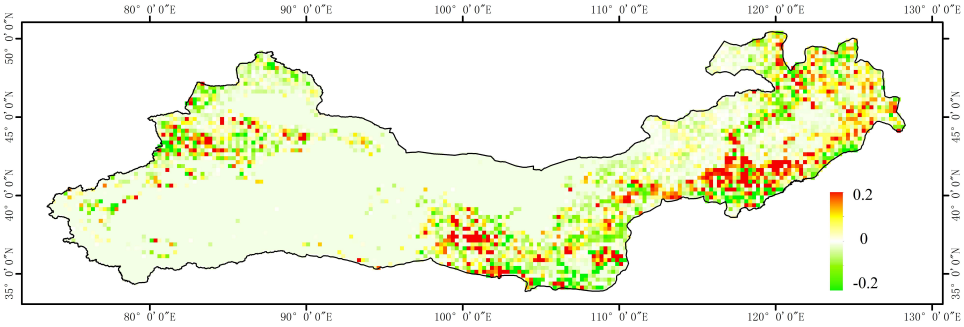

Figure 5

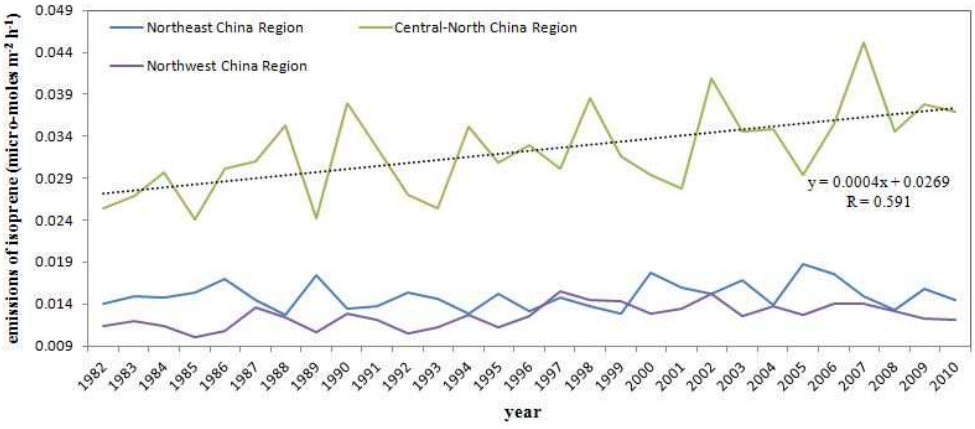

Figure 6

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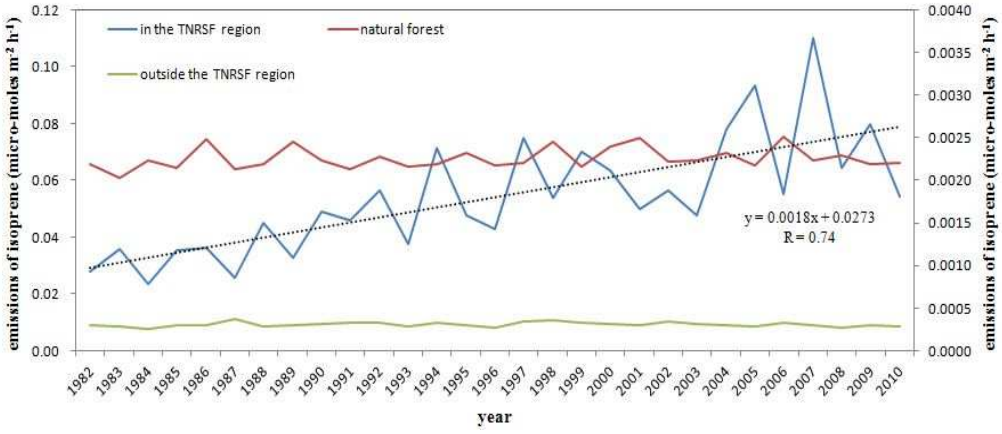

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903 **Figure 7**

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