Responses to reviewer's comments

Dr. K. Sindelarova, Reviewer #1

General comments

The paper touches an interesting topic of impact of human induced ecosystem changes on air quality. It studies trends of isoprene emission in Northern China with focus on artificially grown ecosystem of Three Northern Regions Shelter Forest (TNRSF). By using model of biogenic VOCs the paper shows that there is an increasing trend in biogenic isoprene emissions in the TNRSF region over the period of 1982 to 2010, which is likely to increase with further plantation of this human induced forest. Particularly, the study shows that promoted tree plantation in Central-North China region close to agglomerations of Beijing and Tianjin brings higher isoprene emissions to the vicinity of potentially strong NO_x sources, which can have significant impact on local air quality (e.g. surface ozone).

The base of the study is in modeling of isoprene emissions with the MEGAN model (Guenther et al., 2012). Additionally, the authors perform an uncertainty analysis of model inputs using the Monte Carlo method. And furthermore, they carry out a model evaluation by converting the measurements of total VOCs (TVOC) at several stations inside the forest to emissions of isoprene. Although the applied methodology of estimation of isoprene emission fluxes from measured TVOC concentrations is rather approximative, it provides a qualitative evaluation of modeled isoprene emissions. The paper is comprehensibly structured, written in appropriate level of English. I recommend its publication in ACP after minor revisions. Please see my specific comments and technical corrections below.

Response: We are very grateful for Dr. Sindelarova's detailed advice and constructive comments on the manuscript which benefit to a large extent to the significant improvements of this paper. We agree with all of the suggested revisions and comments from the reviewer. Following the comments from Dr. , Sindelarova (Reviewer #1), we have revised the manuscript and address all comments from Dr. , Sindelarova. Our detailed responses and revisions in accordance with Dr. Sindelarova's comments are presented below.

.

Specific comments

1] Since the manuscript does not show any results on the impact of BVOC emissions on the ‘ozone formation’, it should not be included among the Key words.

Response: ‘ozone formation’ was removed from the key words.

2] P2L10 : ": : : emit harmful gases into the air : : : ” – gases that trees emit are not harmful per se, but they indeed contribute to air pollution through atmospheric chemistry. Please rephrase this sentence.

Response: In the revised manuscript, we have rewritten text as "they also contribute

to air pollution through atmospheric chemistry".

3] In section 2.1 authors do not mention which meteorological fields they used to drive the MEGAN model.
Response: In addition to air temperature mentioned previously in our paper, we have added "solar radiation, wind speed, humidity," in the revised paper.

4] P11L7-L9 : Comparison of Northern China emissions with emissions calculated for regions in the US. This sentence is a bit vague. Authors should specify why they chose the US regions for comparison and be more precise, e.g. add numbers of total amounts.
Response: We thought that MEGAN model has been applied extensively in the US. The results from the MEGAN modeling in the US might be used as a reference to validate our modeling results in China. Nevertheless, the text on the comparison of isoprene emissions between the US and Northern China have been deleted in the revised paper.

5] It would be helpful for orientation in the Northern China geography, if the figures with maps of emissions and emission trends (Figs. 3-5, S4, S6a, S7) included indications of meridians and parallels of latitude in the model domain.
Response: Following the reviewer's suggestion, meridians and parallels of latitude have been presented in the revised Figs. 3-5, S4, S6a, and S7, respectively.

6] It is not quite clear what is shown in Fig. 5. The description in the main text (P14L1) is not clear and the figure caption is the same as in Fig. 4b.
Response: There was indeed an error in the description and caption of Fig. 5. Figure 5 shows **summer** gridded trends of isoprene emissions whereas Figure 4b shows the **annual** trends. In the revised paper we have replaced "annual biogenic isoprene emissions" by "summer biogenic isoprene emissions". The same change was made in Fig. 5 caption. We have also added new text, indicating that the summer emission fluxes 'show a similar annual pattern to the annual emissions (Fig. 4b) but are greater than the annual emissions, as shown by Fig. 5" in the revised paper.

7] P16L4: Authors compare their results of isoprene emissions in Central-North China regions with emission estimates by Li et al. (2013). They claim the results are comparable. However, the upper limit of their emission range is about 4 times lower than that of Li et al. (2013). Can authors comment on that, what could be the possible differences?
Response: We agree with the reviewer's comment. In the revised paper we acknowledged the difference of the upper limits of isoprene emissions between Li et al (2013) and our results and listed potential reasons causing this difference. 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 used hourly and diurnal meteorological

(temperature, radiation, winds) data. Our estimated fluxes were obtained using the emission factors specified in the MEGAN2.1 (Guenther et al., 2012) and vegetation types classified by the surface roughness lengths (Zhang et al., 2015). In addition, our model input daily meteorological data. These different input data to the MEGAN model likely resulted in the difference of the isoprene emission fluxes between Li et al (2013) and our result.
These texts have been incorporated into the revised manuscript.

8] P22L2 – Discussion of the comparison of emissions in Northeast China and Inner Mongolia in 2010 and 1982 doesn't seem to be correct. While I agree with the authors conclusion that emissions are lower in 2010 than in 1982 (shown in Fig. 3) due to lower air temperatures (Fig. S7), the premises seem to be confused. The emissions in this region do not have a trend (as shown in Fig. 4b and Fig. 6), but the forest coverage increased between 1982 and 2010 (Fig. S6a). Assumption that the mixed forest reaches a steady state is unclear though. Can you be more specific?
Response: Reviewer raised a good question! We agree with the reviewer that, compared with the increasing trend of LAI in the Northeastern China region of the TNRSF (**Fig. S6a**), no statistically significant increasing trend of the isoprene emissions are discerned in this region. In addition to the LAIs, isoprene emissions also respond to light and temperature in terms of the MEGAN model. Considering that the long-term changes in BVOC emissions are more sensitive to temperatures, we estimated the trends of gridded surface air temperatures (SATs, ^{o}C) over the Northeastern China region of the TNRSF from 1982 to 2010. The result is presented in a new figure (**Figure S7b,** attached with this respond) in the revised Supplementary Materials. As shown, compared with the Central-North China region, the SATs in most places of the Northeast China region exhibit a declining trend during this period of time. Again, since BVOC emissions are highly sensitive to changes in ambient temperatures (Guenther et al., 2012; Li et al., 2013), the lack of the incline trend of the isoprene emission fluxes in the Northeastern China region might be attributable to the decreasing SATs from 1982 to 2010.
The above argument and point have been incorporated into the revised manuscript. In the revised manuscript, we have removed text on steady state of mixed forest in the Northeastern China region.

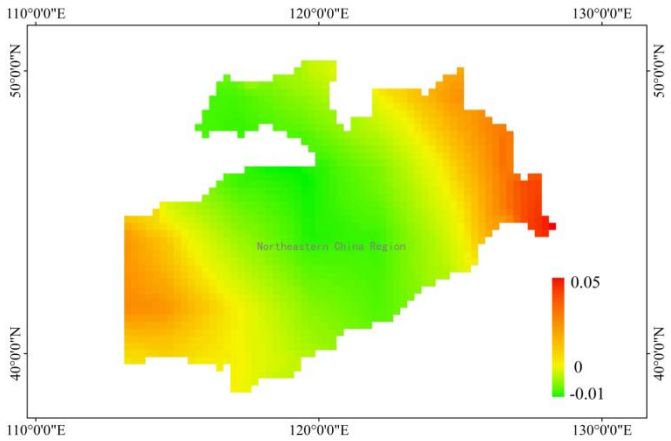

Figure S7b. Trends of surface air temperatures in Northeastern China region from 1982 to 2010.

Technical corrections

Main text:

In the whole text please replace ‘BVOCs emissions‘ by ‘BVOC emissions’, similarly ‘VOCs emissions’ by ‘VOC emissions’

Response: Done! Thanks！

P2L17: replace ‘anthropogenic emissions’ by ‘anthropogenic sources’

Response：Done！

P2L18: isoprene is a subgroup of terpenes (hemiterpene), please replace ‘terpenes’ by ‘monoterpenes’ or ‘monoterpenes and sesquiterpenes’

Response：Following the reviewer's suggestion, ‘terpenes’ has been replaced by ‘monoterpenes'.

P3L10: replace ‘monoterpene’ by ‘monoterpenes’

Response: Following the reviewer's suggestion, ‘monoterpene’ has been replaced by ‘monoterpenes’ in the revised paper.

P3L14: replace ‘was from isoprene emission’ by ‘was isoprene’

Response: Done!

P4L10: replace ‘tens percent’ by ‘tens of percent’

Response: Done!

P5L11: replace ‘modeled increased dry deposition’ by ‘increased modeled dry deposition’

Response: Done!

P11L14: replace ‘increased’ by ‘increase’

Response: Done!

P12L1 : reference to Fig.1 seems to be redundant

Response: Reference to Fig. 1 has been deleted.

P12L5: reference to Fig.3 seems to be redundant

Response: Reference to Fig. 3 has been deleted.

P13L1: I’d recommend to replace ‘applicable model grids’ by ‘model grids that fall within the TNRSF domain’ or similar

Response: Following the reviewer's comment, 'applicable model grids’ has been replaced by ‘model grids that fall within the TNRSF domain' in the revised

manuscript.

P13L7: Fig.1 is not the right reference here since it does not show arid or semi-arid regions.
Response: Reference to Fig. 1 has been deleted.

P19L15: misspelled reference of Arneth et al.
Response: Corrected. Thanks!

P19L17; replace ‘tens percent’ by ‘tens of percent’
Response: Done! Thanks for the correction.

P21L7: Sentence starting ‘However, : : :’ does not make sense. Did the authors mean ‘However, it is not yet clear : : :’ ?
Response: Reviewer is right! 'yet' is 'not yet'. We have corrected this typo error.

P22L4: Missing space in ‘between1982’
Response: Thanks to the reviewer for the correction! The space between two words has been added.

P22L14: Reference to Fig. 4b is misleading here. Either remove it, or refer to Fig. 4b directly after ‘Northeastern China’ in the same sentence and refer to Fig. 4a after ‘2000’.
Response: Following the reviewer's suggestion, we have removed the reference to Fig. 4b in the revised paper.

References:
- missing year of publication for Guenther et al., Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements.
Response: Missing year and full authors list have been added in the revised reference.

Figure caption to Fig. 6 – please edit the text, only one dotted line is shown in the figure.
Response: Following the reviewer's comment we have edit the text and made corresponding changes in the figure caption of Fig. 6.

Supplementary material:
- in section of Simplified Gaussian model for an area source – variable ‘Cis’ is not defined.
Response: Cis has been defined in the revised Supplementary material.

Figure caption to Fig. 6b – replace ‘LAT’ by ‘LAI’
Response: Yes LAT is 'LAI'. This error has been corrected. Thanks!

Responses to reviewer's comments

Anonymous Reviewer #2

Zhang et al have made MEGAN model simulations of isoprene emissions in China for the period 1982-2010, with special emphasis on the effects of the massive afforestation currently underway in the Three Northern Regions Shelter Forest (TNRSF) area. Model simulations showed an increase of isoprene fluxes over the years in the areas where forested cover also increased, suggesting that the man-made afforestation played a major role in the change of isoprene emissions.

This paper deals with the impact of human activities on the vegetation cover of a big land area that in turn impacts the concentrations of isoprene, an atmospherically relevant volatile organic compound that participates in the photochemistry of the atmosphere and can have an active role in the pollution episodes that China has been suffering in recent years. Thus this paper is within the scope of ACP and I would recommend its publication after addressing some concerns. The text needs some rewriting to make it clearer to the reader, especially the part reporting the TVOC measurements and the modeling of fluxes from those measurements.

Response: We thank Anonymous Reviewer#2 for his or her comments and appreciate the constructive criticisms which improve largely the presentations and interpretations in our manuscript. Based on the comments from the Reviewer #2, we have made corresponding revisions to the manuscript. Following are reviewer's comments and our responses

Specific comments:

P2L2: correct the number "R2=0014", there must be a decimal point missing.
Response: Corrected. Thanks!

P2L10: defining reactive BVOCs emitted by plants as "harmful gases" is not appropriate. Authors can argue that they have implications for atmospheric generation of pollutants such as ozone, but not that these gases are harmful.
Response: We agree with the reviewer's comment. In the revised manuscript, we have rewritten text as "they also contribute to air pollution through atmospheric chemistry"

P6L19: Reference to Guenther et al 2006, is it correct? If the MEGAN version was 2.1, should this reference be Guenther et al 2012? Otherwise, MEGAN version should be 2.0.
Response: The reference should be Guenther et al 2012. We have changed '2006' to '2012'. Thanks!

P9L1: Should L (oxidation rate) be replaced with C (isoprene concentration) in the

text? Table S3 does not list L but C, and it is reasonable that L will actually vary with OH and O3 concentrations, which are also listed in this list.
Response: We agree with the reviewer's comment! The texts have been changed to ' the measured isoprene concentration (*C*)'.

P10L7: Please write the genus name Populus starting with capital letter. Was it only one species of poplars that were planted in the region? If so, please give the scientific name, otherwise list as Populus spp and refer to this trees in plural in the text.
Response: Thanks for the suggested changes！We have rewritten 'populus' to '*Populus spp'* and referred to this trees in plural in the revised text (e.g., changing 'poplar' to 'poplars').

P10L10: Please list the variety of P. sylvestris or otherwise remove the word “var”.
Response: We have removed 'var' following the reviewer's comment.

P13L13: The slope of -0.534 applies to northern China without including the TNRSF, according to Fig S5. Please clarify in the text.
Response: The text has been rewritten as '... the relatively strong increasing trend (**Fig. 2**) in the TNRSF (slope=0.881, R^2=0.335) has reversed the negative trend (slope=-0.533, R^2=0.05) of the total annual isoprene emissions in Northern China, which did not take the isoprene emissions in the TNRSF into consideration, to the positive trend (slope=0.347, R^2=0.014)...'.

P14L14: Did the authors do any statistical analysis to support the statement that the trends of isoprene emissions in the Central-North region are statistically significant whereas those from the other two regions are not?
Response: In the revised manuscript, we added *p* values for each trend in the three regions. As shown, the *p* value=0.002 for the isoprene emission trend in the Central-North region，indicating statistically significant trend. Relatively weak significant trend was found in the Northwestern China region (*p*=0.012), and no statistically significant trend existed in the Northeastern China (*p*=0.484). These have been incorporated in the revised paper.

P17L8-P18L2: Please clarify this part of the text. If the surface of a model grid square is not completely covered by vegetation, wouldn’t this imply that the calculated MEGAN fluxes do not compare so nicely with the estimates using Eq (1), mainly because the MEGAN fluxes calculated for these sites where TVOC measurements were performed would be higher (more vegetation coverage than the model grid square)?
Response: The reviewer raised a good point! To address the reviewer's question, we have extended discussions on potential reasons causing the difference between MEGAN modeled and TVOC measurements converted fluxes. Except for the reason the reviewer questioned, we also considered an additional cause: in the simplified Gaussian model (Supplementary) we choose the fetch Δl =3km which is related

directly to the magnitude of the converted emission fluxes which were 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.

These discussions have been incorporated into the revised manuscript.

P18L14: was vehicular exhaust the dominant source of atmospheric isoprene? Do the authors want to say that vehicular exhaust was the dominant source of atmospheric VOCs? Same for line 17 of this page.
Response: We have rephrased text in these two sentences. In the revised text, we made clear that 'the atmospheric isoprene during the wintertime was emitted mostly from vehicular exhaust', and 'the summertime isoprene was released from biogenic sources'.

P19L15: Thanks for this correction! We have corrected Arneths to Arneth.
Response: Done! Thanks!

P20L10-13: Please clarify this sentence.
Response: Following the reviewer's comment, we have rephrased this sentence to make our point more clear.

P22L1: This sentence needs more information to make sense. As it currently reads, it may seem that 2007 was a bad year for the trees, but looking at Fig. 2, isoprene emissions are at or near the historical maximum. I suspect the authors have something else in mind that is not clear to me. What is the time span that the authors describe as showing a “considerable decline of forest coverage and isoprene emissions”?
Response: We thank the reviewer to point out this inconsistence. The forests collapse took place *since* 2007 rather than *in* 2007 (see Zhang, X., et al., 2015 in the Reference). We have replaced 'in' by 'since' in the revised paper. We further indicated that the mortality of trees since 2007 caused visible decline of the forest coverage and isoprene emissions in this region after 2007.

P22L7-8: the authors assume steady state of the mixed forest of Northeast China, regarding which variable? LAI? If so, have the authors checked whether the LAI information on Fig S6 agree with this assumption?
Response: The LAI data did show no trend in Northeast China. But in the revised manuscript we have deleted 'steady state'. Instead, we added new text, a new Fig. S7b which shows annual temperature averaged over Northeastern China, and corresponding discussions in the revised paper.

P27L10: Please list the year of publication (1996) and the complete list of authors.
Response: Done!

FigS6 (caption): LAT should be LAI?
Response: Yes, 'LAT' is 'LAI'. This error was corrected in the revise paper. Thanks!

Responses to reviewer's comments

Anonymous Reviewer #3

Long term trend of isoprene emission in the Three Northern Regions Shelter Forest (TNRSF) from 1982 to 2010 was evaluated, using a biogenic emission model for gases and aerosols (MEGAN). Isoprene emission flux has increased substantially in many places in the TNRSF due to the increase of trees and vegetation coverage, especially in the Central-North China region. The estimated isoprene emissions suggest that the TNRSF has altered the long-term emission trend in North China. I recommend its publication after addressing some questions. Please see the questions and comments bellow:

Response: We appreciate Anonymous Reviewer#3 for his or her comments and the constructive criticisms which help us to improve considerably our manuscript. Based on the comments from the Reviewer #3, we have made relevant revisions to the manuscript. Following are reviewer's comments and our responses.

Specific comments:

P2L10: they also emit harmful gases into the air. By our understanding, these gases are not harmful, please correct it, or cite references here.

Response: We agree with the reviewer's comment! In the revised manuscript, we have rewritten text as "they also contribute to air pollution through atmospheric chemistry"

P6L12: 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. Please introduce these data sources in the calculation for past three decades, the uncertainties of all these parameters used in the model for TNRSF, for example PAR, emission factor.

Response: Following the reviewer's comment, in the revised paper we have added text describing the data sources of meteorological data used in the modeling 30 years isoprene emissions, including a website and a new reference (Zhang et al., 2002). In the uncertainty analysis, we referred to Situ et al's work (2014) for the uncertainty analysis of the MEGAN model in which PAR and temperature were found to be most important environmental factors contributing to the uncertainties of the MEGAN model. We also further introduced PAR as one of the MEGAN model input parameters in our uncertainty analysis and rerun the Monte Carlo model. New results are presented in revised Fig. S1 and Table S2 of Supplementary materials.

P9L6: What are the sampling numbers at 8 sites in a field campaign? More introductions should be given for the measurements, such as VOC species and concentrations.

Response: The sampling frequency was set at 1 min. Since the GreyWolf VOC sensor can only measure TVOC, the concentration of individual VOC species is not reported here. These have been mentioned in sections 2.4 and 3.4 in the previous and revised paper. Figure 8 illustrates sampled TVOC concentrations per minute.

P12L10: It's better to use mg m-2h-1 instead of micro-moles m-2 hr-1.
Response: Thanks for the suggestion! The use of this unit followed Guenther et al. (2012, see Reference list). We figured out that using this unit we could better compare and illustrate emission fluxes inside and outside the TNRSF. For instance, Figure 7 compares isoprene emission fluxes within the TNRSF, a natural forest in Northeastern China, and outside the TNRSF. Using micro-moles m-2 hr-1 the annual variation of the emission fluxes in these three regions can be nicely presented in the same panel of the figure. Whereas, the use of mg m-2 h-1 the annual fluxes outside the TNRSF cannot be shown in Fig. 7 because the fluxes become too small using this unit as compared with those within forests. Therefore, we prefer to use micro-moles m-2 hr-1.

P14L17 (and P22L14): These natural forests already reached the steady state, is there any evidence from botanical field?
Response: We don't have botanical data to show evidence of steady-state natural forest in Northeast China. Instead, we added two references which indicated that a natural forest could be assumed to be in a steady state. In the revised manuscript, we rewrote the text as " This implies that this natural forest was likely under a steady state from which the biogenic isoprene emissions were not altered on the decadal basis (Sanderson et al., 2003; Purves et al., 2004)".

P15L13: No direct measurements of BVOCs emission data across the TNRSF have been ever reported before. This sentence should be corrected. Some measurements of BVOC emissions and concentrations in TNRSF region had been carried out, for example:
Klinger L.F., Li Q.J., Guenther A. et al. 2002. Assessment of volatile organic compound emissions from ecosystems of China, J. Geophy. Res., 107(D21). Wang Z.H., Bai Y.H., Zhang S.Y., 2003. A biogenic volatile organic compounds emission inventory for Beijing. Atmospheric Environment. 37, 3771-3782. Bai J.H., Baker B., Liang B.S., Greenberg J., Guenther A., 2006. Isoprene and monoterpene emissions from an Inner Mongolia grassland. Atmospheric Environment. 40(30), 5753-5758. There should be more others that can be used for the evaluation.
Response: We thank the Reviewer#3 for letting us know these references. We did not cite some of these references because the field measurements reported in these references were not conducted in the TNRSF. e.g., Wang et al.'s field work was done in Beijing and Bai et al.'s study was focused on the grassland of Inner Mongolia. Nevertheless, following the reviewer's comment we have revised the text as "No extensive and direct measurements of BVOC emission across the TNRSF have been ever carried out. Several field campaigns have been conducted to measure BVOC

emissions in Northern China but they were not typically designated for the TNRSF (Klinger et al., 2002; Wang et al., 2003)". These two references are also added to the Reference list.

P19L12: The increasing biogenic isoprene emissions can be attributed to the development of the TNRSF (i.e., LAI), how about the roles of other factors, PAR, temperature. My suggestion is to consider these parameters in all analysis, including P24L3. Where are figures Fig. S6a and b?
Response: We agree with Reviewer's comments! BVOC emissions do depend on other parameters and factors. We have shown that lower temperature in 2009 than 1982 in the Northeast China region of the TNRSF led to lower isoprene fluxes in 2009 in this region. In the revised manuscript, we have also added Fig. S7b which further shows decreasing trends of annually averaged temperature in the Northeast China region where LAI showed the incline (Fig. S6a) but BVOC emissions exhibited negative trends (Figs. 4 and 5). We suggested that declining temperatures in this region might cause the decreasing trend of isoprene emissions. Corresponding discussions have been incorporated in the Discussion section in the revised manuscript. We also wrote " Another environmental factor that may exert strong influence on the trend of isoprene emissions is solar radiation/PAR (Situ et al., 2014). Analogous to the response of the BVOC emissions to temperature, increasing radiation could also enhance the isoprene emissions, or vice versa, particularly on daily or monthly basis." in the revised manuscript.

Fig. S6a and b are cited in Discussion section and presented in Supplementary materials.

P24L16: emission minus dry deposition? please make it clear.
Response: Thanks to the Reviewer to indicate this error. We have removed texts in the revised manuscript.

Marked-up manuscript

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

Authors:
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]*

Affiliation:
[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

***Corresponding author:** Jianmin Ma, Tao Huang
Tel: +86 15293166921, fax: +86-931-8911843, email: 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 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, ~~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 contribute to air pollution through atmospheric chemistry~~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~~VOC emissions from biogenic sources have far exceeded those from anthropogenic ~~emissions~~sources (Guenther et al., 1994, 1995; Aydin et al., 2014).

Among the three dominant VOCs (isoprene, monoterpene~~sterpenes~~, oxygenated compounds) contributing to ~~BVOCs~~BVOC emission fluxes, isoprene accounts for 70% of the total ~~BVOCs~~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 ~~BVOCs~~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 ~~BVOCs~~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 ~~BVOCs~~BVOC emission in Eastern China was 11.3 $\times 10^6$ t, of which 44.9% was isoprene, followed by monoterpene~~s~~ 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~~BVOC emission as 42.5Tg, of which 55% was ~~from~~ isoprene emission.

~~BVOCs~~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 ~~BVOCs~~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 ~~BVOCs~~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 ~~BVOCs~~BVOC emissions. Their results revealed that the increasing anthropogenic emissions of VOCs subject to urbanization overall enhanced total ~~VOCs emissions~~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 (**Fig. 1**). 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 ~~modeled~~ 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 ~~VOCs emissions~~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 ~~BVOCs~~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 ~~BVOCs~~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. ~~BVOCs~~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 ~~BVOCs~~BVOC emissions in Northern China. This new version includes additional compounds, emission types, and various controlling processes. For ~~BVOCs~~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 radiation (PAR), wind speed, humidity, 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. Meteorological data used in the MEGAN2.1 employed the 6-hourly objectively analyzed data from the 1°×1° latitude/longitude NCEP (National Centers for Environmental Prediction) Final Operational Global Analysis (http://dss.ucar.edu/datasets/ds083.2/). These data were then interpolated into the TNRSF grids on the spatial resolution of 0.25×0.25 latitude/longitude. PAR was calculated from solar radition provided by the Big-leaf dry deposition model (Zhang et al., 2002). 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. (201206) reported the differences in MEGAN2.1 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

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

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 ~~BVOCs~~BVOC emissions model was well established for different vegetation types, there were uncertainties in the estimate of ~~BVOCs~~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 ~~BVOCs~~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~~4.38~~ micro-mole m^{-2} h^{-1} with the variation from 97~~.1~~%-211~~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~~Z~~$_i$, the measured isoprene concentration~~oxidation rate of isoprene~~ (~~*L*~~*C*)~~ 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 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 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 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 (*P~~p~~opulus 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 ~~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 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~~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 Central-North region of the TNRSF exhibited the strongest increasing trend with the highest emissions increase~~d~~ 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 Mongolia region of the TNRSF 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~~BVOC 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.

The total annual isoprene emission, summed from annual emissions of the model grids that fall within the TNRSF domain~~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 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 Northern China and 42% of 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^{o}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 (slope=0.881, R^2=0.335) has reversed the negative trend (slope=-0.533~~4~~, R^2=0.05) of the total annual isoprene emissions in Northern China, which did not take the isoprene emissions in the TNRSF into consideration, 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).

Figure 5 presents the gridded trends of the summer~~annual~~ biogenic isoprene

emissions (Eq. 1) across the TNRSF from 1982 to 2010. The summer emission fluxes exhibit similar annual pattern to the annual emissions (**Fig. 4b**) but are 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, ~~there were almost no~~ statistically insignificant ~~trends~~ and relatively weak trends of isoprene emissions were found in the Northeastern China (slope=0.00003, R^2=0.032, p=0.484) and Northwestern China (slope=0.00009, R^2=0.27, p=0.012) regions of the TNRSF, respectively~~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. As shown by **Fig. 4b**, the isoprene emissions in most places of Northeast China show almost no trends in most places of Northeast China. The 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 TNRSF (marked by the red circle in the inner map of **Fig. 1**), a farmland outside the TNRSF (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 extensive and direct measurements of ~~BVOCs~~BVOC emission ~~data~~ across the TNRSF have been ever carried out.~~ reported before~~ Several field campaigns were conducted to measure BVOC emissions in Northern China but these monitoring

programs were not typically 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. ~~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}. While the lower limit of their estimated flux agrees well ~~which were comparable~~ with our ~~results of~~ 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 ~~to~~ (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 result. Song et al. (2012) simulated ~~BVOCs~~BVOC 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 could also ~~likely resulted in~~lead to 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 with sampling frequency of 1 min. Detailed descriptions of these sites and sampling procedures are presented in Methodology section, **Fig. S3**, and Table S4, respectively. Higher TVOC air concentrations were observed at all forest sites than those sites outside 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 (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~~s~~ of 2~~-3~~ higher than the MEGAN2.1 estimated fluxes. Results are presented in Supplementary Materials. ~~Nevertheless, it~~ 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, ~~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 × 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~~ BVOC~~s~~ emissions might be lower.~~were emitted.~~ 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~~. 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 the summertime isoprene was released from biogenic ~~emissions~~ sources ~~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 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 Arneth~~s~~ 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 ~~BVOCs~~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 ~~BVOCs~~BVOC emissions may be even stronger with continuous increase of vegetation coverage till the end of the program in 2050.

While ~~BVOCs~~BVOC emissions vary on short time scales, the global ~~BVOCs~~BVOC 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). Identification of the impact of climate change on ~~Temporal uniformly distributed BVOCs~~ BVOC emissions is not straightforward if regional or global forests reach a steady state. ~~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~~ BVOC emissions via large-scale afforestation exert strong influence on long-term ~~BVOCs~~ 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 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 not 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~~ BVOC emissions 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 since~~in~~ 2007 (Zhang et al., 2013; Tan and Li, 2015), causing ~~considerable~~visible decline of the forest coverage and isoprene emissions in this region after 2007, 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 the Northeast China region did not show considerable change between 1982 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. S7a**), 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~~ In addition, compared with the increasing trend of LAI in the Northeastern China region of the TNRSF (**Fig. S6a**), no statistically significant increasing trends of the isoprene emissions are discerned in this region. **Figure S7b** displays the trend of annual surface air temperatures (SAT, ^{o}C) in the Northeast China region of the TNRSF from 1982 to 2010. Overall the SATs exhibited a decreasing trend, caused mostly by declining SATs since the late 1990s. Since temperature plays a key role in canopy

BVOC emissions (Guenther et al., 2012; Li et al., 2013), the lack of the incline trend of the isoprene emission fluxes in the Northeastern China region of the TNRSF might be attributable to the decreasing SAT from the late 1990s. Another environmental factor that may exert the influence on the trend of isoprene emissions is solar radiation/PAR (Situ et al., 2014). Analogous to the response of the BVOC emissions to temperature, increasing radiation could also enhance the isoprene emissions, or vice versa, particularly on daily or monthly basis.

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~~ BVOC 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 was likely~~has~~ under ~~reached~~ a steady state from which the biogenic isoprene emissions were not altered on the decadal basis (Sanderson et al., 2003; Purves et al., 2004).

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 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~~VOC emissions, particularly on their decadal variation, though the magnitude of emissions might not be higher than that from natural forests in Northeastern 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 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^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 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 on the ~~BVOCs emissions~~BVOC emissions in Northern China 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~~BVOC emissions. The comparison of isoprene emission fluxes among the Central-North China region of the TNRSF, farmland, and the boreal forest in Northeastern 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~~BVOC 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.: 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 observation 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., Pollock, W., Westberg, H., Allwine, G., Geron, C.: Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements, J. Geophys. Res.-Atmos., 101(D1), 1345-1359， 1996.

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).

Klinger, L. F., Li, Q. J., Guenther, A., B., Greenberg， J. P., Baker, B., and Bai, J.: Assessment of volatile organic compound emissions from ecosystems of China, J. Geophy. Res., 107(D21), 4603, doi:10.1029/2001JD001076, 2002..

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.

Wang, Z. H., Bai, Y. H., Zhang, S. Y.: A biogenic volatile organic compounds emission inventory for Beijing, Atmos. Environ. 37, 3771-3782, 2003

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.

Zeman~~Kova,~~ 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, L., Moran, M. D., Makar, P. A., Brook, J. R., and Gong, S.: Modelling gaseous dry deposition in AURAMS: a unified regional air-quality modelling system, Atmos. Environ. 36,537-560, 2002.

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 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 Northern China~~the TNRSF~~.

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

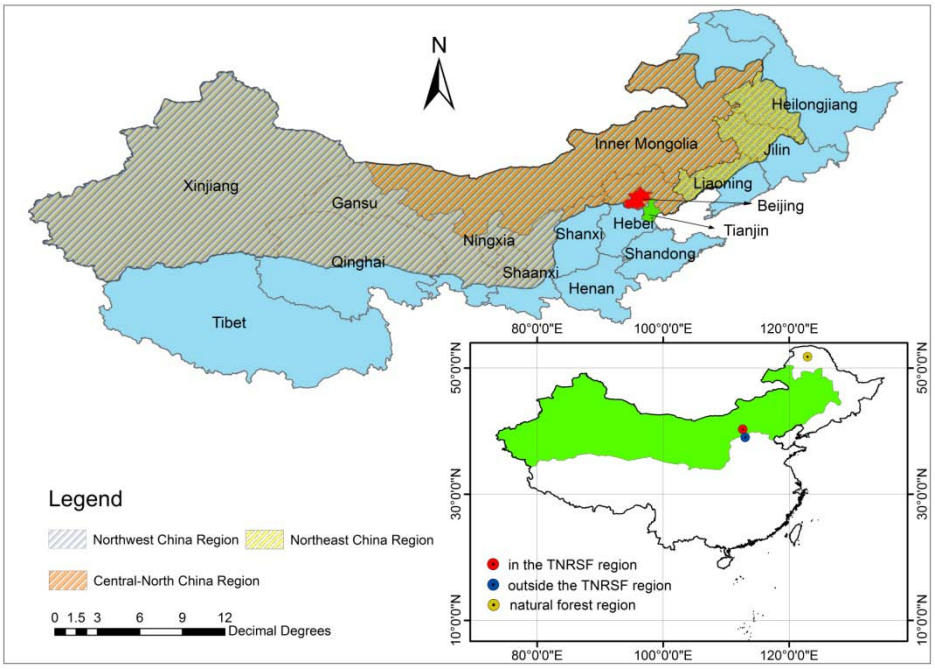

Figure 1

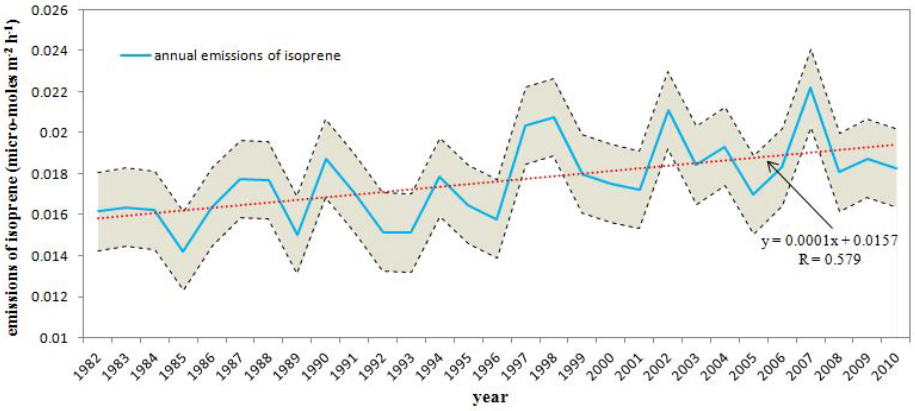

Figure 2

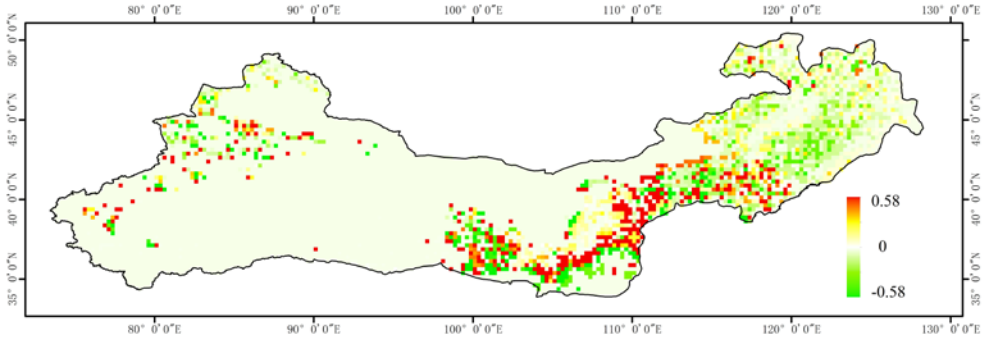

Figure 3

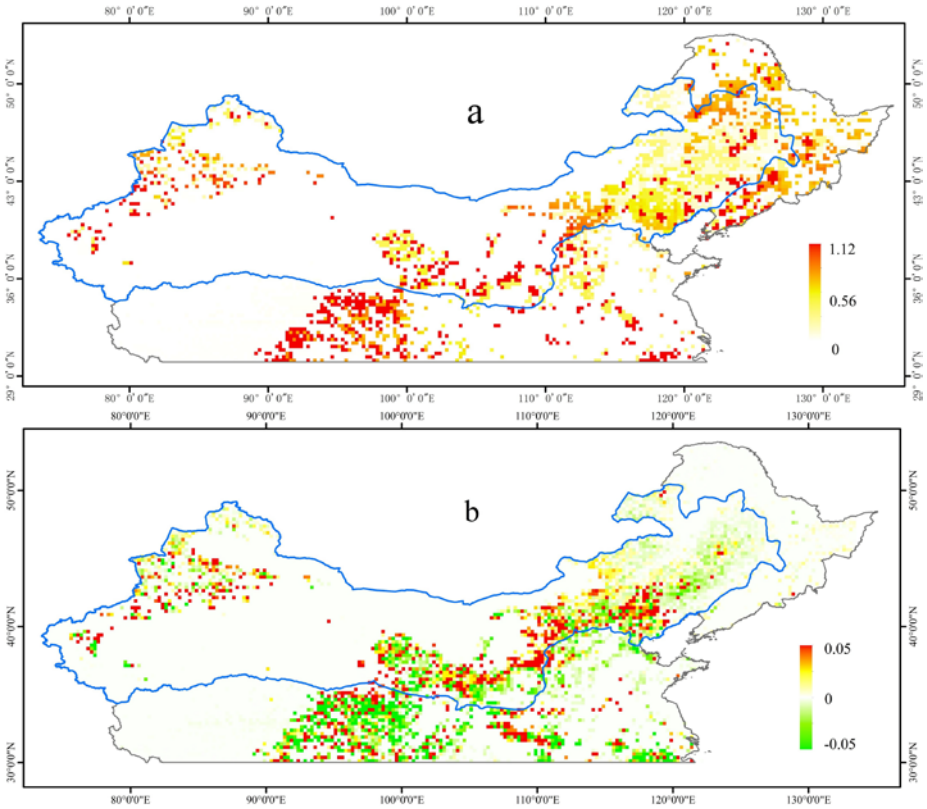

Figure 4

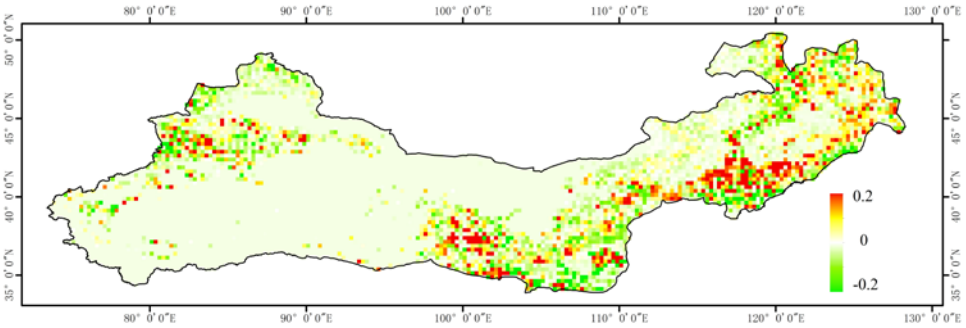

Figure 5

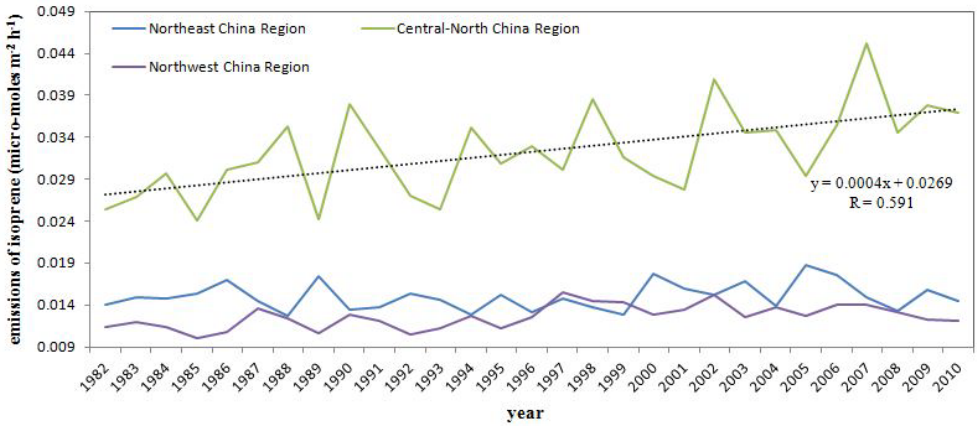

Figure 6

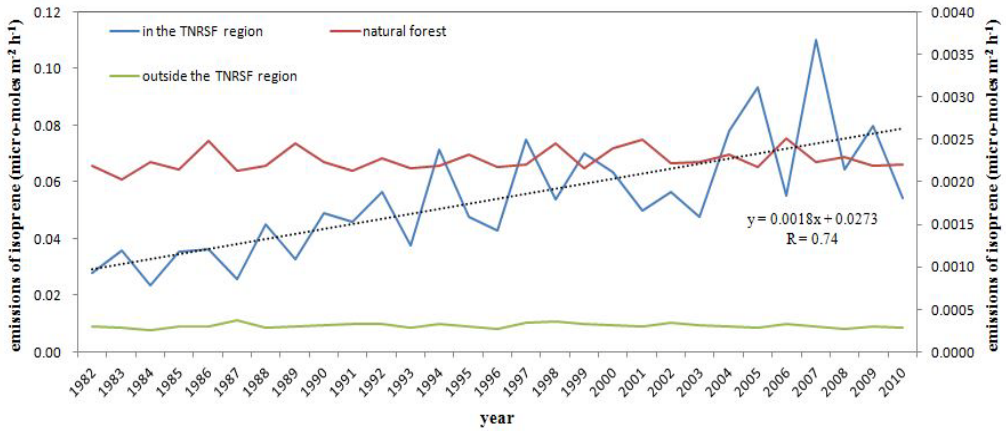

Figure 7

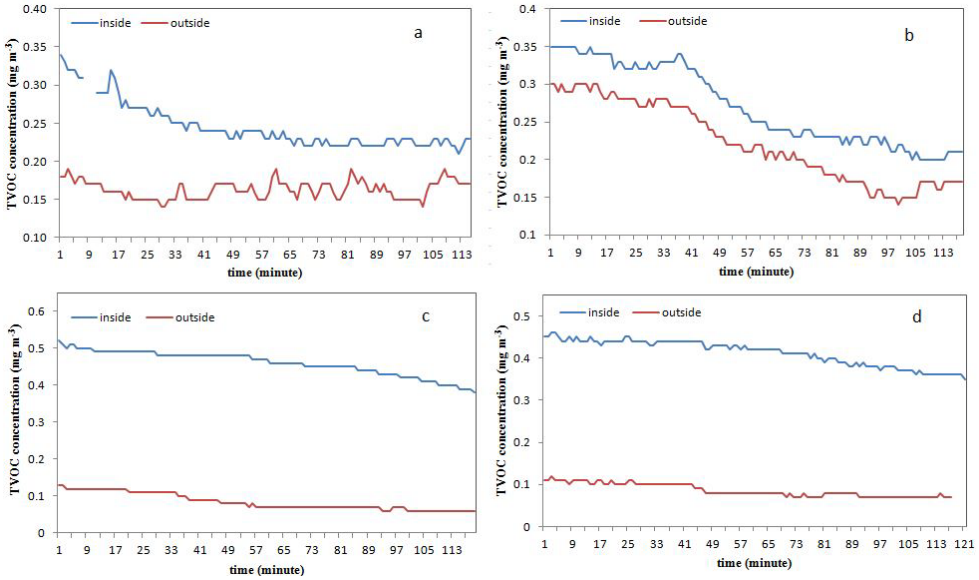

Figure 8