NOTE: This file includes two sections. Section 1 presents comments from referees, the corresponding point-by-point responses, and the related changes in the manuscript. Section 2 is the marked-up manuscript.

Section 1: (the black font are comments from referees, and the red font are authors' responses as well as the related change clarifications.)

(1) Detailed response to comments from referee #1:

General comments :

The study by Sun et al reports the column and partial columns of HCN, a known biomass indicator, along with the column CO from Heifei in China. The authors compare their data with other similar measurements from the NDACC community, and use the standard agreed protocol for retrieve these columns. They derive emission ratios of HCN with respect to CO, and also use back trajectory analyses to trace where the air masses originated. The trajectories from various global sectors are discussed and compared in the context of the seasonality in the HCN to CO enhancements, which the authors conclude is consistent with the same sources. Finally global fire counts are used to show that fires from various sources explain the observed seasonality in the HCN column enhancements.

In general the paper is well written, organised, and follows NDACC recognised analysis procedures. The skill level of this group Heifei is very good, and improves all the time. The paper is therefore recommended for publication in ACP subject to the list of mainly minor corrections, but also a few not so minor points for the authors to correct/address.

Response: This paper has been subjected to a revision based on the comments from two referees. All your comments are appreciated and have been addressed in the revised version. Main changes/improvements are listed as follows:

Specific comments:

1) P2 line 41: replace “in polluted troposphere in eastern China at middle latitude . . .“ with “in the polluted troposphere over eastern China at middle latitudes . . .”

2) P2/3 line 57/1: suggest replacing last sentence on page 2 with “Both HCN and CO are regularly measured at Hefei (32N) using the FTIR observations, where

influences from biomass burning occurring at long distances or locally can be assessed."

3) P3, line 12: ". . . evaluation of global .." => ". . .evaluation of the global . . ."

4) P3, line 30/31: spelt out the "&"

Response: We have done above corrections in the revised version

5) P3 line33: The field stop is employed to maximise the S/N consistent with the maximum frequency possible for the wavenumber range that is selected. Is this is what adapt means? Explain.

Response: We have changed this sentence to "The entrance field stop size ranging from 0.80 to 1.5 mm was employed to maximise the SNR consistent with the maximum frequency possible for the selected wavenumber range."

6) P3 caption of figure 1: what is significant about these star spots? Refer to the text for an explanation (just a simple, see section xx). Even so it is not clear on page 16 where this is mentioned, exactly why these points were chosen. Are they the middle of the selected source regions?

Response: We have included a new Figure 1 in the revised paper, where the star spots are replaced by six rectangles for tagged CO definitions. It looks more clear than the old ones. Please check.

7) P5, fig 2: Why show the averaging kernel plot of HCN with these two layers when the actual partial column used in this study is from 0 to 15 km? HCN has a dof of 1.3 so there are not 2 independent layers, unlike CO. Perhaps it would be better to plot two averaging kernels for HCN, the total column and the 0-15 km layer?

Response: We have done this as your suggestion and plotted two averaging kernels for HCN, the total column and the 0-15 km layer.

8) P5 table 2: I am not sure about the tabulated error for the line intensity for CO and HCN, they seem to be the wrong way around? The reported uncertainty for the line intensity in hitran2008 for CO and HCN is 2-5% and 5-10% respectively. So why is the reported % error for the CO line intensity higher than HCN?

Response: In the error analysis, we assume *a priori* error covariance of line intensity as 5% for both CO and HCN. The error in table 2 randomly selected from all

measurements shown that the resulting % error for the CO line intensity in the troposphere is higher than HCN.

Some remarks should be clarify: 1, the error analysis may site, measurement, and layer dependent. For the selected retrieval, the tropospheric AK uncertainties of CO used for error analysis (Rodgers, 2000) are larger than HCN. 2, the error analysis were performed after retrieval, the error in line intensity estimation for either CO or HCN would not impact the time series and thus would not alter the point of this paper. In the revised version, we still set *a priori* error covariance of line intensity to 5% for both CO and HCN, and don't make any revision.

9) P6 line 16: Combine these sentences to read ". . .September > December, while for the tropospheric CO column, ..."

10) P6 line 18: perhaps "phase" is a better word than "timing"? This word is used elsewhere as well.

Response: We have done above corrections in the revised version

11) P7, line 6: type in the word "Fig. A"

Response: We have moved this figure to supplement. Now Fig.A1 is Fig. S2 in the supplement.

12) P7, line 27: be more specific about what timeframes you are actually comparing, what exactly do you mean by "counterpart"?

Response: In the revised version, the "counterpart" has been replaced by "concurrent". The timeframes of NDACC selected for comparison are the same as that of Hefei. This sentence has been changed to " Enhancements of both tropospheric HCN and CO columns between September 2015 and July 2016 at Hefei (32°N) were observed compared to the measurements in other years."

13) P7, line 32: combine these sentences to read ". . .2016, while. . ."

Response: We have done this in the revised version.

14) P7/8: Maybe summarise all this information in this paragraph in a table? It is otherwise tedious for any reader.

Response: We have condensed all this information to "The enhancements of both tropospheric HCN and CO columns within the same period were also observed at the

selected NDACC stations except Ny Alesund (79°N) and Kiruna (68°N). The winter enhancements were not shown over Ny Alesund (79°N) and Kiruna (68°N) because of the polar night in the Arctic which interrupted the observations in winter. The magnitude of the enhancement in tropospheric HCN column at the selected NDACC stations between September 2015 and July 2016 ranges from 3 to 213%, and for CO ranges from 4 to 62%."

15) P9, line 2,: "proceed" is not the correct word here. Should be something like "using a linear ..."

16) P10, line 28: "seasonal" => "seasonally"

17) P10, line 31: ". . .occurred before the timing of tropospheric HCN enhancements within one month period. Then, we" replace with "occurring before the timing of tropospheric HCN enhancements within a one month period. Finally, we . . ."

Response: We have done above corrections in the revised version.

18) P13, fig 8 caption: What is the ratio in fig 8a, what is being ratioed against what?

Response: In the revised version, this figure has been replaced by Fig. 11.

19) P13, fig 8 caption, line 5: Do you mean the each red dot is a fire over the 10 day period. What is written here implies a fire that occurred 10 days before. So this is cumulative over the 10 days, yes?

Response: Correct. In the revised version, this figure has been replaced by Fig. 11.

20) P14, fig 9b: These plots are really hard to make out. Perhaps explore another way of plotting so it clearly shows the different datasets. My suggestion is to try different plotting symbols as the one you use seem too large.

Response: In the revised version, this figure has been replaced by Figs. 13 and 14. Now it should be more clear.

21) P15, line 13, "Particularly," => "In particular, "

Response: We have done this in the revised version.

22) P16, line 8: "cause"

23) P16, line 15: "lifetimes ..." => "where lifetimes ..."

24) P17, line 7: These numbers from other studies though should be entered as a range in table 5, that is, a column that says "literature values" to give the reader a

sense of where the emission ratios in this study fall.

Response: We have removed this paragraph in the revised version. Instead, a tagged CO simulation was included as response to referee # 2's request. Please check.

(2) Detailed response to comments from referee #2:

General comments :

The authors presented a multi-year timeseries (2015-2018) of HCN partial columns observed at a densely populated Chinese city, Hefei, using a ground-based high spectral resolution Fourier transform infrared (FTIR) spectrometer. CO columns were also presented for comparison. The authors identified the seasonal maxima of tropospheric HCN columns at this site and compared their seasonality and interannual variations to the HCN columns obtained from other NDACC sites. Drivers of HCN seasonality and interannual variations at Hefei were determined through GEOS-Chem tagged CO simulations, as well as the global fire maps and a back-trajectory analysis technique. They also used CO measurements to estimate the HCN/CO emission enhancement ratios to quantify biomass burning emissions.

This version (manuscript-version2) has been significantly improved from the original submission in terms of analysis and presentation. The results are valuable to the community. I suggest some minor corrections, which are detailed below. The authors should perform a thorough proof-reading of the manuscript to further improve the presentation in order to meet the publishing standards of ACP.

Response: This paper has been subjected to a revision based on the comments from two referees. We also perform a thorough proof-reading of the manuscript to further improve the presentation. All your comments are appreciated and have been addressed in the revised version. Main changes/improvements are listed as follows:

Specific comments:

1) Page 1, Line 35: Are these values multi-year mean or are they the maximum values throughout the whole period? Please clarify.

Response: They are monthly means based on multi-year measurements. We have clarified this in the revised version.

2) p2, line 34-35: Could you also point out where these regions are located in China?

Response: In the revised version, we have included a map of China showing the three most developed regions—Jing-Jin-Ji (Beijing-Tianjin-Hebei), Yangtze River Delta (including Shanghai), and Pearl River Delta (including Guangzhou and Hong Kong–Shenzhen) in Fig. S1. It looks more clear than put these regions in the world map in Figure 1.

3) p2, line 53: add "where" before "influences from biomass . . ."

4) p3, line 6: replace "can improve" with "aims to improve"

5) p3, line 17: replace "it is planned to" with "plan to"

6) p3, line 20: replace "a highest" with "the highest"

Response: The above corrections have been done in the revised version.

7) p3, line 22: "to ensure a higher signal to noise . . . and a faster. . ." compared to what?

Response: To avoid misleading, we have changed it to " However, all mid-infrared (MIR) spectra are recorded with a spectral resolution of 0.005 cm^{-1} to follow NDACC convention".

8) p3, line 26-27: can you spell out "&" as appropriate here.

Response: We have done this in the revised version.

9) P4, line 8: change to "Whole-Atmosphere Community Climate Model (WACCM) v6"

Response: We have done this in the revised version.

10) P4, line13-15: spell out all species names when they first appear.

Response: We have done this in the revised version.

11) P4, line 24: did you calculate the tropopause height from the NCEP reanalysis data? If so, replace "deduced" with "calculated".

Response: Yes, and we have done this in the revised version.

12) P5, line 19: please spell out GEOS-FP.

Response: We have done this in the revised version.

13) P6, line 5: the order should be "Global Fire Assimilation System (GFAS) v1.2"

Response: We have done this in the revised version.

14) P6, line 9: change to "period of"

Response: We have done this in the revised version.

15) P6, line 11: Please be consistent in placing acronyms. Should be "the Multi-resolution Emission Inventory for China (MEIC)".

Response: We have done this in the revised version.

16) P6, line 18-19: It is confusing here, as the GEOS-Chem OH shown in Shindell et al. (2006) is lower than the multi-model mean (Table 1). Could you clarify?

Response: We have consulted the GEOS-Chem team at Harvard university during the ACPD phase. The developer told me that what we actually used in this paper was "monthly mean OH concentrations archived from a previous full-chemistry simulation" rather than that used from Shindell et al. (2006). In the revised version, we have changed this sentence to " The OH fields were obtained from monthly mean OH concentrations archived from a previous full-chemistry simulation."

17) P6, line 31-33: this sentence can be modified as "In this study, we only investigate the influence from the biomass burning sources. The regional definition. . ."

Response: We have done this in the revised version.

18) P6: at the beginning of section 2.3, could you briefly say the purpose of using PSCF in this study? Just add some context.

Response: We have done this in the revised version.

19) P7, line 37: delete "total" before "troposphere"

Response: We have done this in the revised version.

20) P8, line 6-10: these few lines can be re-organised to make the statements clearer. For example, "Note that the largest seasonal peak of HCN occurs in May which is 3 months later than that of CO which occurs in February, but the other two seasonal peaks for both species occur in the same months, i.e., in September and December respectively. Otherwise, their seasonal cycles show similarities."

Response: We have done this in the revised version.

21) P10, line 11-17: could you elaborate a bit more on possible mechanisms why correlations between CO and HCN are negative or weak at these sites, especially at Bremen? Have you checked the seasonal correlation between CO and HCN at Bremen?

Response: Actually, here are the overall correlations by using all measurements from 2015 to 2018. We have doubled check the programing script for this figure, and found that all fittings are correct. We have included more explanations in the revised paper, i.e., "Biomass burning is the dominant source of HCN and industrial emissions only contribute additional minor sources (Bange and Williams, 2000; Holzinger et al., 1999; Lobert et al., 1990). In contrast, anthropogenic, biomass burning, CH_4 and NMVOC oxidations are major sources of CO, and their contributions are season and location dependent. Therefore, the correlation between HCN and CO tropospheric column is also season and site dependent. High correlation of these two species is supposed to be observed if biomass burning dominates the CO variability, and vice visa."

22) P10, line 24: how about ". . .is an effective quantity to identify biomass burning emissions. . ."?

23) P10, line 31: should be "indicating that these. . ."

24) P10, line 32: change to "throughout the year"

25) P11, line 1: change to "is located . . ., therefore emissions. . ."

26) P14, line 22: change to "both the first and the second half of the year"

27) P14, line 24: change to "in the second half of the year"

28) P14, line 25: same as above "in the first half of the year"

29) P14, line 27: change to "As shown in Figs. . ."

30) P14, line 34: replace "Drives" to "Driven"

31) P15, line 3: "meteorological conditions"

32) P15, line 7-8: change to "through large-scale atmospheric circulation"

33) P17, line 2: replace "driven" with "drove"

Response: We have done above corrections in the revised version.

34) P17, first paragraph: Are these elevated fire counts related to ENSO? Can you discuss the possible ENSO link here, rather than at the end of the section?

Response: We have moved the last paragraph here and analyzed the possible ENSO link. "Many studies have revealed that the El Niño Southern Oscillation (ENSO) can cause large scale variations in the convection, circulation, and air temperature of the global atmosphere-ocean system (Liu et al., 2017; Zhao et al., 2002), which could

affect the distribution, frequency, and intensity of biomass burning emissions (Schaefer et al., 2018). Furthermore, ENSO could also alter the destruction processes of tropospheric species through their photochemical reactions with tropospheric OH (Zhao et al., 2002). Zhao et al. (2002) found that the abnormally enhancement of tropospheric CO and HCN observed in northern Japan in 1998 were associated with the 1997–1998 ENSO events (Zhao et al., 2002). There is a close correlation between ENSO and HCN columns at Lauder (45°S) (Zeng et al., 2012; Schaefer et al., 2018), and Schaefer et al. (2018) quantified a detectable ENSO influence on biomass burning of up to 51-55% (Schaefer et al., 2018; Zeng et al., 2012). Very likely, the elevated fire counts which caused significant enhancements between September 2015 and July 2016 for tropospheric CO and HCN columns at Hefei and most selected NDACC stations were related to the 2015 – 2016 ENSO events."

35) P17, lines 28: should it be "Zhao et al. (2000) or (2002)" here?

Response: We have changed it to Zhao et al (2002).

36) P17, line 30-31: please re-phrase this sentence as "There is a close correlation between ENSO and HCN columns at Lauder (45^{o}S) (Zeng et al., 2012; Schaefer et al., 2018), and Schaefer et al. (2018) quantified a detectable ENSO influence on biomass burning of up to 51-55%".

37) P17, line 32: replace "presumably" with "very likely".

38) P17, line 37: delete "amounts" and "s" to "HCN column"

Response: We have done above corrections in the revised version.

39) In Conclusion, could you provide some further remarks on the long-term outlook of FTIR observations at this site.

Response: In the revised version, we have included the sentence "Most high resolution FTIR instruments are located in Europe and Northern America, whereas the number of sites in Asia, Africa, and South America is very sparse. As one of few FTIR stations on Asian continent, the long-term observations of trace gases at Hefei are crucial to understand global warming, regional pollution, long term transport, and contribute to the evaluation of satellite data and model simulations."

Section 2: marked up file, as follows

In briefly, we have revised the paper based on referees' comments, and tried our best

to improve the language problem.The marked up file is as follow, please check the red sentences for details:

FTIR time series of tropospheric HCN in eastern China: seasonality, interannual variability and source attribution

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Abstract:

We analyzed seasonality and interannual variability of tropospheric HCN columns in densely populated eastern China for the first time. The results were derived from solar absorption spectra recorded with ground-based high spectral resolution Fourier transform infrared (FTIR) spectrometer at Hefei (117°10′E, 31°54′N) between 2015 and 2018. The tropospheric HCN columns over Hefei, China showed significant seasonal variations with three monthly mean peaks throughout the year. The magnitude of the tropospheric HCN column peak in May > September > December. The tropospheric HCN column reached a maximum monthly mean of (9.8 ± 0.78) × 10^{15} molecules/cm^2 in May and a minimum monthly mean of (7.16 ± 0.75) × 10^{15} molecules/cm^2 in November. In most cases, the tropospheric HCN columns at Hefei (32°N) are higher than the FTIR observations at Ny Alesund (79°N), Kiruna (68°N), Bremen (53°N), Jungfraujoch (47°N), Toronto (44°N), Rikubetsu (43°N), Izana (28°N), Mauna Loa (20°N), La Reunion Maido (21°S), Lauder (45°S), and Arrival Heights (78°S) that are affiliated with the Network for Detection of Atmospheric Composition Change (NDACC). Enhancements of tropospheric HCN column were

observed between September 2015 and July 2016 compared to the same period of measurements in other years. The magnitude of the enhancement ranges from 5 to 46% with an average of 22%. Enhancement of tropospheric HCN (ΔHCN) is correlated with the concurrent enhancement of tropospheric CO (ΔCO), indicating that enhancements of tropospheric CO and HCN were due to the same sources. The GEOS-Chem tagged CO simulation, the global fire maps and the Potential Source Contribution Function values (PSCFs) calculated using back trajectories revealed that the seasonal maxima in May is largely due to the influence of biomass burning in South Eastern Asia (SEAS) (41 ± 13.1%), Europe and Boreal Asia (EUBA) (21 ± 9.3%) and Africa (AF) (22 ± 4.7%). The seasonal maxima in September is largely due to the influence of biomass burnings in EUBA (38 ± 11.3%), AF (26 ± 6.7%), SEAS (14 ± 3.3%), and Northern America (NA) (13.8 ± 8.4%). For the seasonal maxima in December, dominant contributions are from AF (36 ± 7.1%), EUBA (21 ± 5.2%), and NA (18.7 ± 5.2%).The tropospheric HCN enhancement between September 2015 and July 2016 at Hefei (32°N) were attributed to an elevated influence of biomass burnings in SEAS, EUBA, and Oceania (OCE) in this period. In particular, an elevated fire number in OCE in the second half of 2015 dominated the tropospheric HCN enhancement in September – December 2015. An elevated fire number in SEAS in the first half of 2016 dominated the tropospheric HCN enhancement in January – July 2016.

1 Introduction

Atmospheric hydrogen cyanide (HCN) is an extremely hazardous gas that threaten human health and terrestrial ecosystems (Andreae and Merlet, 2001; Akagi et al., 2011; Rinsland et al., 2002). Improved knowledge of the physical and chemical mechanisms which drive the observed HCN variability is of great significance because HCN plays an important role in the global nitrogen cycle (Andreae and Merlet, 2001; Li et al., 2003). It is well established that biomass burning is the major source of tropospheric HCN and industrial emissions contribute additional minor sources of HCN (Bange and Williams, 2000; Holzinger et al., 1999; Lobert et al., 1990). Li et al. (2009) estimates a global source of HCN from biomass burning of 0.4 – 3.2 Tg N yr^{-1} and from burning domestic biofuel of 0.2 Tg N yr^{-1} (Li et al., 2009). Bertschi et al. (2003) estimates a global fossil fuel combustion source of 0.04 Tg N yr^{-1}, negligibly small in comparison (Bertschi et al., 2003). The principle pathway for HCN sink is ocean uptake which accounts for 0.73 to 1.0 Tg N/year (Li et al., 2009). Additional minor sinks of HCN are attributed to atmospheric reaction with hydroxyl radical (OH) and $O(^1D)$, and photolysis (Li et al., 2000; Nagahama and Suzuki, 2007). The life time of HCN is 2 – 5 months in the troposphere and several years in the stratosphere. Li et al. (2003, 2009), Lupu et al. (2009), Vigouroux et al. (2012), and Zeng et al. (2012) showed that the observed variability of HCN can be reproduced by the chemical model simulations where biomass burning and ocean uptake provide the main source and sink, respectively (Li et al., 2009; Li et al., 2003; Lupu et al., 2009; Vigouroux et al., 2012; Zeng et al., 2012).

With the rapid economic growth in China over the past three decades, the anthropogenic emissions have increased dramatically, raising concerns about worsening air quality in China (Tang et al., 2012; Chan, 2017; Xing et al., 2017; Wang et al., 2017). These emissions are from automobile exhaust, industrial processes and biomass burning. Many researchers have evaluated regional emissions in various pollution regions (e.g., the Jing-Jin-Ji region, the Yangtze River Delta region, and the Pearl River Delta region, Fig. S1), but the relative contribution of the biomass burning, automobile exhaust, and industrial processes is seldom mentioned in the literature (Tang et al., 2012; Chan, 2017; Wang et al., 2017; Sun et al., 2018a; Xing et al., 2017). This is because both industrial emissions and biomass burning are major sources of the trace gases (e.g. carbon monoxide (CO), formaldehyde (HCHO) and carbon dioxide (CO_2)) that were used to evaluate regional emissions in the literature, and it is hard to quantify their relative contribution under the complex pollution condition in China (Chan et al., 2018; Tang et al., 2012; Wang et al., 2017; Xiaoyan et al., 2010; Xing et al., 2017). It has been proved that HCN is an unambiguous tracer of biomass burning emission due to its inactive chemical feature and long lifetime (Rinsland et al., 2002; Zhao et al., 2002). Therefore, measurements of HCN made in the polluted troposphere over eastern China at middle latitudes are particularly useful in determining the potential biomass burning sources that drive the observed tropospheric HCN seasonality and interannual variability in China.

Ground based high-resolution Fourier Transform Spectroscopy (FTIR) measurements of trace gases made by Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences

(AIOFM-CAS) at Hefei (117°10′E, 31°54′N, 30 m a.s.l. (above sea level)) is one of few multiyear time series of trace gases on Asian continent (Sun et al., 2018a; Sun et al., 2018b). These measurements are crucial to understanding global warming, regional pollution, and long term transport. Both HCN and CO are regularly measured at Hefei (32°N) using the FTIR observations, where influences from biomass burning occurring at long distances or locally can be assessed.

In this study, we analyze the first multiyear measurements of tropospheric HCN in densely populated eastern China. In section 2 the retrieval strategy to derive HCN from high resolution FTIR spectrometry and the methods for a GEOS-Chem tagged CO simulation and potential source contribution function (PSCF) calculation are summarized. In section 3 we present the seasonal and interannual variability of tropospheric HCN columns measured at Hefei (32° N), China and comparisons with the measurements affiliated with Network for Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org/, last accessed on 3 June 2019). The potential sources that drive the observed HCN variability are determined by using the GEOS-Chem tagged CO simulation, the global fire maps and the PSCFs analysis in section 4. The work concludes with a summary in section 5. This study aims to improve our understanding of regional biomass burning characteristic and transport, and contribute to the evaluation of the global nitrogen cycle.

2 Methods

2 FTIR observations

2.1.1 Site description and instrumentation

The routine observations of atmospheric trace gases using ground based high-resolution FTIR spectrometer at Hefei (117°10′E, 31°54′N, 30 m a.s.l.) started in July 2014. Location of Hefei site alongside those of the NDACC FTIR stations selected for comparison are shown in Fig.1. Geographical source regions used in the standard GEOS-Chem tagged CO simulation are also marked in Fig.1. Detailed description of Hefei site can be found in Tian et al., 2017. We follow the NDACC requirements, and plan to apply for acceptance within the NDACC in the future.

A Bruker IFS 125 HR with maximum optical path difference (OPD) of 900 cm is used to take the solar spectra (Tian et al., 2017). Defined as 0.9/OPD, this instrument can reach the highest spectral resolution of 0.001 cm^{-1}. However, all mid-infrared (MIR) spectra are recorded with a spectral resolution of 0.005 cm^{-1} to follow NDACC convention. This spectral resolution is sufficient to resolve the optical absorption structure of all gases in the atmosphere. The FTIR spectrometer covered a wide spectral range (about 600 – 4500 cm^{-1}) but, depending on the species, specific detectors and band-pass filters are applied (Sun et al. 2018a). In this study, the instrument is equipped with a KBr beam splitter, an InSb detector, and a filter centered at 2900 cm^{-1} for HCN measurements, and a KBr beam splitter, an InSb detector, and a filter centered at 2400 cm^{-1} for CO measurements. The entrance field stop size ranging from 0.80 to 1.5 mm was employed to maximise the signal to noise ratio (SNR) consistent with the maximum frequency possible for the selected wavenumber range. The number of measurements within a day varies from 1 to 20. In total, there were 651 and 649 days of qualified measurements between 2015 and 2018 for CO and HCN, respectively.

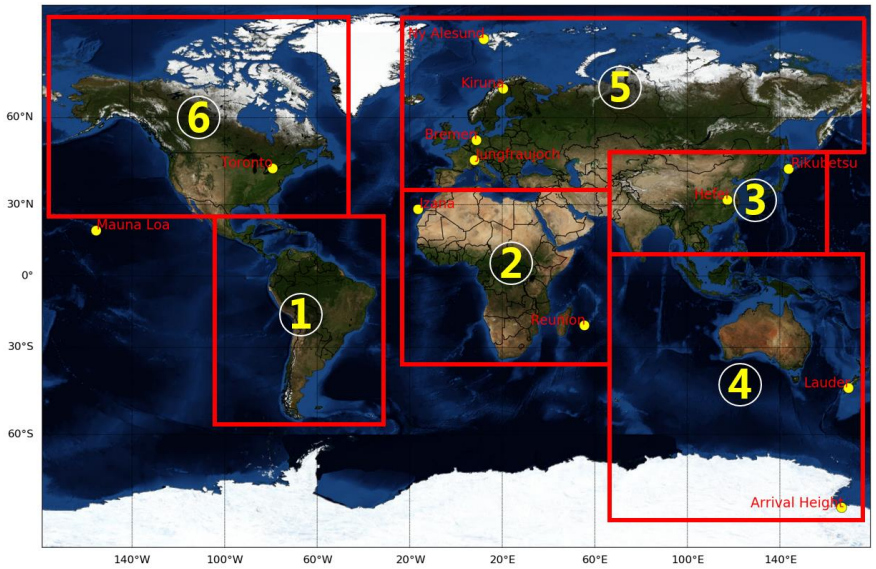

Fig. 1 Location of Hefei site alongside those of the NDACC FTIR stations (yellow dots) that are selected for comparison. Geographical source regions used in the standard GEOS-Chem tagged CO simulation are also shown. See Table 3 for latitude and longitude definitions

2.1.2 Retrieval strategy

The SFIT4 (version 0.9.4.4) algorithm is used to retrieve the vertical profiles of CO and HCN (Viatte et al., 2014). Both CO and HCN are standard NDACC species, and we follow the NDACC recommendation for micro windows (MWs) selection and the interfering gases consideration (http://www.ndaccdemo.org/, last accessed on 23 May 2019). The retrieval inputs for CO and HCN are summarized in Table 1. Time series of tropospheric CO columns between 2014 and 2017 at Hefei (32°N) measured from the FTIR have been reported in Sun et al. (2018a) and the detailed description of CO profile retrieval can be found therein. Time series of tropospheric HCN columns at Hefei (32°N) are presented for the first time. Temperature and pressure profiles are extracted from National Centers for Environmental Protection (NCEP) 6-hourly reanalysis data (De Maziere et al., 2018) and all spectroscopic absorption parameters are prescribed from HITRAN 2008 database (Rothman et al., 2009). The water vapor (H_2O) *a priori* profile is interpolated from the NCEP 6-hourly reanalysis data and a priori profiles of other gases are from the Whole-Atmosphere Community Climate Model (WACCM) v6 special run for NDACC.

Three MWs were used for CO: a strong line at 2057.7–2058 cm^{-1} and two weak lines at 2069.56–2069.76 cm^{-1} and 2157.5–2159.15 cm^{-1} (Sun et al., 2018a). For HCN, two MWs were used: 3268.00 – 3268.38 cm^{-1} and 3287.00 – 3287.48 cm^{-1} (Mahieu et al., 1997; Lutsch et al., 2016; Notholt et al., 2000). In order to minimize the cross absorption interference, profiles of ozone (O_3) and nitrous oxide (N_2O) and columns of H_2O, carbonyl sulfide (OCS) and CO_2 are simultaneously retrieved in addition to the CO profile. Profile of H_2O and columns of O_3, C_2H_2, and CH_4 are simultaneously retrieved in addition to the HCN profile. No de-weighting SNR is used for HCN and a de-weighting SNR of 500 is used in the three MWs for CO.

The diagonal elements of *a priori* profile covariance matrices $\mathbf{S}_a$ are set to standard deviation of the WACCM v6 special run for NDACC, and its non-diagonal elements are set to zero. The diagonal elements of the measurement noise covariance matrices $\mathbf{S}_\varepsilon$ are set to the inverse square of the SNR calculated from each individual spectrum and its non-diagonal elements are set to zero. The measured instrument line shape (ILS) is included in the retrieval (Hase, 2012; Sun et al., 2018a).

Table 1. Retrieval inputs used for CO and HCN.

Gases	CO	HCN
Code	SFIT4 v 0.9.4.4	SFIT4 v 0.9.4.4
Spectroscopic parameters	HITRAN 2008	HITRAN 2008
P, T, H_2O profiles	NCEP reanalysis data	NCEP reanalysis data
A priori profiles of all gases except H_2O	WACCM v6	WACCM v6
Micro windows for profile retrievals (cm^{-1})	2057.7 – 2058 2069.56–2069.76	3268.00 – 3268.38 3287.00–3287.48

	2157.5–2159.15	
Retrieved interfering gases	O_3, N_2O, CO_2, OCS, H_2O	H_2O, O_3, C_2H_2, CH_4
SNR for de-weighting	500	None
$\mathbf{S}_a$	WACCM v6 standard deviation	WACCM v6 standard deviation
$\mathbf{S}_\varepsilon$	SNR calculated from each individual spectrum within 2526.23 – 2526.62	SNR calculated from each individual spectrum within 3381.16 – 3381.54
ILS	LINEFIT145 analysis	LINEFIT145 analysis
Error analysis	Systematic error: line intensity, line pressure broadening, line temperature broadening, solar zenith angle, background curvature, solar line strength, optical path difference, field of view, phase	
	Random error: -Measurement error -Smoothing error -Interference errors: interfering species, retrieval parameters - Other errors: zero level, temperature	

2.1.3 Averaging kernels and error budget

The partial column averaging kernels of CO and HCN at selected layers are shown in Fig. 2. The CO averaging kernels have three maxima at the surface, 7 km, and 14 km, respectively. The HCN averaging kernels only have one maxima at 10 km. Both CO and HCN retrievals show good vertical sensitivity in the whole troposphere where CO exhibits the best sensitivity with two maxima in the troposphere (Sun et al., 2018a). We can see in Table 2, the typical degrees of freedom (DOFS) obtained at Hefei (32°N) over the total atmosphere for CO and HCN are about 2.8 ± 0.3 (1σ) and 1.3 ± 0.2 (1σ), respectively. In this study, only partial columns of CO and HCN within a broad layer between surface and 15 km are considered. The selected layer corresponds roughly to the total troposphere over eastern China, as the mean tropopause height calculated from NCEP reanalysis data is around 15 km over four seasons. The selected layer corresponds to 2.3 ± 0.2 (1σ) and 1.0 ± 0.1 (1σ) of DOFS for CO and HCN, respectively.

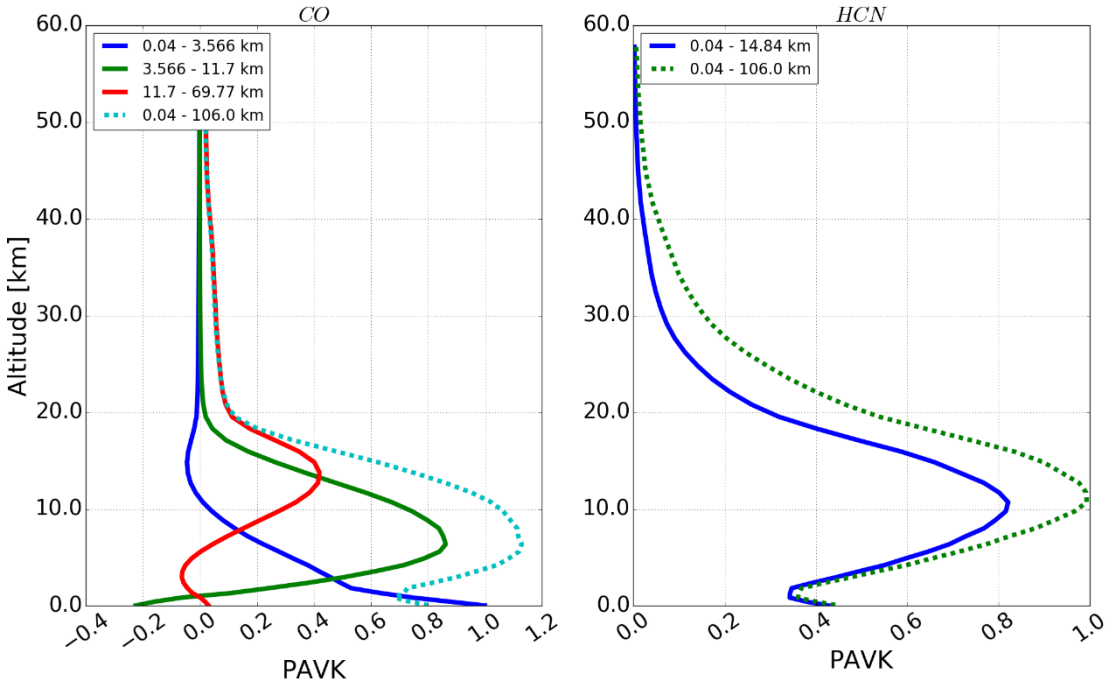

Fig. 2 Partial column averaging kernels (PAVKs) (ppmv / ppmv) for CO and HCN retrievals.

We calculated the error budget following the formalism of Rodgers, 2000, and separated all error items into systematic error or random error depending on whether they are constant over consecutive measurements, or vary randomly. Table 2 summarizes the random, the systematic, and the combined error budget of tropospheric CO and HCN columns. The error items included in the error budget are listed in Table 1. For CO, the major systematic error is line intensity uncertainty, and the major random error are zero level uncertainty and temperature uncertainty. For HCN, the major systematic error are line intensity uncertainty and line pressure broadening uncertainty, the major random error are smoothing error and measurement error. Total retrieval errors for tropospheric CO and HCN columns between surface and 15 km are estimated to be 8.3 and 14.2%, respectively.

Table 2. Retrieval error budgets and DOFs for tropospheric CO and HCN.

Gases	CO	HCN
Temperature uncertainty	2.5%	0.2%
Zero level uncertainty	5.2%	1.5%
Retrieval parameters uncertainty	< 0.1%	2.0%
Interfering species uncertainty	< 0.1%	1.3%
Measurement Error	< 0.1%	6.8%
Smooth Error	0.1%	11.0%
Total Random Error	5.7%	13.2%
Background curvature uncertainty	< 0.1%	*
Optical path difference uncertainty	< 0.1%	< 0.1%
Field of view uncertainty	< 0.1%	< 0.1%
Solar line strength uncertainty	< 0.1%	< 0.1%
Phase uncertainty	*	< 0.1%
Solar zenith angle uncertainty	0.1%	< 0.1%
Line temperature broadening uncertainty	0.13%	0.3%
Line pressure broadening uncertainty	0.87%	3.5%
Line intensity uncertainty	6.0%	3.7%
Total Systematic Error	6.1%	5.1%
Total Errors	8.3%	14.2%
DOFS (-)	2.2	1.0

* Not included into error budget since they are retrieved together with the target gas

2.2 GEOS-Chem tagged simulation

To interpret the influence of biomass burning sources on HCN columns at Hefei (32°N), the GEOS-Chem chemical transport model is used (http://geos-chem.org/; Bey et al., 2001b) in a tagged simulation of CO at a horizontal resolution of 2°×2.5° with 47 vertical hybrid levels. GEOS-Chem version 12.2.1 was used and driven by the Goddard Earth Observing System-Forward Processing product (GEOS-FP) assimilated meteorological data observations from the NASA Global Modeling and Assimilation Office (GMAO). For driving the GEOS-Chem model, the GEOS-FP meteorological data with a native horizontal resolution of 0.25° latitude × 0.3125° longitude were downgraded to 2° latitude × 2.5° longitude and a vertical resolution of 72 hybrid levels (extending from surface to 0.01 hPa). The temporal resolution of surface variables and boundary layer height are 1hr and other variables are 3 hr.

The GEOS-Chem simulation was initialized with a 1-year spin-up from July 2014 to July 2015. Chemical and transport operator time-steps of 1 hr and 10 min, respectively, were used. Biomass burning emissions are from Global Fire Assimilation System (GFAS) v1.2 (Kaiser et al., 2012; Giuseppe et al., 2018; Erik et al, 2019) which assimilates Moderate Resolution Imaging Spectroradiomter (MODIS) burned area and fire radiative power (FRP) products to estimate emissions for open fires. GFASv1.2 emissions have a 0.1◦×0.1◦ horizontal resolution with 3-hourly temporal resolution. GFAS was chosen for the availability of emissions over the analysis period of 2015 - 2018. Global anthropogenic and biofuel emissions are from the Community Emissions Data System (CEDS) inventory (Hoesly et al., 2018). In particular, the latest Multi-resolution Emission Inventory for China (MEIC) is used to provide Chinese anthropogenic emissions (Li et al., 2017). Biogenic emissions of precursor VOCs are from the Model of Emissions of Gases and Aerosols from Nature (MEGANv2.1; Guenther et al., 2012) and biofuel emissions are taken from Yevich and Logan (2003). The main loss mechanism for CO is from photochemical oxidation by the hydroxyl radical (OH). The OH fields were obtained from monthly mean OH concentrations archived from a previous full-chemistry simulation. Surface emissions in GEOS-Chem are released within the boundary layer, and boundary layer mixing is implemented using the non-local mixing scheme of Holtslag and Boville (1993). Biomass emissions are released by uniformly distributing emissions from the surface to the mean altitude of maximum injection based on the injection height information as described in Rémy et al. (2017) which includes an injection height parameterization by Sofiev et al. (2012) and a plume rise model by Freitas et al. (2007).

GEOS-Chem version 12.2.1 tagged CO simulation includes the improved secondary CO production scheme of Fisher et al. (2017), which assumes production rates of CO from CH_4 and NMVOC (non-methane volatile organic compounds) oxidation from a GEOS-Chem full-chemistry simulation therefore reducing the mismatch between the CO-only simulation and the full-chemistry simulation.

The tracers of anthropogenic, biomass burning, CH_4 and NMVOC oxidations are implemented following the standard GEOS-Chem tagged CO simulation (Giglio et al., 2013). In this study, we only investigate the influence from the biomass burning sources. The regional definition of all biomass burning tracers are shown in Fig. 1 and tabulated in Table 3.

Table 3. Regional definitions of all biomass burning tracers implemented in the standard GEOS-Chem tagged CO simulation

No.	Tracer	Description	Region
1	SA	Biomass burning CO emitted over South America	112.5°W - 32.5°W; 56°S - 24°N
2	AF	Biomass burning CO emitted over Africa	17.5°W -70.0°E; 48.0°S - 36.0°N
3	SEAS	Biomass burning CO emitted over Southeast Asia	70.0°E - 152.5°E; 8.0°N - 45.0°N
4	OCE	Biomass burning CO emitted over Oceania	70.0°E - 170.0°E; 90.0°S - 8.0°N
5	EUBA	Biomass burning CO emitted over Europe and Boreal Asia	17.5°W - 72.5°E; 36.0°N - 45.0°N and 17.5°W - 172.5°E; 45.0°N - 88.0°N
6	NA	Biomass burning CO emitted over North America	173°W - 50°W; 24.0°N - 88.0°N

2.3 Potential source contribution function

We used the potential source contribution function (PSCF) analysis method to identify air masses associated with high levels of air pollutants. The PSCF assumes that back trajectories arriving at times of higher concentrations likely point to the more significant pollution directions (Ashbaugh et al., 1985). PSCF has been applied in many studies to locate air masses associated with high levels of air pollutants (Kaiser et al., 2007; Dimitriou and Kassomenos, 2015; Yin et al., 2017). In this study, PSCF values were calculated using back trajectories that were calculated by HYSPLIT. The top of the model was set to 10 km. The PSCF values for the grid cells in the study domain were based on a count of the trajectory segment that terminated within each cell (Ashbaugh et al., 1985). The number of endpoints that fall in the ij^{th} cell is designated n_{ij}. The number of endpoints for the same cell having arrival times at the sampling site corresponding to concentrations higher than an arbitrarily set criterion is defined to be m_{ij}. In this study, we calculated the PSCF values based on trajectories corresponding to concentrations that exceeded the monthly mean level of tropospheric HCN column during measurement. The PSCF value for the ij^{th} cell is then defined as:

$$PSCF_{ij} = m_{ij}/n_{ij} \quad (1)$$

The PSCF value can be interpreted as the conditional probability that the concentrations of a given analyte greater than the criterion level are related to the passage of air parcels through the ij^{th} cell during transport to the receptor site. That is, cells with high PSCF values are associated with the arrival of air parcels at the receptor site that have concentrations of the analyte higher than the criterion value. These cells are indicative of areas of 'high potential' contributions for the constituent.

Identical $PSCF_{ij}$ values can be obtained from cells with very different counts of back-trajectory points (e.g., grid cell A with m_{ij} = 400 and n_{ij} = 800 and grid cell B with m_{ij} = 4 and n_{ij} = 8). In this extreme situation grid cell A has 100 times more air parcels passing through than grid cell B. Because of the sparse particle count in grid cell B, the PSCF values are more uncertain. To account for the uncertainty due to low values of n_{ij}, the PSCF values were scaled by a weighting function W_{ij} (Polissar et al., 1999). The weighting function reduced the PSCF values when the total number of endpoints in a cell was less than approximately 3 times the average value of the end points per cell. In this case, W_{ij} was set as follows:

$$W_{ij} = \begin{cases} 1.00 & n_{ij} > 3N_{ave} \\ 0.70 & 3N_{ave} > n_{ij} > 1.5N_{ave} \\ 0.42 & 1.5N_{ave} > n_{ij} > N_{ave} \\ 0.05 & N_{ave} > n_{ij} \end{cases} \quad (2)$$

where *Nave* represents the mean n_{ij} of all grid cells. The weighted PSCF values were obtained by multiplying the original PSCF values by the weighting factor.

3 FTIR time series and comparisons with NDACC counterparts

The new HCN data are compared with the concurrent measurements regularly measured at eleven NDACC stations to investigate the representativeness of the observation site at Hefei (32°N) in polluted eastern China. These NDACC stations cover over a wide latitude range from 77.8°S to 78.9°N and a wide longitude range from 79°W to 170°E (http://www.ndaccdemo.org/, last access on 19 July 2019). Most of these NDACC stations use the same instrument and retrieval algorithm as those of Hefei (32°N). Alternatively, the high resolution spectrometers Bruker 125M, 120HR, or Bomem DA8 and the retrieval algorithm PROFFIT are used in other stations. It has been demonstrated that the profiles derived from these different instruments and algorithms are in excellent agreement (Hase et al., 2004; De Maziere et al., 2018). In addition, we show the time series of tropospheric CO columns, also measured with FTIR spectrometer, because we will discuss the correlation between HCN and CO, and quantify the influence of biomass burning sources on HCN columns at Hefei (32°N) by using a tagged CO simulation. The upper limit of 15 km is above the tropopause at most of the NDACC stations. For most NDACC stations, the surface – 15 km layer is a mixture of troposphere and a part of stratosphere. However, we did not find major changes in the results of this study when choosing a lower upper limit such as 12 km. Thus we have chosen the same upper limits for all stations. The geolocations of all FTIR stations and their seasonal maximum, minimum and variabilities are summarized in Table 4.

Table 4. Tropospheric HCN and CO columns at Hefei (32°N), China from 2015 to 2018 alongside those of the NDACC FTIR stations. All stations are organised as a function of decreasing latitude.

Station	Location (Lon., Lat., Alt. in km)	Instrument	Algorithm	Maximum (molecules cm^{-2})		Minimum (molecules cm^{-2})	
				HCN (10^{15})	CO (10^{18})	HCN (10^{15})	CO (10^{18})
Ny Alesund	(12°E, 79°N, 0.02)	125HR	SFIT4	5.94± 1.20 (August)	2.11 ± 0.11 (March)	3.75 ± 0.37 (March)	1.56 ± 0.12 (July)
Kiruna	(20°E, 68°N, 0.42)	125HR	PROFFIT	5.81 ± 0.58 (August)	2.1 ± 0.01 (January)	2.43 ± 0.27 (January)	1.45 ± 0.09 (July)
Bremen	(9°E, 53°N, 0.03)	125HR	SFIT4	6.11 ± 0.87 (August)	2.32 ± 0.13 (March)	2.85 ± 0.25 (January)	1.63 ± 0.19 (July)
Jungfraujoch	(8°E, 46.5°N, 3.58)	125HR	SFIT4	4.68 ± 0.63 (May)	1.14 ± 0.08 (March)	2.1 ± 0.29 (February)	0.88 ± 0.08 (July)
Toronto	(79°W, 44°N, 0.17)	Bomem DA8	SFIT4	5.92 ± 1.13 (May)	2.19 ± 0.15 (April)	3.12 ± 1.02 (November)	1.74 ± 0.1 (October)
Rikubetsu	(144°E, 43°N, 0.38)	125HR	SFIT4	7.0 ± 1.92 (May)	2.32 ± 0.31 (March)	2.86 ± 0.44 (February)	1.79 ± 0.14 (October)
Hefei	**(117°E, 32°N, 0.03)**	**125HR**	**SFIT4**	**9.8 ± 0.78 (May)**	**3.38 ± 0.43 (February)**	**7.16 ± 0.75 (November)**	**2.29 ± 0.48 (July)**
Izana	(16°W, 28°N, 2.37)	125HR	PROFFIT	5.33 ± 1.2 (May)	1.41 ± 0.14 (April)	2.59 ± 0.28 (October)	1.1 ± 0.08 (October)
Mauna Loa	(24°W, 20°N, 3.40)	125M	SFIT4	4.49 ± 1.8 (April)	1.36 ± 0.31 (April)	2.07 ± 0.43 (August)	0.8 ± 0.04 (August)
La Reunion Maido	(55°E, 21°S, 2.16)	125HR	SFIT4	6.91 ± 2.45 (November)	1.46 ± 0.17 (October)	2.56 ± 0.48 (May)	1.0 ± 0.1 (April)
Lauder	(170°E, 45°S, 0.37)	120HR	SFIT4	5.29 ± 1.18 (November)	1.28 ± 0.19 (October)	1.94 ± 0.28 (July)	0.89 ± 0.09 (February)
Arrival Heights	(167°E, 78°S, 0.2)	120HR	SFIT4	3.22 ± 0.51 (February)	1.0 ± 0.04 (October)	1.78 ± 0.21 (September)	0.67 ± 0.03 (April)

3.1 Seasonal variation

The monthly means of the tropospheric CO and HCN columns at the twelve FTIR stations are shown in Fig. 3. As commonly observed at Hefei (32°N), three monthly mean peaks are evident for tropospheric HCN and CO columns. The magnitude of the tropospheric HCN peak at Hefei (32°N) in May > September > December, while for tropospheric CO column, the magnitude of the peak at Hefei (32°N) in February > September > December. Note that the largest seasonal peak of HCN occurs in May which is 3 months later than that of CO which occurs in February, but the other two seasonal peaks for both species occur in the same months, i.e., in September and December respectively. Otherwise, their seasonal cycles show similarities.

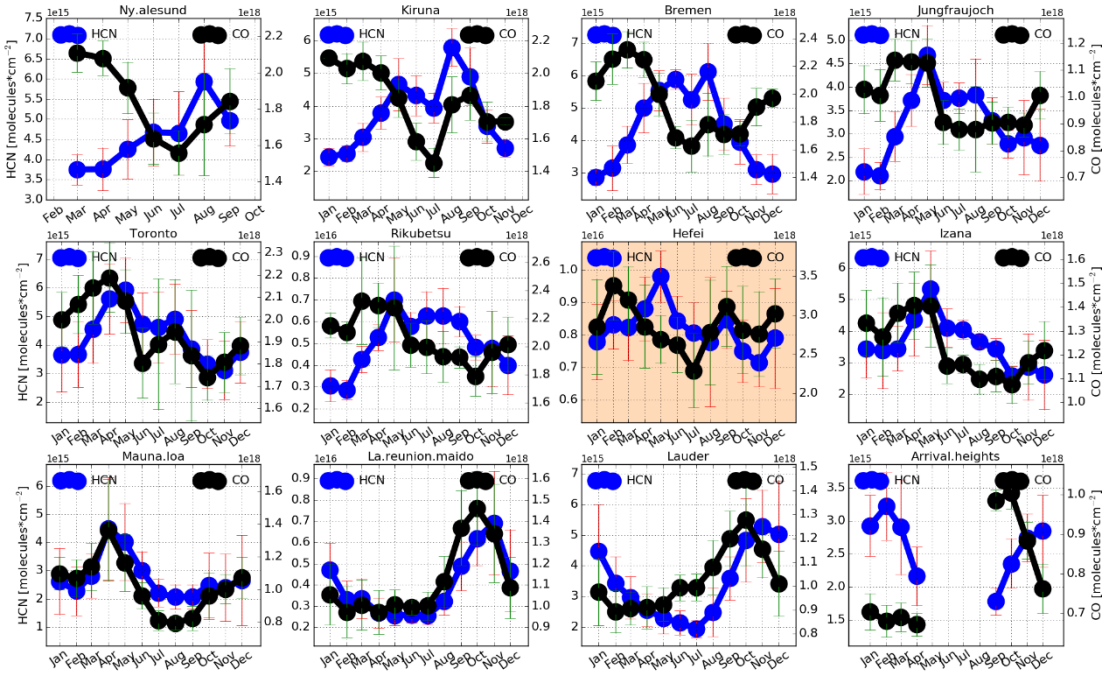

Fig. 3. Monthly means of the tropospheric CO and HCN columns at Ny Alesund, Kiruna, Bremen, Jungfraufoch, Toronto, Rikubetsu, Hefei, Izana, Mauna Loa, La Reunion Maido, Lauder, and Arrival Heights from 2015 to 2018. Vertical error bars represent 1σ within that month. All stations are organised as a function of decreasing latitude.

The tropospheric HCN and CO columns at Hefei (32°N) are higher than the NDACC FTIR observations (see Fig. S2). The tropospheric HCN column reached a maximum of (9.8 ± 0.78) × 10^{15} molecules/cm^2 in May and a minimum of (7.16 ± 0.75) × 10^{15} molecules/cm^2 in November. The tropospheric CO column reached a maximum of (3.38 ± 0.43) × 10^{18} molecules/cm^2 in February and a minimum of (2.29 ± 0.48) × 10^{18} molecules/cm^2 in July (Table 4). In comparison, the seasonal maxima and minima of tropospheric HCN columns at the selected NDACC FTIR stations varied over (3.22 ± 0.51) to (7.0 ± 1.92) × 10^{15} molecules/cm^2 and (1.78 ± 0.21) to (3.75 ± 0.37) × 10^{15} molecules/cm^2, respectively. The seasonal maxima and minima of tropospheric CO columns at the selected NDACC FTIR stations varied over (1.0 ± 0.04) to (2.32 ± 0.31) × 10^{18} molecules/cm^2 and (0.67 ± 0.03) to (1.79 ± 0.14) × 10^{18} molecules/cm^2, respectively (Table 4).

In the northern hemisphere, the phase of the seasonal maxima for tropospheric HCN columns generally occur in spring or summer, and for CO occur in winter or spring. While in the southern hemisphere, the phase of the seasonal maxima for both tropospheric HCN and CO columns occur in autumn or winter.

3.2 Interannual variability and enhancement

In order to study the interannual variability of HCN and CO, fractional differences in the tropospheric HCN and CO columns relative to their seasonal mean values represented by the cosine fitting at the twelve FTIR stations are shown in Fig.4 and Fig.5, respectively. Enhancements of both tropospheric HCN and CO columns between September 2015 and July 2016 at Hefei (32°N) were observed compared to the same period of measurements in other years. For HCN, the magnitude of the enhancement ranges from 5 to 46% with an average of 26%. The significant enhancements occurred in December 2015 and May 2016 with peaks of 46% and 38%, respectively. By contrast, the magnitude of the enhancement in tropospheric CO column at Hefei (32°N) between September 2015 and July 2016 ranges from 4 to 59% with an average of 27%.The tropospheric CO columns were elevated over its seasonal means by more than 20% from March to April 2016. In addition, an enhancement magnitude of more than 40% were occasionally observed in August and September for both HCN and CO at Hefei (32°N).

The enhancements of both tropospheric HCN and CO columns within the same period were also observed at the selected NDACC stations except Ny Alesund (79°N) and Kiruna (68°N). The winter enhancements were not shown over Ny Alesund (79°N) and Kiruna (68°N) because of the polar night in the Arctic which interrupted the observations in winter. The magnitude of the enhancement in tropospheric HCN column at the selected NDACC stations between September

2015 and July 2016 ranges from 3 to 213%, and for CO ranges from 4 to 62%.

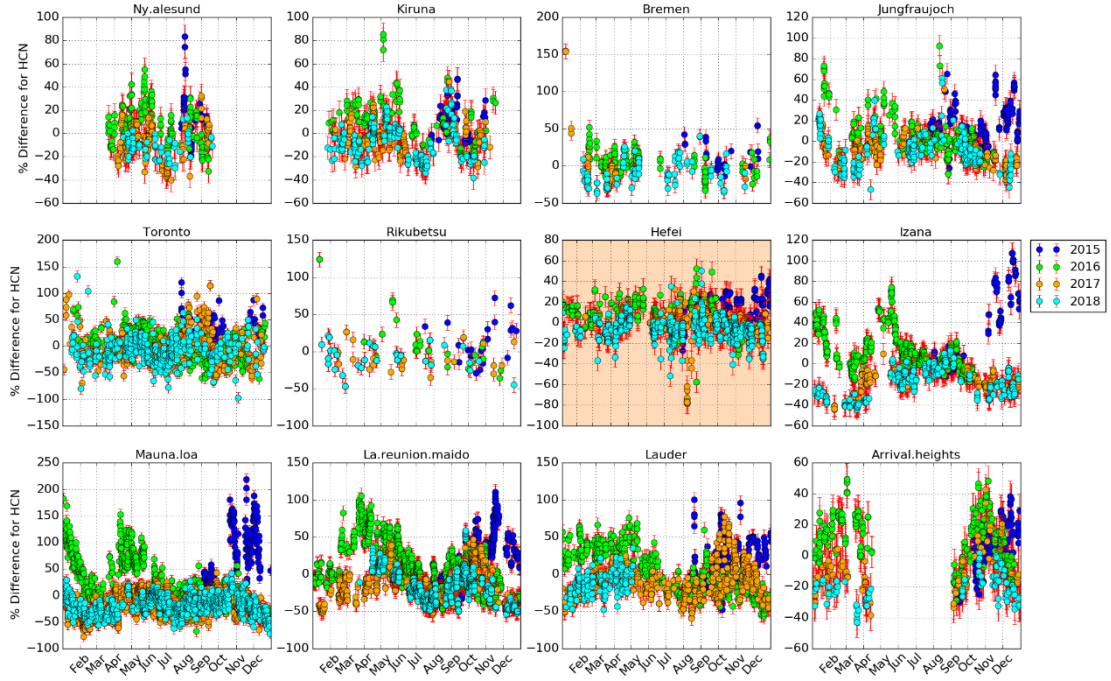

Fig.4. Fractional difference in the partial columns (surface - 15 km) of HCN from 2015 to 2018 at Ny Alesund, Kiruna, Bremen, Jungfraufoch, Toronto, Rikubetsu, Hefei, Izana, Mauna Loa, La Reunion Maido, Lauder, and Arrival Heights relative to their seasonal mean values. Vertical error bars represent the estimated retrieval errors. All stations are organised as a function of decreasing latitude.

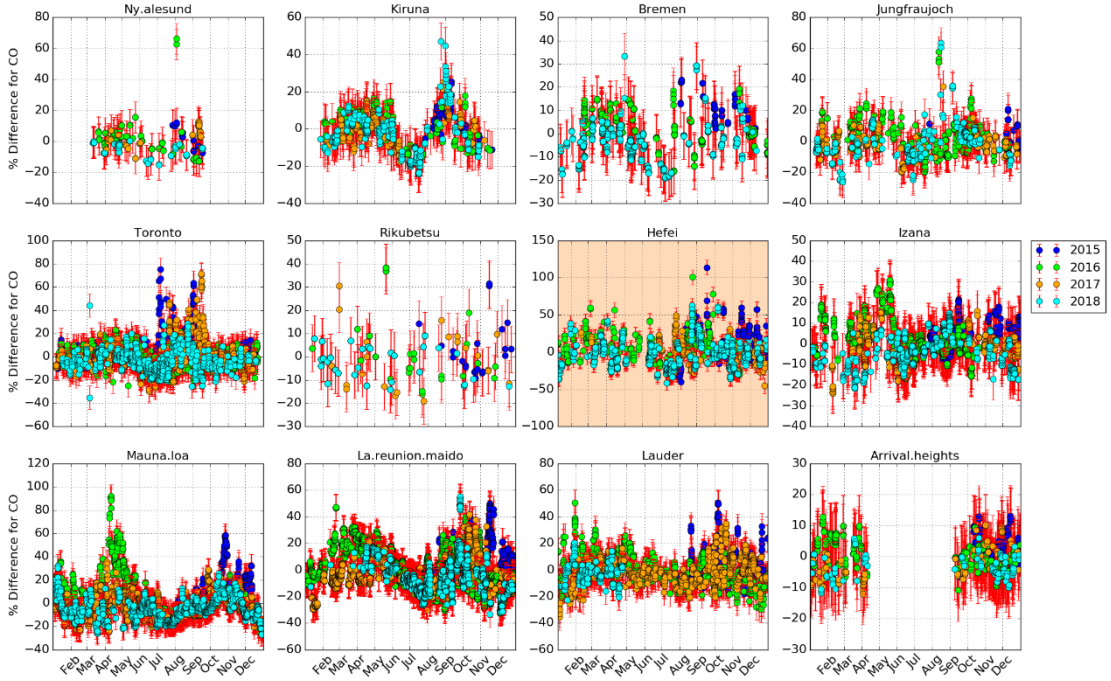

Fig.5. The same as Fig.4 but for CO.

3.3 Correlation with CO and enhancement ratios

The tropospheric HCN columns at the twelve FTIR stations from 2015 to 2018 have been plotted against the coincident CO partial columns (Fig.6). In Fig.7, the correlations between the tropospheric HCN and CO columns at Hefei (32°N) for all spectra recorded throughout the year (gray dots) and those recorded within the selected periods (green dots) are compared. We followed the least squares procedure of York et al., 2004 to fit the coincident measurements using a linear regression, and incorporated the errors in both ordinal and abscissa coordinates into the uncertainty estimation.

Biomass burning is the dominant source of HCN and industrial emissions only contribute

additional minor sources (Bange and Williams, 2000; Holzinger et al., 1999; Lobert et al., 1990). In contrast, anthropogenic, biomass burning, CH_4 and NMVOC oxidations are major sources of CO, and their contributions are season and location dependent. Therefore, the correlation between HCN and CO tropospheric column is also season and site dependent. High correlation of these two species is supposed to be observed if biomass burning dominates the CO variability, and vice visa. For the period of 2015 to 2018 in this study, moderate overall correlations between HCN and CO tropospheric columns were present at Jungfraujoch (47°N) and Rikubetsu (43°N), and negative overall correlations were present at Ny Alesund (79°N), Kiruna (68°N), Bremen (53°N), and Arrival Heights (78°S). However, high correlation of these two species were seen at Toronto (44°N), Hefei (32°N), Izana (28°N), Mauna Loa (20°N), La Reunion Maido (21°S), and Lauder (45°S) throughout the year probably because the portion of the fire-affected seasonal measurements at these stations are larger than those at other stations (Fig.6). For the measurements at Hefei (32°N), the high correlations between HCN and CO tropospheric columns deduced from the measurements without March and April (R=0.67, Fig.7 (a)), in May (R=0.69, Fig.7 (b)), in September(R=0.77, Fig.7 (c)), and in December (R=0.65, Fig.7 (d)) are consistent with that deduced from all measurements (R=0.70) (Table 5). However, the correlation slope for the May, September, and December tropospheric columns differ from the annual one, indicating different biomass burning sources in different periods.

For fire-affected measurements, the slope ΔHCN/ΔCO defined as enhancement ratio ($EnhR_{HCN}$) is an effective quantity to identify biomass burning emissions (Holzinger et al., 1999; Lutsch et al., 2016; Rinsland et al., 2002; Viatte et al., 2015; Vigouroux et al., 2012; Zhao et al., 2000). Depending on the burnt biomaterials, fire type, the phase of the fire, and the travel time of the plumes, the reported $EnhR_{HCN}$ varied by 2 orders of magnitude. The mean $EnhR_{HCN}$ of 1.34×10^{-3} at Hefei (32°N) falls between the wide range of the HCN/CO ratios measured in laboratory ($0.4 – 7.1\times10^{-3}$ in the work of (Yokelson et al., 1997) and $0.4 – 2.6\times10^{-3}$ in the work of (Holzinger et al., 1999), and $0.94 – 7.4\times10^{-3}$ in the NDACC FTIR measurements (Fig. 6). The mean $EnhR_{HCN}$ at Hefei (32°N) is close to that at Rikubetsu (43°N) indicating that these two Asian stations share similar biomass burning sources throughout the year. The mean $EnhR_{HCN}$ at Hefei (32°N) is lower than those measured at Jungfraujoch (47°N), Toronto (44°N), Izana (28°N), Mauna Loa (20°N), Lauder (45°S), and La Reunion Maido (21°S) because the emissions of crop residue burning which dominates the HCN enhancements at Hefei (32°N) is lower than those of the boreal or tropical forest burning, which account for the HCN enhancements at aforementioned NDACC stations (Akagi et al., 2011; Akagi et al., 2012; Rinsland et al., 2007; Vigouroux et al., 2012). On the other hand, the Hefei (32°N) site is located in the densely populated part of China, therefore emissions of fossil fuel combustion such as automobile exhaust and industrial processes could elevate the CO background level and hence lessen the $EnhR_{HCN}$.

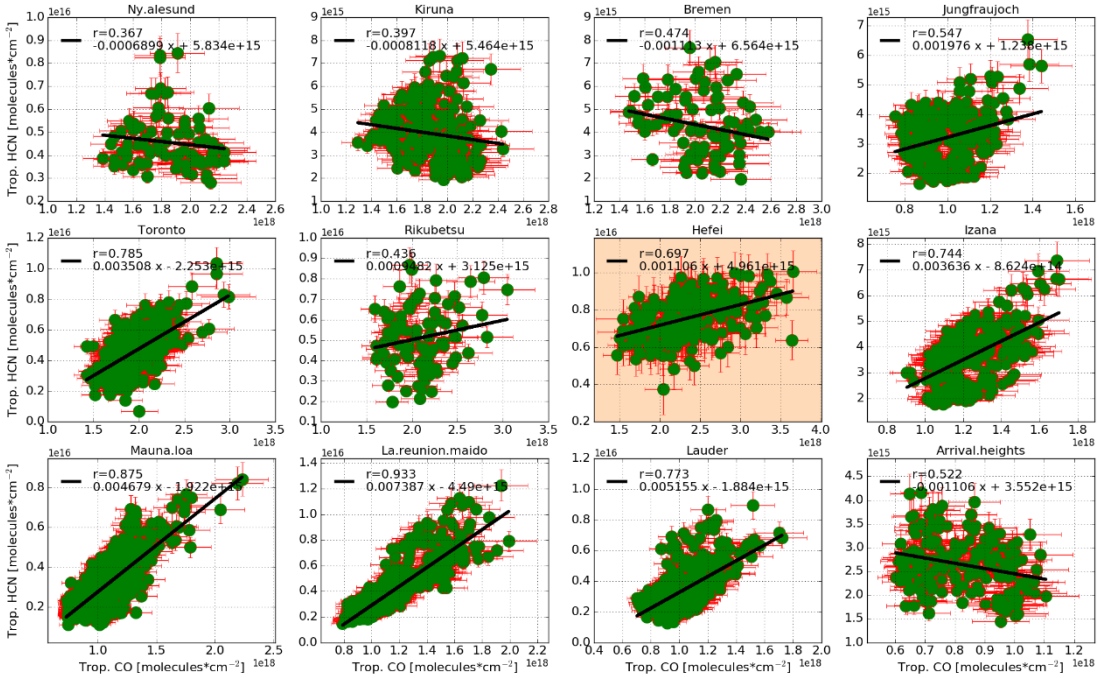

Fig. 6. Correlation plots of daily mean partial columns (surface - 15 km) of HCN versus CO (molecules/cm^2). The linear equation of the fit and the resulting correlation coefficient *r* are shown. The black line is a linear least-squares fit of respective data. All stations are organised as a function of decreasing latitude. Error bars represent the retrieval uncertainties.

Table 5. Correlation between HCN and CO tropospheric columns within each selected period at Hefei (32°N), China. *N* is the number of points, *R* is the correlation coefficient and $EnhR_{HCN}$ is the enhancement ratio.

Gas	Period	without March and April	May	September	December	Mean
HCN	*N*	239	26	56	35	-
	R	0.67	0.69	0.77	0.65	0.7
	EnhR×10^{-3}	1.06	1.48	1.29	1.52	1.34

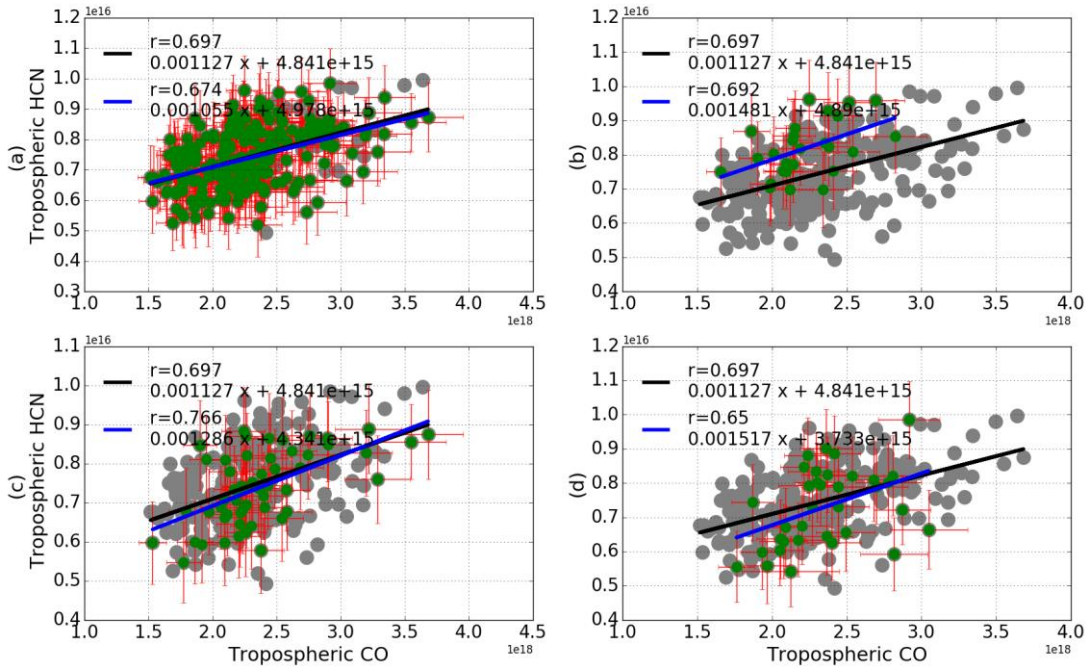

Fig. 7. Correlation plots of daily mean tropospheric columns of HCN versus CO (molecules/cm^2) at Hefei (32°N). The gray dots represent all measurements and the green dots represent the measurements within the selected period: (a) measurements without March and April; (b) measurements in May; (c) measurements in September; (d) measurements in December. The linear equation of the fit and the resulting correlation coefficient *r* are shown. The black line is a linear least-squares fit of the gray data and the blue line is for the green data. Error bars represent the retrieval uncertainties.

4 Source attribution

In order to determine what drives the seasonality and interannual variability of tropospheric HCN in eastern China, it is necessary to match the observed time series with actual biomass burning events, and show that the generated plumes are capable of travelling to the observation site. We did this by using various independent data sets.

1. The 1-hourly instantaneous CO VMR (volume mixing ratio) profiles of the tracers listed in Table 3 provided by a GEOS-Chem tagged CO simulation performed as described in Section 2.2.

2. The global fire atlas data archived by the Fire Information for Resource Management System (FIRMS) which generates fire information from NASA's Moderate Resolution Imaging Spectroradiometer (MODIS) and NASA's Visible Infrared Imaging Radiometer Suite (VIIRS) (https://firms.modaps.eosdis.nasa.gov/download/, last access on 23 May 2019). We have only taken the fire number with a retrieval confidence value of larger than 60% into account.

3. Three dimensional kinematic back trajectories at designated elevations calculated by the Air Resources Laboratory (ARL, http://ready.arl.noaa.gov/HYSPLIT.php, last accessed on 23 May 2019) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model using Global Data Assimilation System (GDAS) meteorological fields (https://ready.arl.noaa.gov/gdas1.php, last accessed on 23 May 2019).

4. The PSCF values calculated by MeteoInfo as described in Section 2.3 using HYSPLIT back trajectories (http://meteothink.org/index.html, last accessed on 17 December 2019).

4.1 Attribution for the seasonality

The GEOS-Chem tagged CO simulation provides a means of evaluating the contribution of CO from anthropogenic, biomass burning and oxidation sources to the measured CO columns at Hefei (32°N). Source attribution is performed as follows. First, the GEOS-Chem CO VMR profiles of all tracers in the grid box containing the Hefei (32°N) site were converted to partial column profiles and linearly interpolated and regridded onto the FTIR vertical retrieval grid. This was necessary in order to account for the differences in the vertical levels of the model and the FTIR (Barret et al., 2003). Then, The GEOS-Chem CO partial column profiles are smoothed by the normalized FTIR CO total column averaging kernel following Rodgers and Connor (2003). The GEOS-Chem CO profiles, FTIR CO profiles and total column averaging kernels are daily averaged and the daily averaged GEOS-Chem profiles are subsequently smoothed. Fig.8 shows the daily-averaged GEOS-Chem and FTIR CO tropospheric columns (surface-15 km) for the simulation period from 2015 - 2018. The relative contribution of anthropogenic, biomass burning and oxidation tracers are also shown. The GEOS-Chem and FTIR CO tropospheric columns are in good agreement.

The combination of the anthropogenic source and the oxidations of CH_4 and NMVOCs is the greatest contribution to the tropospheric CO column at Hefei (32°N). The magnitude of this combination source varies over 80 to 95% throughout the year. In contrast, the magnitude of biomass burning source varies over 5 to 20%. As shown in Fig.9, the anthropogenic, biomass burning and oxidation sources are all seasonal dependent due to the magnitude of the emissions and the influence of seasonally variable transport. The onset of the anthropogenic contribution begins in July with a maximum in December. In contrast to the anthropogenic influence, the onset of the oxidation contribution begins in January with a maximum in July, as a result of maximum NMVOC emissions in Summer (Sun et al., 2018b). For biomass burning contribution, two onsets were observed. One begins in January with a maximum in April and the other one begins in July with a maximum in October.

After normalizing each biomass burning tracer listed in Table 3 to the total biomass burning contribution, the normalized relative contribution of each individual biomass burning tracer to the total biomass burning associated CO tropospheric column was obtained in Fig.10. The results show that the seasonal maxima in May is largely due to the influence of SEAS biomass burning (41 ± 13.1%). Moderate contributions from EUBA (21 ± 9.3%) and AF (22 ± 4.7%), and small contributions from SA (7.8 ± 2.9%), OCE (1.5 ± 0.8%), and NA (7.7 ± 1.9%) are also observed. The seasonal maxima in September is largely due to the influence of EUBA (38 ± 11.3%) and AF (26 ± 6.7%) biomass burnings. Remaining contributions are from SA (5.1 ± 2.7%), SEAS (14 ± 3.3%), OCE (8.9 ± 7.4%), and NA (13.8 ± 8.4%). For the seasonal maxima in December, contributions from AF, SA, SEAS, EUBA, OCE, and NA are 36 ± 7.1%, 11 ± 1.9%, 11 ± 3.6%, 21 ± 5.2%, 4.8 ± 2.7%, and 18.7 ± 5.2%, respectively.

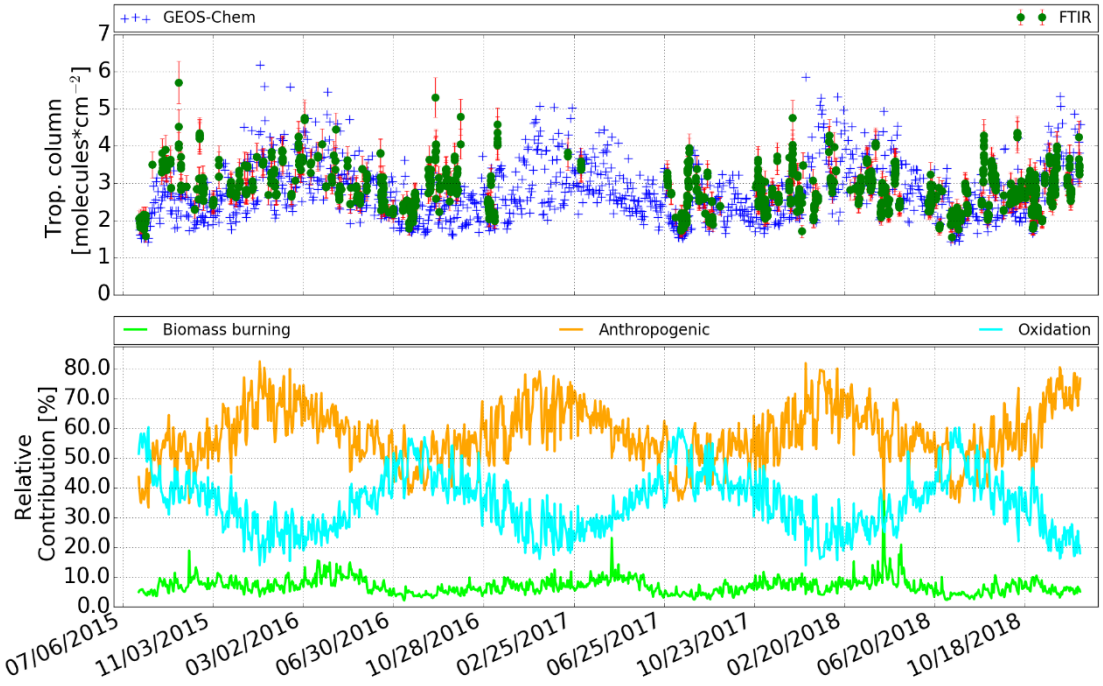

Fig. 8. Daily-mean CO tropospheric column time series of FTIR and GEOS-Chem (top panel) from 2015-2018 at Hefei (32°N). The bottom panel shows the relative contribution (%) of the anthropogenic, biomass burning, and oxidation tracers in the GEOS-Chem simulation to the total CO tropospheric column.

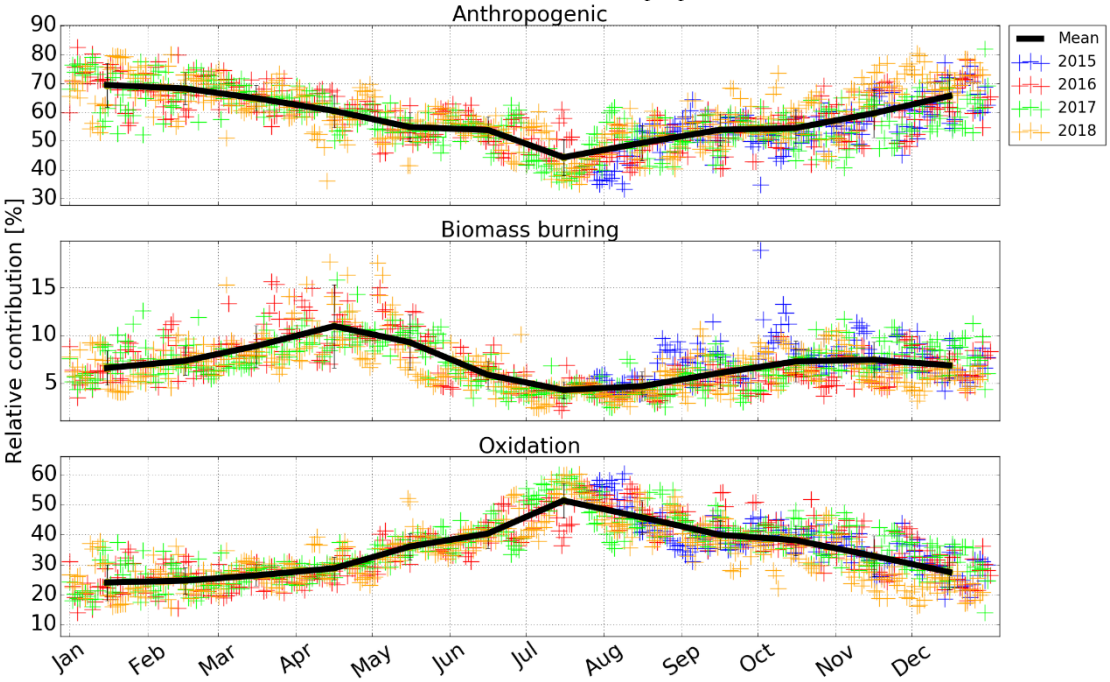

Fig. 9. Seasonality of the relative contribution (%) of the anthropogenic, biomass burning, and oxidation tracers in the GEOS-Chem simulation to the total CO tropospheric column.

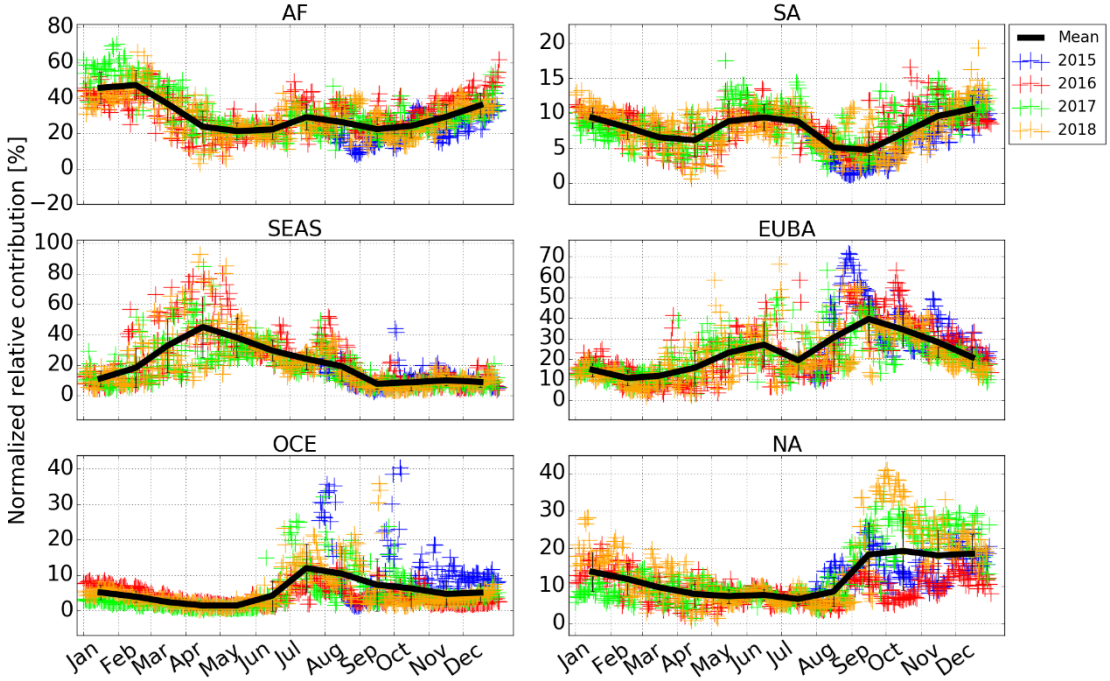

Fig. 10. Seasonality of the normalized relative contribution (%) of the AF, SA, SEAS, EUBA, OCE, and NA biomass burning tracers in the GEOS-Chem simulation to the total biomass burning associated CO tropospheric column.

4.2 Attribution for transport pathway

For each seasonal enhancement of the tropospheric HCN, transport pathway is determined as follows. First, the GEOS-Chem tagged CO simulation is used to calculate the relative contribution of each biomass burning tracer (Fig. 10). For the tracer with a high contribution, the FIRMS global fire map is used to search for potential fire events occurring before the phase of tropospheric HCN enhancement within a one month period. Then, we generated an ensemble of HYSPLIT back trajectories with different travel times and arrival altitudes to judge whether these plumes are capable of travelling to the observation site. For example, for each intensive biomass burning

event detected at a specific period, we generated ten back trajectories at different arrival altitudes ranging from 1.5 to 12 km, and modified the end time of these back-trajectories within one day of the observed enhancement. If the back-trajectories intersect a region where the FIRMS fire data indicates an intensive fire event and the travel duration is within a reasonable range, then this specific fire event could contribute to the observed enhancements at Hefei (32°N) in eastern China. The transport pathway for this enhancement is finally determined.

Fig. 11 demonstrates travel trajectories of the plumes occurred in AF, SEAS & OCE, EUBA, and NA that reached Hefei (32°N) through long range transport. Fig. 12 shows the PSCFs calculated using 13-day HYSPLIT back trajectories that are coincident with the FTIR measurement time. The eastern China, South Asia, Central Asia, Eastern Europe, and Northern Africa had high PSCF weight values in both the first and the second half of the year. The large areas of Southeastern Asian countries including Philippines, Malaysia, and Indonesia, and the Eastern North America were the additional regions with potentially high PSCF weight values in the second half of the year. Generally, trajectories with the same travel time in the second half of the year are longer than those in the first half year, resulting in broader areas with potentially high PSCF weight values.

As shown in Figs.13 and 14, the seasonal biomass burning typically occurs in July – September in southern Africa and in November – February in central Africa. These AF emissions can be transported to eastern China along with the southwestern wind which contributed 25 – 45% of the tropospheric HCN in these periods. The seasonal biomass burning typically occurs in March – May and July – November in central Europe, and in June – September in Siberia. These EUBA emissions can be transported to eastern China along with the northwestern or northern wind which contributed 27 – 40% of the tropospheric HCN in these periods. The seasonal biomass burning typically occurs in March – May in India and South Asia peninsula. Driven by the Asian monsoon anticyclone (AMA), the dominant circulation feature in the Indian–Asian upper troposphere–lower stratosphere region during the Asian monsoon, these emissions can be transported to eastern China which contributed to the tropospheric HCN peak in May. The seasonal biomass burning typically occurs in March – May, July – September, and November – December in the eastern part of China. All these emissions can be transported to the observation site at Hefei (32°N) under favorable meteorological conditions and thus contribute to all the seasonal tropospheric HCN peaks. The SEAS contribution (mainly China, India and South Asia peninsula) varies over 25 to 80% in March to August.

Additionally, a small to moderate portion of wildfire events in central SA, eastern NA, and Northern OCE in autumn or winter could transport to the observation site through large-scale atmospheric circulation, which contributed 5 – 20% of the tropospheric HCN in these periods.

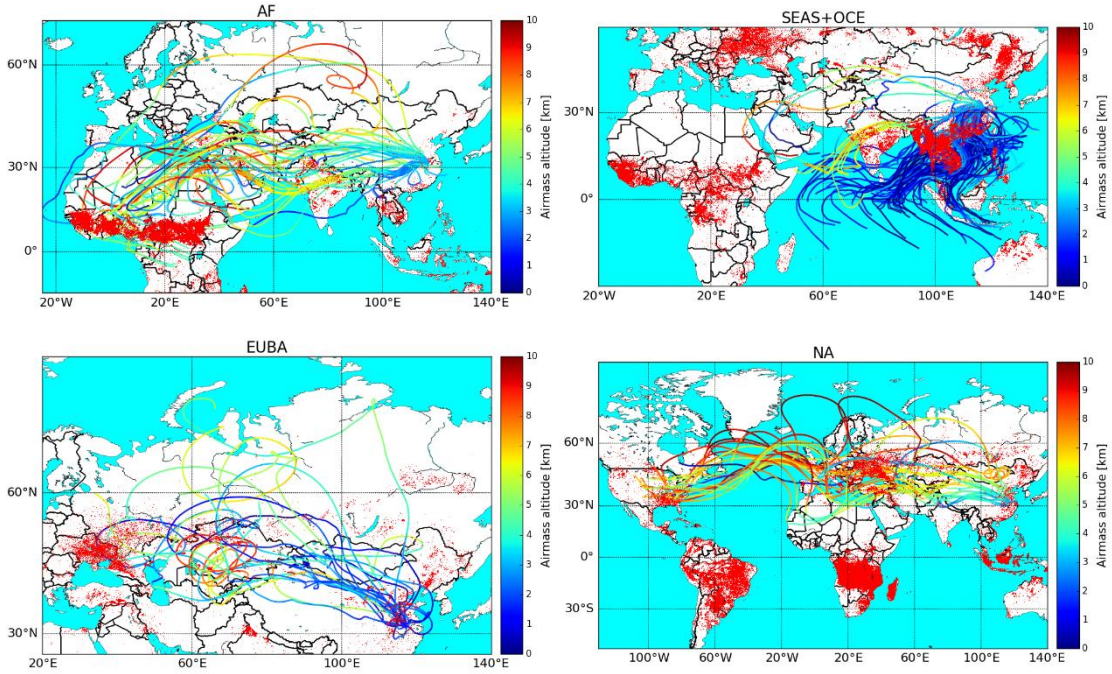

Fig.11. Travel trajectories of the plumes occurred in AF, SEAS & OCE, EUBA, and NA that reached Hefei (32°N)

through long range transport. Travel times are 13, 7, 10, and 14 days, respectively. For clarity, only few trajectories are selected for demonstration.

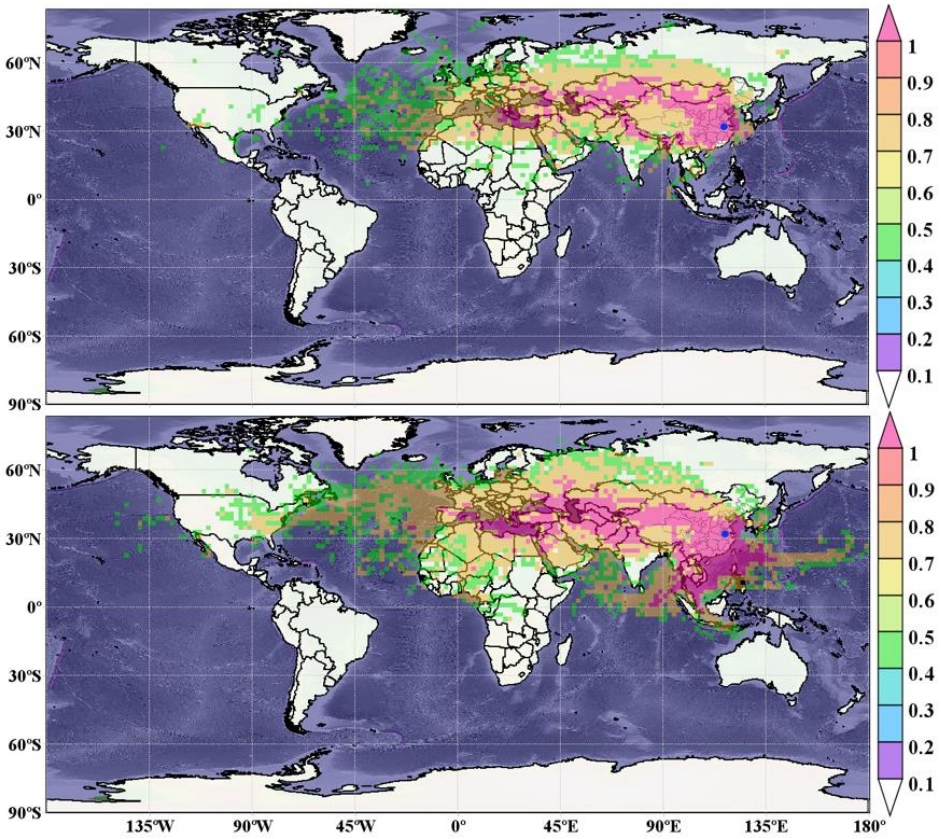

Fig.12. Likely source areas of air mass associated with higher HCN concentrations at Hefei (32°N) in the first half year (top panel) and the second half year (bottom panel) identified using PSCF.

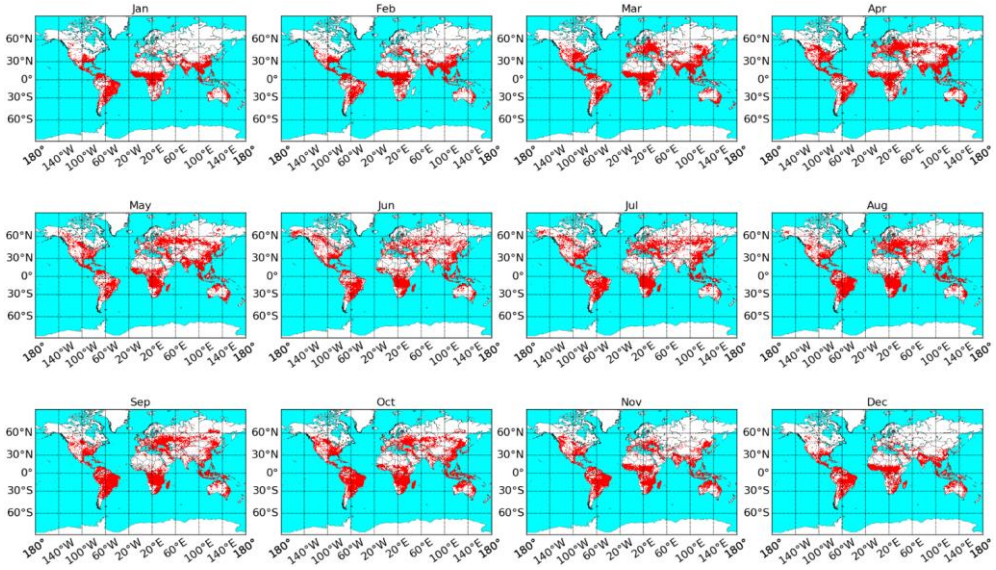

Fig. 13. Global fire map in January to December 2015 accumulated from the FIRMS fire atlas.

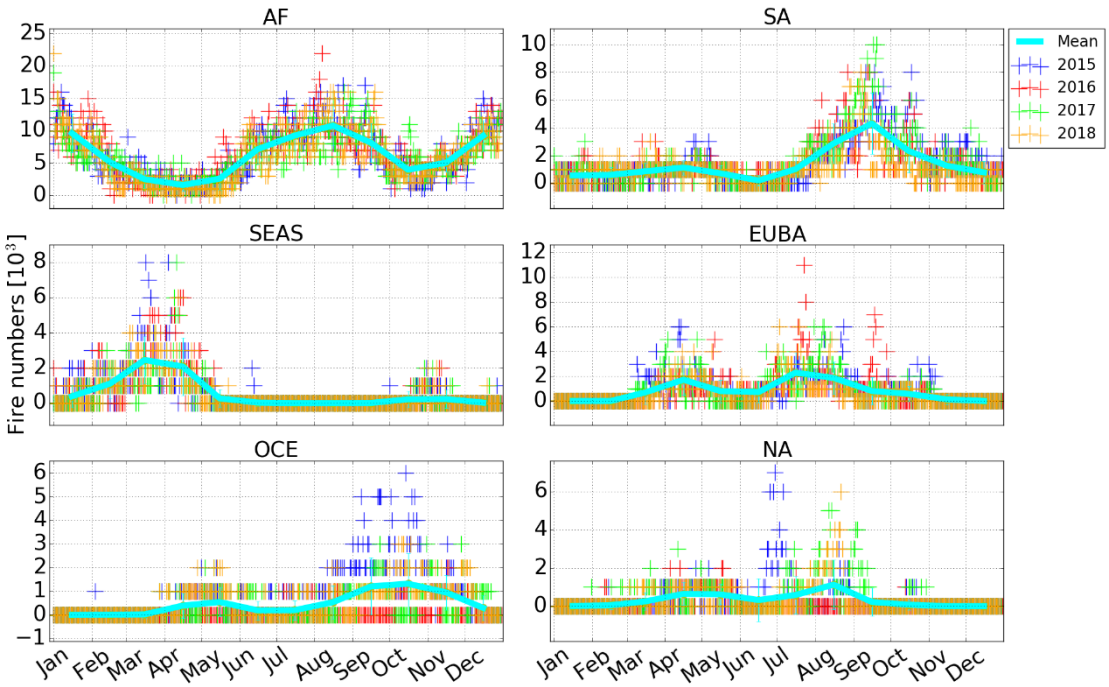

Fig.14. Seasonality of total fire numbers within the AF, SA, SEAS, EUBA, OCE, and NA tracers. All data are accumulated from the FIRMS fire atlas.

4.3 Attribution for interannual variability

In Fig. 9, the biomass burning contribution was elevated by 5 – 15% between September 2015 and July 2016, while no elevations were observed for anthropogenic and oxidation influence. As a result, enhancements of both tropospheric HCN and CO columns between September 2015 and July 2016 at Hefei (32°N) were attributed to an elevated influence of biomass burning. In Fig.10, the relative contribution (%) of the SEAS, EUBA, and OCE biomass burning tracers to the total biomass burning associated CO tropospheric column were elevated by 5 – 20%, 8 – 27%, 8 – 31%, respectively, in the second half of 2015 compared to the same period in other years. The relative contribution (%) of the SEAS and OCE biomass burning tracers to the total biomass burning associated CO tropospheric column were elevated by 8 – 39% and 2 – 7%, respectively, in the first half of 2016 compared to the same period in other years.

The statistical results of the FIRMS fire atlas data in Fig.14 show that, the fire numbers in the SEAS, EUBA, and OCE regions elevated by 21.89%, 15.72%, and 32.68% between September 2015 and July 2016 compared to the same period in other years. These elevated fire numbers in EUBA, SEAS and OCE drove the enhancements of tropospheric HCN and CO columns between September 2015 and July 2016 at Hefei (32°N). In particular, the number of fires in OCE in the second half of 2015 was greatly elevated in comparison with the other years, acting as a dominant source of tropospheric HCN enhancement in September – December 2015. The fire numbers elevated significantly in the SEAS region in the first half of 2016, which dominated the tropospheric HCN enhancement in January – July 2016.

Many studies have revealed that the El Niño Southern Oscillation (ENSO) can cause large scale variations in the convection, circulation, and air temperature of the global atmosphere-ocean system (Liu et al., 2017; Zhao et al., 2002), which could affect the distribution, frequency, and intensity of biomass burning emissions (Schaefer et al., 2018). Furthermore, ENSO could also alter the destruction processes of tropospheric species through their photochemical reactions with tropospheric OH (Zhao et al., 2002). Zhao et al. (2002) found that the abnormally enhancement of tropospheric CO and HCN observed in northern Japan in 1998 were associated with the 1997–1998 ENSO events (Zhao et al., 2002). There is a close correlation between ENSO and HCN columns at Lauder (45°S) (Zeng et al., 2012; Schaefer et al., 2018), and Schaefer et al. (2018) quantified a detectable ENSO influence on biomass burning of up to 51-55% (Schaefer et al., 2018; Zeng et al., 2012). Very likely, the elevated fire number which caused significant enhancements between September 2015 and July 2016 for tropospheric CO and HCN columns at Hefei and most selected NDACC stations were related to the 2015 – 2016 ENSO events.

Compared to the northwestern part of China such as the Xinjiang province and the Tibet plateau, the densely populated eastern parts of China are more suitable for crop planting because of fertile soil and adequate water resources. Historically, Chinese farmers burned their crop residue (such as rice, corn, and wheat straws) after harvest to fertilize the soil for the coming farming season. Post-harvest crop residue is a fine fuel that burns directly in the field and mostly by flaming in many mechanized agricultural systems. In contrast, when crops are harvested by hand the residue is often burned in large piles that may smolder for weeks.

This seasonal crop residue burning season typically occurs in the spring and summer seasons and also occasionally occurs in the autumn and winter. Pollution gases, dust, and suspended particle matters resulting from crop residue burning emissions result in poor air quality that threaten human health and terrestrial ecosystems. The Chinese presidential decree included the prohibition of crop residue burning into the Law of the People's Republic of China on the Prevention and Control of Atmospheric Pollution in August 2015 (http://www.chinalaw.gov.cn, last access on 17 July 2019), and since then the crop residue burning events were banned throughout China. Therefore, we obtain a decrease in fire numbers in China since 2015.

6 Conclusion

The first multiyear measurements of HCN in the polluted troposphere in densely populated eastern China have been presented. Tropospheric HCN columns were derived from solar spectra recorded with ground-based high spectral resolution Fourier transform infrared (FTIR) spectrometer at Hefei (117°10′E, 31°54′N) between 2015 and 2018. The seasonality and interannual variability of tropospheric HCN columns in eastern China have been investigated. The potential sources that drive the observed HCN seasonality and interannual variability were determined by using the GEOS-Chem tagged CO simulation, the global fire maps and the PSCFs (Potential Source Contribution Function) calculated using HYSPLIT back trajectories.

The tropospheric HCN columns over eastern China showed significant seasonal variations with three monthly mean peaks throughout the year. The magnitude of the tropospheric HCN peak in May > September > December. The tropospheric HCN column reached a maximum monthly mean of $(9.8 \pm 0.78) \times 10^{15}$ molecules/cm^2 in May and a minimum monthly mean of $(7.16 \pm 0.75) \times 10^{15}$ molecules/cm^2 in November. In most cases, the tropospheric HCN columns at Hefei (32°N) are higher than the NDACC FTIR observations. Enhancements of the tropospheric HCN columns were observed between September 2015 and July 2016 compared to the same period of measurements in other years. The magnitude of the enhancement ranges from 5 to 46% with an average of 22%. Enhancement of tropospheric HCN (ΔHCN) is correlated with the coincident enhancement of tropospheric CO (ΔCO), indicating that enhancements of tropospheric CO and HCN were due to the same sources.

The GEOS-Chem tagged CO simulation, the global fire maps and the PSCFs analysis revealed that the seasonal maxima in May is largely due to the influence of biomass burning in South Eastern Asia (SEAS) (41 ± 13.1%), Europe and Boreal Asia (EUBA) (21 ± 9.3%) and Africa (AF) (22 ± 4.7%). The seasonal maxima in September is largely due to the influence of biomass burnings in EUBA (38 ± 11.3%), AF (26 ± 6.7%), SEAS (14 ± 3.3%) and NA (13.8 ± 8.4%). For the seasonal maxima in December, dominant contributions are from AF (36 ± 7.1%), EUBA (21 ± 5.2%), and NA (18.7 ± 5.2%).

The enhancements of both tropospheric HCN and CO columns between September 2015 and July 2016 at Hefei (32°N) were attributed to an elevated influence of biomass burnings in SEAS, EUBA, and Oceania (OCE) in this period. In particular, an elevated fire numbers in OCE in the second half of 2015 dominated the tropospheric HCN enhancement in September – December 2015. An elevated fire numbers in SEAS in the first half of 2016 dominated the tropospheric HCN enhancement in January – July 2016.

Most high resolution FTIR instruments are located in Europe and Northern America, whereas the number of sites in Asia, Africa, and South America is very sparse. As one of few FTIR stations on Asian continent, the long-term observations of trace gases at Hefei are crucial to understand global warming, regional pollution, long term transport, and contribute to the evaluation of satellite data and model simulations.

Data availability. The CO and HCN measurements at the selected NDACC sites can be found by the link http://www.ndaccdemo.org, and the CO and HCN measurements at Hefei are available on request.

Author contributions. YS conceived the concept and prepared the paper with inputs from all coauthors. CL, WW, CS, HY, XX, MZ, and JL carried out the experiments. The rest authors contributed to this work via provide refined data or constructive comments.

Competing interests. The authors declare that they have no conflict of interest.

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