Changing characteristics of atmospheric CH4 on the Tibetan Plateau, records from 1994 to 2017 at Mount Waliguan station

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Abstract. A 24-year long-term observation of atmospheric CH$_4$ was presented at Mt. Waliguan (WLG) station, the only WMO/GAW global station in inland of Eurasia. Overall, during 1994-2017, continuously increase of atmospheric CH$_4$ was observed at WLG with yearly growth rate of 5.1 ± 0.1 ppb yr$^{-1}$, although near-zero and even negative growth appeared in some particular periods, e.g., 1999-2000, and 2004-2006. The average CH$_4$ mole fraction was only 1805.8 ± 0.1 ppb in 1995, but unprecedented elevated ~100 ppb and reached a historic high of 1903.8 ± 0.1 ppb in 2016. The seasonal averages of atmospheric CH$_4$ at WLG were ordered by summer, winter, autumn and spring, and the correlation slopes of ΔCO/ΔCH$_4$ showed a maximum in summer and minimum in winter, which was almost opposite to other sites in the northern hemisphere, e.g., Mauna Loa, Jungfraujoch, and was caused by regional transport. Strong potential sources at WLG were predominately identified in northeast (cities, e.g., Xining, Lanzhou) and southwest (the Northern India), and air masses from west and northwest regions were accompanied with higher CH$_4$ mole fractions than that from city regions.

What is interesting is that obviously changes appeared in different observing periods. Generally, i) the amplitudes of diurnal or seasonal cycles were continuously increasing over time, ii) the wind sectors with elevated CH$_4$ moved from ENE-…-SSE sectors in early periods to NNE-…-E sectors (city regions) in later years, iii) the area of source regions was increasing along with the years, and strong sources gradually shifted from northeast to southwest, iv) the annual growth rates in recent years (e.g., 2013-2016) were significantly larger than that in early periods (e.g., 1998-2012). We conclude that the site was more and more affected by regional sources along with the time. Northern India was possibly becoming the strongest source area to WLG rather than city regions before. The case study in the Tibetan Plateau showed that the atmospheric CH$_4$ observed in Qinghai-Tibetan Plateau changed not as expected, the annual growth rate was even larger than that in city regions in some period (e.g., 7.3 ± 0.1 ppb yr$^{-1}$ in 2013-
2016). It is unambiguous that the anomalously fluctuations of atmospheric CH$_4$ in this region are a warning to the world, its increasingly annual growth rate may be a dangerous signal to global climate change.
1 Introduction

Since the pre-industrial era, the emissions of greenhouse gases (GHGs) have increased continuously, and larger absolute increases were found in recent years with the concentration higher than ever now (WMO, 2019). The GHGs could perturb the infrared radiation balance, trap the heat in the atmosphere, which contributes to global warming, melting glaciers, extreme weather events and many other global climate changes (IPCC, 2014). The recent 30-years from 1983 to 2012 were the warmest of the last 800-years in the Northern Hemisphere, and half of the rising surface temperature was due to increased GHGs emissions (IPCC, 2014). As one of the most important GHGs, the global warming effect of methane (CH4) is just after carbon dioxide (CO2) (Etminan et al., 2016). It has an 8-12 years atmospheric lifetime (Battle et al., 1996), with the global warming potential of ~23 times greater than CO2 over a 100 year horizon (Weber et al., 2019). About 17% of radiative forcing by long-lived greenhouse gases was contributed by CH4 during 1750-2016 (Etminan et al., 2016). Since the beginning of the industrial era, the concentration of CH4 is rapidly increased because of the influence of anthropogenic activities (Saunois et al., 2016). The result by the analyses of ice cores in Antarctica showed that the atmospheric concentration of CH4 has reached unprecedented over the last 0.8 million years (IPCC, 2014).

In the beginning of 1990s, CH4 concentration appeared a decreasing trend in global scale. However, high growth rates were found in 1998, which was possibly due to the higher global mean temperature (Dlugokencky et al., 1998; Nisbet et al., 2014). Subsequently, a low growth rate sustained over 1999 to 2006, except for special years (2002/2003) with El Niño events (Dlugokencky et al., 1998). The annual growth rates dropped from ~12 ppb yr\(^{-1}\) to near 0 from late 1980s to 1999-2006 (Nisbet et al., 2019). But thereafter, the atmospheric CH4 concentration keeps rising from 2007. During 2007-2013, the annual growth rate of methane was 5.7 ± 1.2 ppb yr\(^{-1}\). After 2013, the atmospheric CH4 grew even at rates not observed after 1980s, such as 12.7 ± 0.5 ppb yr\(^{-1}\) in 2014 and 10.1 ± 0.7 ppb yr\(^{-1}\) in 2015 (Nisbet et al., 2016, 2019). The overall
global growth rate was 7.1 ppb yr\(^{-1}\) in recent 10 years (WMO, 2019). And the not expected increase since 2007 would make it difficult to meet the targets of carbon emission reduction in the future. The World Meteorological Organization/Global Atmospheric Watch programme (WMO/GAW) annual greenhouse gas bulletin revealed that globally averaged CH\(_4\) mole fraction reached a new high with 1869 ± 2 ppb in 2018 (Rubino et al., 2019), which was ~259% of pre-industrial levels (~722 ppb around 1750 C.E.) (Etheridge et al., 1998; WMO, 2019).

The atmospheric CH\(_4\) is mainly emitted from natural sources (about 40%, e.g., ruminants and wetlands) and anthropogenic sources (about 60%, e.g., paddies, cattle ranch, coal mine, fossil fuel and biomass burning) (Hausmann et al., 2016; Saunois et al., 2016). Studies from GAW observations indicated that the causes of recent increase were likely attributed to anthropogenic emissions at mid-latitudes in the northern hemisphere and the wetlands in the tropics (WMO, 2019). The rapid development of population growth, economic expansion and countries urbanization has led to more and more fossil fuel production and consumption (e.g., the large-scale exploitation of natural gas, oil and coal) and biomass burning, consequently large amounts of anthropogenic CH\(_4\) were emitted around the world in recent years (Galloway, 1989; Streets and Waldhoff, 2000; Wang et al., 2002; Lin et al., 2014; Hausmann et al., 2016). The recent carbon isotope study revealed that biogenic emissions might also have driven CH\(_4\) increase, including microbial sources whether from rice, paddies, ruminants, termites, enteric fermentation or all of these (Nisbet et al., 2016; Schaefer et al., 2016; Wolf et al., 2017). 90% of CH\(_4\) destruction in the atmosphere are mainly from the reaction with hydroxyl radicals (OH) (Vaghjiani and Ravishankara, 1991; Bousquet et al., 2011), an important oxidant in the troposphere (Logan et al., 1981). Therefore, the interannual variability of OH or the decline oxidative capacity of the atmosphere may also cause the recently increased CH\(_4\) growth rates (Rigby et al., 2017; Turner et al., 2017).

To get accurate understanding of atmospheric CH\(_4\), a systematic observations
network would perform the best. Hundreds of CH$_4$ observation stations worldwide are running under the framework of WMO/GAW. Since 1978, systematic measurements of atmospheric CH$_4$ began around the world (Blake et al., 1982; Rasmussen and Khalil, 1984; Dlugokencky et al., 1994). On the northern slope of the Mauna Loa volcano, Hawaii, there exists the first global station Mauna Loa (MLO), which was performed about 3397m above sea level (a.s.l.) and far away from local sources and sinks. It has the longest records of continuous atmospheric CH$_4$ observation (Keeling et al., 1976). Later, many types of the sites were installed CH$_4$ observation system, such as the Barrow (BRW), South Pole (polar site, SPO) (Dlugokencky et al., 1995), Cape Grim (CGO) in Australia (coastal/island sites) (Pearman and Beardsmore, 1984), Minamitorishima (MNM) in Japan (coastal/island sites) (Wada et al., 2007), Jungfraujoch (JFJ) in Switzerland and Mount Waliguan in China (continental mountain site) (Zhou et al., 2004; Loov et al., 2008). Even though, the exact causes of significantly increased CH$_4$ emissions in past years are still remained unclear and debated, especially for the anomalous periods with suddenly large growth, due to the time and space sparsity of measurements and the crude model approaches, which limited our understanding of the global variation of atmospheric CH$_4$ (Saunois et al., 2019; Weber et al., 2019). As long as the reasons for rising CH$_4$ emissions contributed by natural sources (e.g. wetlands), anthropogenic sources (e.g. fossil fuels), or climate change feedbacks remain uncertainties, it will be impractical to predict CH$_4$ trends in the future, and then to develop realistic management (Nisbet et al., 2019). Therefore, it is essential to establish typical observing regions and perform long observations.

China has the largest anthropogenic CH$_4$ emissions in the world (Janssens-Maenhout et al., 2019). Qinghai-Tibetan Plateau has an average altitude over 4000m a.s.l., which has long been recognized as the roof of the world. By coincidence, the two largest CH$_4$ source regions in the world (i.e. Eastern China and Northern India) trapped the Tibetan Plateau in the middle (Zhang et al., 2011; Fu et al., 2012; Wilson and Smith, 2015). Under the characteristics of special geographical conditions, lower population
density, rarely industrial activities and high sensitivity to external disturbances, the Tibetan Plateau is undoubtedly one of ideal regions to observe continual CH4 signal (Zhou et al., 2005; Fu et al., 2012; Zhang et al., 2013). Most of the previous studies reported the short-term CH4 variations in China and concluded the importance of long-term observation (Cai et al., 2000; Zou et al., 2005; Wang et al., 2009; Fang et al., 2013), which is of great value to enhance the understanding of the global carbon cycle (Yuan et al., 2019). As the rapid development of China and India, the year to year difference as well as the sources and sinks of CH4 on the Tibetan Plateau might change significantly over time. Since 1994, in-situ measurements of atmospheric CH4 have been launched at Mt.Waliguan (WLG) station. To study the long-term variations of atmospheric CH4 at the WLG and get a new insight of its characteristics in the inland of the Eurasia, in this study, we evaluated the performance of a 24 year long-term in situ observations of CH4 at Mt.Waliguan baseline observatory, which is the longest time observing records in China. Temporal patterns, annual variations, long-term trends, air mass transports, spatial distribution of potential sources were analyzed. In addition, the case studies combining atmospheric CO measurements and a separate analysis between the Tibetan Plateau and the city regions were performed to constrain the contribution of anthropogenic emissions.

2 Methodology

2.1 Measurement site

The Mt.Waliguan (WLG, 36.28° N, 100.09° E, 3816m a.s.l.) station is situated at the edge of northeastern of the Tibetan (Qinghai-Xizang) Plateau, which was in remote western China and isolated from populated and industrial regions (Fig. 1). WLG was the only WMO/GAW global background station in Eurasia and running by the China Meteorological Administration (CMA). The surrounding areas of the site are pristine with sparse vegetation, naturally arid and semi-arid grasslands. Small farms with yak
and sheep are in the valley. Two adjacent large cities Xining (~2.2 million populations) and Lanzhou are located about 90km northeast and 260km east of the station, respectively. The Longyangxia hydroelectric station (~380 km²) is located approximately 13km south to southwest of the WLG. The predominant winds at WLG are mainly from southwest and east in winter and summer, respectively (Zhou et al., 2004; Zhang et al., 2011), which is controlled by Tibet Plateau monsoon. Simultaneously, dial variations of vertical winds at WLG is influenced by mountain-valley breezes, where upslope flow brings heated air masses from the boundary layer to the site in daytime and downslope flow results in cool air masses transport from mountain peak to the site. Under this unique location, the observation at WLG could obtain essential information on CH₄ sources and sinks from Eurasia (Zhou et al., 2005; Zhang et al., 2013).

2.2 Instrumental setup

Atmospheric CH₄ has been measured quasi-continuously using a HP 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) since July 1994, and an Agilent 6890N GC equipped with a FID since June 2008. Both of the systems used the same sampling procedures. A Cavity Ring Down Spectroscopy system (Picarro G1301) began in January 2009 and the instrument was upgraded to Picarro G2401 in 2015. Ambient air is delivered to the above systems at about 5 L/min by a KNF Neuberger N2202 vacuum pump via a dedicated 0.95 cm o.d. sample line from an 80m intake line attached to an 89m steel triangular tower located approximately 15m from the main observatory. The residence time of the ambient air from the top of the tower to the instrument is 30 s. The ambient air is first passed through a 7 mm stainless steel membrane filter located upstream of the pump and then (after the pump) passed through a pressure relief valve set at 1 atm to release excess air and pressure. The ambient air is then dried to a dew point of approximately -60°C by passing it through a glass trap submerged in a -70°C methanol bath. All standard gases supplied to the instruments are
from pressurized 37.5 L treated aluminum alloy cylinders fitted with high-purity, two-stage gas regulators. Stainless steel tubing (0.32 cm o.d., 0.22 cm i.d.) is used for the standard gas sample line and the ambient sample line after the cold trap. The automated sampling module equipped with a VICI 8 ports valve is designed to sample from separate gas streams (standard tanks and ambient air). According to the comparability target of WMO/GAW program (WMO, 2019), methane mole fractions are referenced to a Working High standard (WH) and a Working Low standard (WL). Additionally, a calibrated cylinder filled with compressed ambient air is used as a Target gas (T) to check the precision and stability of the system routinely. Diagram of the observing system during different periods could be seen at Zhou et al. (2004) and Fang et al. (2013). Here, we focus on the longest continuous measurements of CH$_4$ from August 1994 to May 2017 at WLG. Data gaps in limited periods are because of the malfunction of instrument and the maintenance of the sampling system.

The records of CO in this study was initially observed by an RGA-3 gas chromatograph (GC) equipped with an HgO reduction detector (Trace Analytical Inc.) since 1994. An automated sampling module was designed to sample from ambient air and a series of 9 standards. Detailed diagram of the system was described by Zhang et al. (2011). Since 2010, the CO has been measured by the Cavity Ring Down Spectroscopy instrument (Picarro G1302 and G2401 since 2015). The scale for all of the CO measurement were further updated to WMO X2014A.

### 2.3 Data processing

Most on-site CH$_4$ observations were unavoidably influenced by local sources and other complex conditions (e.g., traffic transportation, various topography). As a result, the records cannot fully represent the regional atmospheric CH$_4$ in well-mixed conditions (Liu et al., 2019). To precisely get representative regional records, we exclude CH$_4$ measurements influenced by local sources adjacent to the site (e.g., agricultural fields, cities, traffic emissions). The hourly CH$_4$ data were classified as Local/Regional events.
through the meteorological approach, which was based on essential meteorological information, similar to previous studies by Zhou et al. (2004) and Liu et al. (2019). In this study, the CH$_4$ records associated with surface wind from selected sectors (i.e. NNE-…-ENE in spring, NE-…-SE in summer, NE-…-ESE in autumn, and NE-ENE in winter) were flagged as local representative. Subsequently, we further rejected portion of daytime records to minimize the effect of human activities (e.g., rush hours), including 9:00-13:00 LT (local time) in spring and summer, 9:00-14:00 LT in autumn, 10:00-17:00 LT in winter. Finally, we filtered CH$_4$ data into local events when the surface wind speed was less than 1.5 m s$^{-1}$ to minimize the very local accumulation.

To understand the influence of local surface wind, the hourly CH$_4$ data was calculated versus 16 horizontal wind directions (Fang et al., 2013). In this study, we used the ‘polarPlot’ function located in the ‘openair’ package of the statistical software R (R Core Team, 2020). It shows the bivariate (i.e. wind speed and wind direction) polar plot of CH$_4$ concentrations, and the concentrations are calculated as a continuous surface by modelling using smoothing techniques (Carslaw et al., 2006; Diederich, 2007). Also, conditional probability function (CPF) was used to detect the probability of which wind directions are dominated by high CH$_4$ mole fractions (Uria-Tellaetxe and Carslaw, 2014). In order to study the pollution transport pathways of air masses at WLG, the cluster analysis of 3 days back trajectories was applied using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) dispersion model (Draxier and Hess, 1998; Rousseau et al., 2004) on the strength of gridded meteorological data (2004-2017) from the National Oceanographic and Atmospheric Administration’s Air Resources Laboratory (NOAA-ARL). The trajectories in four months, including January, April, July and October, were calculated to represent the seasons of winter, spring, summer and autumn, respectively. The spatial source distributions of annual CH$_4$ were analyzed using the Potential Source Contribution Function (PSCF) approach, which computed the conditional probability of the residence times of air parcels with greater concentration than threshold transport to the
exactly receptor site (Ashbaugh et al., 1985). In this study, PSCF value was calculated in 0.5×0.5-degree grid cell \((i, j)\):

\[
PSCF_{ij} = \frac{m_{ij}}{n_{ij}}
\]

(1)

\(n_{ij}\) represents the number of endpoints that terminate in the \(i\)th grid cell, while the number of trajectories with concentration exceed the threshold value was defined as \(m_{ij}\) (Polissar et al., 1999). In order to reduce the abnormal influence of small \(n_{ij}\) values in some grid cells, \(PSCF_{ij}\) was further computed by an arbitrary weighting function \(W_{ij}\) as below.

\[
W_{ij} = \begin{cases} 
1.00 & 3n_{ave} < n_{ij} \\
0.70 & 1.5n_{ave} < n_{ij} \leq 3n_{ave} \\
0.42 & n_{ave} < n_{ij} \leq 1.5n_{ave} \\
0.05 & n_{ij} \leq n_{ave}
\end{cases}
\]

(2)

\(W_{ij}\) represents the weight of cell \((i, j)\), \(n_{ij}\) is the number of trajectory endpoints that fall in the \(i\)th grid cell, while the \(n_{ave}\) shows the mean number of the endpoints in all grid cells.

In order to fill the data gaps so as to evaluate the long-term \(CH_4\) trend, we applied the curve fitting approach by Thoning et al. (1989). We also calculated the trend curve that excluded the influence of seasonal variation, and then got the annual growth rates of the average of the first derivative of the trend curve. The function consists of the polynomial part and the annual harmonics part:

\[
f(t) = a_0 + a_1 t + a_2 t^2 + \cdots + a_{(k-1)} t^{(k-1)} + \sum_{n=1}^{nh} c_n \sin(2\pi n t) + \phi_n
\]

(3)

\(k\) represents the number of polynomial part. \(nh\) is the number of harmonics part. We applied \(k = 3\) polynomial terms (a quadratic) for multi-year trends and \(nh = 4\) yearly harmonics for seasonal cycles in this study. The fast Fourier transform (FFT) was utilized to smooth the fitting residuals (Press et al., 1992).

The significant difference test was applied by the ‘scheirerRayHare’ function in the ‘rcompanion’ package of R software, which is a non-parametric test for two-way ANOVA analysis. And the multiple comparison was used by Wilcoxon rank sum test.
with R (R Core Team, 2020). For the correlation analysis between CH$_4$ and CO, we obtained the detrended time series of CH$_4$ and CO from 2004-2017 based on the method by Thoning et al. (1989). The detrended values are denoted as $\Delta$CH$_4$ and $\Delta$CO. To obtain the correlation slopes of $\Delta$CH$_4$ and $\Delta$CO accurately, a rolling linear regression was applied to $\Delta$CH$_4$ and $\Delta$CO time series by the ‘roll_lm’ function in ‘roll’ package of R (R Core Team, 2020). We successively moved a 24-h time window by 1 h over the whole time series. Similar to the study by Tohjima et al. (2014), we set 3 criteria to achieve a better quality control of the slopes. When (i) the number of CH$_4$ record is less than 5 in 24 hours, (ii) the coefficient variation of the correlation slope is more than 15%, (iii) the absolute value of the correlation slope is less than 0.8 ($|R| < 0.8$), the correlation slopes were identified as statistically insignificant and inaccurately and were rejected. In order to understand the year to year variations, we further analyzed the different periods over 1994-2017. The entire CH$_4$ time series were divided according to the significant stages or the critical time period of atmospheric CH$_4$ variations from previously studies (Zhou et al., 2004; Fang et al., 2013; Zhang et al., 2013; Nisbet et al., 2019; WMO, 2020), appropriately every five years a period. Unless special notes, the average values in this study were presented with 95% confidence intervals (CIs).

3 Results

3.1 Diurnal variations

Generally, distinct diurnal cycles were observed in four seasons during 1994-2017. The CH$_4$ mole fraction increased from early morning and reached the maximum at noon and a trough in late afternoon (Fig. 2f). However, differences also existed from different seasons. In spring, the atmospheric CH$_4$ apparently increased from 9:00 to 13:00 LT with the daily amplitude of 5.7 ± 2.4 ppb. In summer, the elevated CH$_4$ also appeared during 9:00-13:00 LT at noon, and the daily amplitude was 4.3 ± 2.6 ppb. In autumn, the diurnal variation showed the mean amplitude of 4.5 ± 2.4 ppb, significantly elevated
CH₄ reached at 9:00-13:00 LT with one peak at noon. In winter, largely increasing
presented in the daytime at 9:00-17:00 LT, with the largest amplitude of 6.2 ± 2.4 ppb
among four seasons. For the diurnal variation over the whole monitoring period, the
highest CH₄ mole fraction was observed in winter and the minimum value was found
in spring (Fig. 2f).

Different patterns for diurnal CH₄ cycles were also found over different periods.
In 1994-1997 and 1998-2002, the CH₄ mole fractions in winter were apparently higher
than the other seasons (Fig. 2a-b). But its value was the highest in summer during the
period of 2003-2007, 2008-2012 and 2013-2017 (Fig. 2c-e). The atmospheric CH₄
values in winter were gradually falling behind the other seasons, and the gaps among
different seasons were increasing, especially for summer. Before 2002, diurnal cycles
in four seasons were ambiguous (Fig. 2a-b), but significant diurnal variations appeared
afterwards (Fig. 2c-e). The peak to trough amplitude almost increased along with the
time in almost all seasons. For example in spring, the amplitude was 6.5 ± 3.0, 4.7 ±
1.8, 5.6 ± 2.6, 6.2 ± 2.4 and 6.8 ± 3.4 ppb over 1994-1997, 1998-2002, 2003-2007,
2008-2012 and 2013-2017, respectively (Table S1).

3.2 The impact of local surface winds

As observed by the previous short-term variations, the atmospheric CH₄ at WLG was
significantly influenced by local surface wind from northeast to southeast sectors (Fig.
3f). Slight differences were also found among seasons. In spring, the atmospheric CH₄
was enhanced by 2.5-6.5 ppb compared to the seasonal average (1839.7 ± 1.4 ppb)
when the wind was originating from NNE-NE-ENE-E sectors. In summer and autumn,
the wind from NNE-NE-ENE-ESE induced higher CH₄ mole fractions, with
enhancement of about 3-9.5 ppb and 4 to 18 ppb, respectively. In winter, the CH₄ mole
fractions significantly elevated from the wind sectors that same as those found in spring,
with value of 7-21 ppb than seasonal average (1854.5 ± 4.8 ppb). Relatively, the
amplitude of enhancements in winter and autumn were larger than those in spring and
summer.

What interesting is that wind sectors elevating CH$_4$ mole fractions vary in different periods. The early periods (i.e. 1994-1997 and 1998-2002) were different from the recent periods (2003-2007, 2008-2012 and 2013-2017). The elevated CH$_4$ was predominately from about ENE-E-ESE-SE-SSE sectors in early years (Fig. 3a-b), but evolved to NNE-NE-ENE-E sectors in later years (Fig. 3c-e). Furthermore, the amplitude of enhancements was almost increasing continuously along with the time. For example, in autumn, the maximum CH$_4$ mole fractions were from E, ENE, ENE, NE and ENE sectors in 1994-1997, 1998-2002, 2003-2007, 2008-2012 and 2013-2017, with the successively increasing enhancements of 8.6, 12.1, 14.7, 16.8 and 19.7 ppb, respectively.

We applied the CPF to hourly CH$_4$ and CO data by considering intervals of entire data percentiles including 0-20, 20-40, 40-60, 60-80 and 80-100 to draw the CPF polar plot. It is clear that different sources only affected CH$_4$ mole fractions on different percentile range. For example, for most wind speed-directions the CPF probability of CH$_4$ being greater than the 60$^{th}$ percentile was tending to zero (Fig. 4). And it is apparent that most sources contributed to the less than 60$^{th}$ percentiles of CH$_4$ mole fraction (e.g. 40-60) (Fig. 4). The specific sources were prominent for specific percentile ranges. The wind from the southwest and southeast was important on the cases of the higher percentiles, resulted in the highest CH$_4$ mole fractions of 1849-1872 ppb for 60-80 percentile and 1872-2031 ppb for 80-100 percentile (Fig. 4). It’s more obvious that the CO showed gradually shifted sources with the increase of percentile ranges. The areas where the CPF probabilities were higher is to the NW-SW sectors when the percentages ranged from 0 to 40$^{th}$. Nevertheless, when the percentages were larger than 60$^{th}$, the high probability areas completely moved to NE-SE sectors (Fig. 4).
3.3 Air mass pathways and potential source distributions

3.3.1 Air mass transports

Figure 5 illustrates the cluster analysis to the 3-day back trajectories to WLG during 2004-2017. In spring, the majority of the air masses were from west and northwest regions, which accounted for about 24% (cluster 3) and 44% (cluster 5) of total trajectories (Fig. 5a). These air masses were also accompanied with higher CH4 mole fractions than those from east and northeast regions, i.e. cluster 1 (13.3% of total) and cluster 4 (11.69%) (Table 1). The largest enhancement was ~18 ppb (relative to spring average) by cluster 3. In summer, 45% of air masses (cluster 1) were from eastern regions. But the high CH4 mole fractions were on cluster 2 and cluster 5 from northwest and west regions, although low percentages were found (cluster 2: 26%; cluster 5: 7%) (Fig. 5b). The highest CH4 mole fraction was associated with cluster 2, with ~9 ppb larger than the average in summer. In autumn, large proportion of air masses was originating from west and southwest station, such as cluster 2 (49%) and cluster 3 (32%) (Fig. 5c). The highest CH4 was from cluster 3 with enhancement of ~4 ppb than the seasonal average. Similar to autumn, the air masses were primarily from northwest in winter, including northwest cluster 3 (59%) and southwest cluster 1 (34%) regions (Fig. 5d). The highest CH4 mole fractions was on cluster 1 with the enhancement of ~7 ppb than the average value.

3.3.2 Spatial distribution of potential source regions

In this study, the potential sources were analyzed over different periods, i.e. 2004-2007, 2008-2012 and 2013-2017. Generally, the strong potential sources were located at the northeast to southeast of the station, especially in summer, but the source regions differed in various seasons as well as years (Fig. 6). The regions of potential source in spring (Fig. 6a-c) and winter (Fig. 6j-l) was obviously larger than that in summer (Fig.
6d-f) and autumn (Fig. 6g-i). There were also trends for the CH₄ source regions along with years: i) the area of potential source regions was increasing with the years, and ii) the location of strong potential sources changed along with the time. For example in autumn and winter, the strength of CH₄ sources were very strong in the southeast to northeast during 2004-2007 (Fig. 6g & i), and then weakened in 2008-2012 (Fig. 6h & k), and finally (i.e. 2013-2017), almost vanished in eastern regions but moved to southwest with very large distribution area (Fig. 6i & l).

3.4 Extracting the well-mixed ambient methane

To precisely understand characteristics of atmospheric CH₄, e.g., seasonal cycle or long-term trend, it is vital to identify the CH₄ records that were influenced by local sources and sinks. In this study, we analyzed hourly CH₄ measurements during 1994-2017, and 47.3% of CH₄ data were classified as regional representative, with the average CH₄ mole fraction of 1847.9 ± 0.3 ppb. The local representative data was obviously larger than regional events, with an average value of 1858.2 ± 0.4 ppb (Table 2). The proportion of regional events increased slightly before 2012, but significantly reduced in recent years (e.g., 2013-2017). The filtered regional/local time series was shown in Figure 7. It can be seen that the CH₄ mole fractions obviously increased from 1994 to 2017. The atmospheric CH₄ showed strong growth and displayed large fluctuation at WLG (Fig. 7). In 1995, the average CH₄ mole fraction was only 1805.8 ± 0.1 ppb, however, the average value increased 98 ppb by the year of 2016 (1903.8 ± 0.1 ppb) (Table 3).

3.5 Correlation analysis between CH₄ and CO

Because part of CH₄ and CO in atmosphere are from the same anthropogenic sources (e.g., fossil fuel combustion), we calculated the regression slopes of ΔCO/ΔCH₄ from 2004 to 2017 (Fig. S1). Figure 8 presents the average seasonal cycles of the ΔCO/ΔCH₄.
slopes. Generally, the slopes were larger in summer and lower in winter during the observing period, except for 2004-2007 with the high slope in autumn. Additionally, the regression slopes increased along with the time, which showed the maximum in 2013-2017 and the minimum in 2004-2007. For the year to year variations, the $\Delta$CO/$\Delta$CH$_4$ slopes showed large fluctuations from 2004 to 2017 at WLG (Fig. 9). The slopes showed decreasing trend during 2004-2007 but then increased from 2007 to 2010, and again decreased after 2010. In spring and summer, increasing trends appeared again after 2014. The slopes in summer were almost the largest but the lowest in winter.

3.6 Variation of long-term records

3.6.1 Seasonal cycles

In order to further investigate the characteristics of atmospheric CH$_4$, we divided the CH$_4$ observations into two main regions according to the above analysis, including geographical conditions, the effect of surface winds, the long-range transports and the potential source distributions. The first region was covered the northeast to southeast (NNE-…SE) of WLG, which was denoted as City Regions (CR). The second region was located south to west (S-…-W) of the station and was well known Tibet (Qinghai-Xizang) Plateau (TP) (Fig. S2). Accordingly, the hourly CH$_4$ records when the surface wind coming from these sectors were divided into two subsets (i.e. TP and CR). The long-term variations between the two regions as well as the total regional time series (Total) were compared and analyzed to explore new sight of atmospheric CH$_4$ variation at WLG.

Overall, at WLG, the seasonal averages of CH$_4$ were ordered by summer (1850.0 ± 0.3 ppb), winter (1847.4 ± 0.3 ppb), autumn (1844.4 ± 0.3 ppb) and spring (1841.2 ± 0.3 ppb), except during 1994-1997 with the maximum in winter and minimum in autumn (Fig. 10). Seasonal averages in CR were significantly different to that in TP and also the entire regional data (Total). The seasonal average in TP was mostly higher than
that in CR, except for wintertime (Table S2). The atmospheric CH$_4$ in August was mostly the maximum and the April was the minimum for the total regional time series (Total), with the seasonal amplitude of 13.4 ppb. The peak to trough amplitude in CR (~15 ppb) was higher than that in TP (~13 ppb) during 1994-2016. Additionally, seasonal amplitudes indicated different trends between CR and TP. For CR, the seasonal amplitude was firstly dropped and then increased along with time, which were similar to the variation of total regional events (Total). But for TP, the amplitude displayed a continuously increasing trend, with values of about 15.9, 19.3, 21.6, 23.4 and 22.4 ppb in 1994-1997, 1998-2002, 2003-2007, 2008-2012 and 2013-2016, respectively.

3.6.2 Long-term trend

In the 1990s, the CH$_4$ growth rates were very low and even negative at WLG. Subsequently, during 2002-2006, a steady period was found with a near-zero growth rates. After 2007, the atmospheric CH$_4$ was raised significantly (Fig. 11a). In the year of 1997/1998, 2000/2001, 2007/2008 and 2011/2012, larger amplitude of the growth rates was found and strong growth appeared (Fig. 11b). The growth rates fluctuated evenly with both positive and negative values before 2009. But almost all of the growth rates showed a positive value after 2009. From 1990s to 2010s, three apparently developing stages (i.e. highlighted green, blue and red blocks) were presented, the CH$_4$ mole fraction slightly decreased in 1998-2000 (green color), and then go through a relative steady period in 2003-2006 (blue color), finally increased steadily after 2007 (red color) (Fig. 11).

The overall annual growth rates were 5.1 ± 0.1 ppb yr$^{-1}$ over 1994-2016 at WLG (Table 4). However, the periodic annual growth rates were 4.6 ± 0.1, 2.6 ± 0.2, 5.3 ± 0.2, 7.6 ± 0.2 and 5.7 ± 0.1 ppb yr$^{-1}$ in 1994-1997, 1998-2002, 2003-2007, 2008-2012 and 2013-2016, respectively. The CH$_4$ growth rate in CR was significantly different from that in TP (Fig. S3). In 1994-1997, 2003-2007 and 2013-2016, the growth rates in TP were obviously larger than that in CR (Table 4). But in 2003-2007 and 2008-2012, the
CR showed higher annual growth rates. In addition, for the entire observing period (i.e. 1994-2016), the growth rates in both TP (5.2 ± 0.1 ppb yr\(^{-1}\)) and CR (5.0 ± 0.1 ppb yr\(^{-1}\)) were similar to the overall annual growth rates (Fig. S3).

3.7 Case study for air mass transport

As described above, the northeast and southeast city regions might act as strong regional sources influencing the atmospheric CH\(_4\) at WLG. Therefore, to analyze the effect of long-distance transport of emissions from cities, we further excluded the regional data by air mass transport, and the rest of regional records were denoted as ‘TR’. We applied the monthly cluster analysis to hourly trajectories over 2005-2007, 2008-2012 and 2013-2017. The cluster results from city regions were presented in detail in Fig. S4 and Table S3.

The proportion of trajectories from cities was 40.3%, 32.5% and 6.8% in 2005-2007, 2008-2012 and 2013-2017, respectively. And about 22.8%, 35.6% and 38.4% of the regional records were associated with air masses transport from city regions in 2005-2007, 2008-2012 and 2013-2017, respectively (Table 5). The average CH\(_4\) value when air masses transport from city regions (1863.0 ± 0.3 ppb) was obviously higher than other sectors (1850.6 ± 0.2 ppb) (Fig. S5). However, after excluding the CH\(_4\) records when air trajectories transport from city regions, the growth rates of TR in 2008-2012 (10.1 ± 0.1 ppb yr\(^{-1}\)) and 2013-2017 (6.3 ± 0.1 ppb yr\(^{-1}\)) (Table 5) were higher than the original regional data series (i.e. 7.6 ± 0.2 and 5.7 ± 0.1 ppb yr\(^{-1}\)) (Table 4). And the overall growth rate for TR in 2005-2016 or 1994-2016 was still similar to original data series (Total), no significant difference was found (Fig. S5).
4 Discussion

4.1 Anthropogenic emission on temporal patterns

In the early years, the daily cycles of atmospheric CH$_4$ at WLG were not distinct and the amplitude was small (Fig. 2a-b), which were similar to the previous studies by Zhang et al. (2013) and Fang et al. (2013). The ambiguous diurnal patterns indicated that the local sources were weak at WLG in the past. The apparent diurnal cycles after 2000 may be attributed to the intense activities by human (e.g., grazing, fuel burning), which was aggravated in daytime and weak in nighttime (Fang et al., 2013). The meteorological conditions (e.g., diffusion and transport) could contribute to the increasing CH$_4$ amplitudes. The WLG was remote from the populate center, the good diffusion condition in daytime may bring high CH$_4$ mole fractions to the site. The increasing amplitude (Table S1) and CH$_4$ mole fractions over time suggested that the WLG was affected by increasingly local sources (e.g., human activities) (Zhou et al., 2004). The maximum was found in summer in recent years (Fig. 2e) could also be ascribed to the transport of anthropogenic sources by the meteorological factors. In summer, the intensely herd or graze activities around WLG might enhance the regional CH$_4$ emissions and hence contribute to the higher CH$_4$ mole fractions. The higher CH$_4$ mole fraction in winter in past years (Fig. 2a) was probably because of the way of heating (e.g., large biomass burning) as well as the adverse diffusion conditions in cold weather.

The previous study by Zhou et al. (2004) found that higher CH$_4$ mole fractions appeared when the winds come from the ENE-E-ESE-SE sectors at WLG during 1991-2002, which was similar to our study in similar period (Fig. 3a-b). Causes of the elevated CH$_4$ from these wind sectors could be attributed to the large plantation of highland barley as well as high population density in those areas (Fang et al., 2013). Two largest cities Xining and Lanzhou are situated in northeast and east of WLG, respectively, which could emit large amount of CH$_4$ by human activities. Besides,
previous studies on black carbon (BC) and carbon monoxide (CO) indicated that the emissions from the Yellow River Canyon industrial area, ~500km away from northeast of WLG may also donate to the high CH4 values originating from ENE and NE sectors (Zhou et al., 2003). In summer, the prevailing wind directions were from NE-…-ESE sectors (~46%) (Fig. S6), and the CH4 mole fractions were also higher in the related sectors. However, in the autumn and winter, although the prevailing wind and high wind speed were from SSW-…-W sectors (~ 40-50%) (Fig. S6), the high CH4 mole fractions were from almost the opposite wind sectors of NNE-…-ESE (Fig. 3f), which indicated that strong local sources were distributed from northeast to southeast (city regions), and even covered the emissions of natural sources. As time goes on, the wind sectors with high CH4 mole fractions changed and concentrated on ESE to ENE sectors, and the amplitudes of enhancements were increasing, which further implied the effect of stronger emissions from anthropogenic sources in city regions in recent years.

4.2 Pollutant sources regions

4.2.1 Sources regions

The air masses from east and northeast regions passed over the cities of Xining and Lanzhou (capital of Gansu province), which is the populated center and industrial area (Fig. 5). However, the highest CH4 values was not observed when air mass was from these sectors. Instead, high CH4 mole fractions were frequently observed when air mass from the northwest to southwest (Table 1). It was possibly due to that the air masses from west and northwest had passed through the northwest of Qinghai province and the central area of Xinjiang Uygur Autonomous Region (XUAR), where located Ge’ermu urban area (the second largest city of Qinghai) with rapid industrial development, natural gas and petroleum resources exploitation and large crops residue burning (Zhang et al., 2013). Similar to the CPF percentile analysis (Fig. 4), the southwest or northwest region away from the site may be also strong source regions.
Most potential source identified in northwestern regions (Fig. 6) was possibly due to CH₄ emissions from the northwest Gansu province, the northwest Qinghai province and the southeast of XUAR. The different source distribution by seasons could be attributed to the effect of westerlies or the southeast monsoons (Zhou et al., 2004). The obviously increasing source region was clear evidence for the strong effect of the expansion of human activity. Moreover, the pattern of source region moved from the east to the southwest, especially in autumn and winter, indicated that the southwest away from the WLG, e.g., Northern India, were gradually becoming a strong CH₄ source region. India has abundant cattle as well as extensive large-scale coal mining, large amount of CH₄ emissions may transport from northern India to the northeastern Tibetan Plateau (Fig. 6i & l). The air mass transport result (Fig. 5d) also support the result that the southwest air masses (cluster 1) contributed the highest CH₄ mole fractions. The studies of atmospheric Hg at WLG by Fu et al. (2012) also revealed this phenomenon.

4.2.2 Different sources between CH₄ and CO

The percentile polar plot clearly showed the specific distribution of different CH₄ mole fractions (Fig. 4). The result revealed that most areas around WLG contributed to low CH₄ mole fractions, the southeast and southwest of the site exist two strong source regions. It is of great possible that the anthropogenic emission from cities (e.g., Lanzhou, Chengdu, etc.) was the only cause for high values in the southeast, and the southwest region away from WLG was possibly due to sources from other countries, such as India. Unlikely to the CH₄, the high CO mole fractions were consistent from east regions (urbanized area) (Fig. 4), indicating strong anthropogenic sources in city regions (i.e. Xining and Lanzhou) (Zhang et al., 2011).

The seasonal cycles of ΔCO/ΔCH₄ slopes (high in summer and low in winter) (Fig. 8) may primarily be due to the effect of monsoons and air mass transport. In summer, air masses arriving at WLG were predominantly transported from the northeast to east
city regions (e.g., Xining, Lanzhou) with the largest CO mole fractions. In contrast, the air masses were mainly from the southwest in winter, which carried strong CH₄ emissions but few CO emissions (Zhang et al., 2011) (Table 1). Hence the opposite two air mass transport lead to a peak in summer and a trough in winter (Fig. 8). Moreover, we could see apparently regional polarization in the concentration ratio of CH₄ and CO (Fig. S7), implying the different strong source distribution between CH₄ and CO at WLG. The cluster results (Fig. 5b & d) and the potential sources analysis (Fig. 6f & l) also support this seasonal variation. Tohjima et al. (2014) found an opposite variation at Hateruma Island, which showed low slope values in summer. It could be attributed to different local sources and sinks, suggested the special topography condition and local source distribution around WLG. The large ΔCO/ΔCH₄ fluctuations (Fig. 9) over the study period was likely because of the anomaly years of different CH₄ or CO mole fractions as well as source regions. In 2007, large increase of ΔCH₄ appeared, and from 2010 to 2013, the ΔCO decreased significantly (Fig. S1). Before 2010, large air masses and potential source regions were identified in eastern regions (city regions) with the highest CO emission (Fig. 5; Fig. 6). After 2010, the southwest regions showed high contributions, with the highest CH₄ emission but relatively lower CO emission. Therefore, obviously variation of the slopes presented with almost an increase in 2007-2010 and a decrease after 2010 (Fig. 9).

4.3 Long-term variations

4.3.1 Seasonal cycles

The seasonal variations with maximum in summer and minimum in spring at WLG (Fig. 10) were consistent with the previously short-term studies, e.g., Zhang et al. (2013) in 2002-2006. However, it was almost opposite to observation in the adjacent stations such as Lin’an, Shangdianzi and Longfengshan in China (Fang et al., 2013, 2016), as well as most global stations in the northern hemisphere, e.g., MLO, BRW and
JFJ (Dlugokencky et al., 1995; Loov et al., 2008). We further compared similar
WMO/GAW global stations in the north hemisphere, including MLO (19.54° N, -
155.58° E, 3397m a.s.l.) (Dlugokencky et al., 1995, 2019a), JFJ (46.55° N, 7.99° E,
3580m a.s.l.) (Zellweger et al., 2016), MNM (24.29° N, 153.98° E, 7.1m a.s.l.)
(Matsueda et al., 2004; Tsutsumi et al., 2006), as well as the marine boundary layer
(MBL) from NOAA/ESRL lab at similar latitude (Dlugokencky et al., 2019b). It can be
seen that the stations in the northern hemisphere (i.e. MLO, JFJ and MNM) and the
MBL showed an opposite trend to WLG with the minimum in summer and maximum
in winter or spring (Fig. 12). And the seasonal amplitude at WLG (~14 ppb) was lower
than many other sites in the northern hemisphere, about 35-70 ppb, e.g., MLO, BRW,
bialystok in Poland, ochenenkopf in Germany and beromunster in switzerland
(Dlugokencky et al., 1995; Thompson et al., 2009; Popa et al., 2010; Satar et al., 2016).
MBL also showed larger amplitude than that in WLG (Fig. 12). The low amplitude at
WLG was possibly because of high elevation of continental mountain sites (e.g., WLG,
JFJ), where were relatively less affected by local influences than the coastal/island sites
(Yuan et al., 2019). The peak in summer at WLG may be attributed to larger grazing
and human activities than other seasons. The CH₄ emissions from yaks and other
ruminants in Tibetan Plateau (alpine pasture) were very strong in summer, preceded
only by paddy emission (Fang et al., 2013; Zhang et al., 2013). Furthermore, the
photochemical capacities were very weak (high altitude) and the dynamic transport by
air flow from polluted northeast/southeast region was also strong in summer at WLG,
which all induced high CH₄ mole fractions in summer and consequently an opposite
trend with other sites (Ma et al., 2002; Xiong et al., 2009).

4.3.2 Long-term trends in different observing periods

The entirely fluctuant trend of atmospheric CH₄ in 1994-2016 at WLG (Fig. 11) was
similar to the global trend reported by quite a few studies (Bergamaschi et al., 2013;
Rigby et al., 2017; Nisbet et al., 2019). The previous study by Zhou et al. (2004) showed
the CH$_4$ annual increase of 4.5 ppb yr$^{-1}$ in 1992-2001, which was similar to that in 1994-1997 (4.6 ± 0.1 ppb yr$^{-1}$) and 1997-2002 (2.6 ± 0.2 ppb yr$^{-1}$) in our study (Table 4). Tohjima et al. (2002) found similar growth rates that the CH$_4$ at Cape Ochi-ishi and Hateruma Island in 1995-2000 was increased about 4.5 and 4.7 ppb yr$^{-1}$, respectively. In early 1990s, the CH$_4$ trend at WLG is very low, which was similar to the global growth rates (Fig. 11b). The levels of OH radicals may have controlled the decrease or increase of CH$_4$ in the atmosphere during this period (Dlugokencky et al., 1998; Rigby et al., 2017; Turner et al., 2017). The growth rates were high in 1998 (Fig. 11b), which may have been due to the high temperatures, large biomass burning and weak destruction (Cunnold et al., 2002; Lelieveld et al., 2004; Simmonds et al., 2005).

The continuously larger CH$_4$ growth rates after 2007 at WLG (Fig. 11), e.g., 7.6 ± 0.2 ppb yr$^{-1}$ in 2008-2012, 5.7 ± 0.1 ppb yr$^{-1}$ in 2013-2016 (Table 4), were similar to the recent study by Nisbet et al. (2016) and (2019), which showed the global CH$_4$ increased by 5.7 ± 1.2 ppb yr$^{-1}$ in 2007-2014, and the much higher of 12.7 ± 0.5 ppb yr$^{-1}$ in 2014, 10.1 ± 0.7 ppb yr$^{-1}$ in 2015, 7.0 ± 0.7 ppb yr$^{-1}$ in 2016 and 7.7 ± 0.7 in 2017 ppb yr$^{-1}$. The average growth rate in the northern hemisphere was 7.3 ± 1.3 ppb in 2007 and 8.1 ± 1.6 ppb in 2008 (Dlugokencky et al., 2009), which was also similar to the observation at WLG (Table 4). After 2007, most sites in the northern hemisphere displayed large CH$_4$ growth rates. Fang et al. (2013) showed that the annual growth rate of CH$_4$ was 9.4 ± 0.2 ppb yr$^{-1}$ in 2009-2011 at WLG, which were a little higher than our study in similar period. The adjacent stations in China also revealed high CH$_4$ growth rates, e.g., 8.0 ± 1.2 ppb yr$^{-1}$ at Lin’an in 2009-2011, 7.9 ± 0.9 ppb yr$^{-1}$ at Longfengshan in 2009-2011, and 10 ± 0.1 ppb yr$^{-1}$ at Shangdianzi in 2009-2013 (Fang et al., 2013, 2016), which was higher than the similar period in 2008-2012 or 2013-2016 at WLG (Table 4). The CH$_4$ measurements in other countries, e.g., Beromünster tall tower station also showed high growth rate of 9.66 ppb yr$^{-1}$ in 2012-2014 (Satar et al., 2016). The very warm temperatures, large biomass burning and the climatic anomaly e.g., El Niño, La Niña event, were likely enhanced the CH$_4$ emissions after 2007 (Dlugokencky et al.,
2009). Additionally, the anomalously sharply increasing or decreasing years (e.g., 2007/2008) may have a significant influence on the overall CH₄ trend (Fig. 11), and these frequent anomalies appeared in most long-term observation stations, e.g., MLO in USA (Dlugokencky et al., 2009), Mount Zugspitze in Germany (Yuan et al., 2019), which were also possibly attributed to climatic forces, such as the exception during the El Niño oscillation, forest fires, volcanic eruptions, and extreme weather events (Keeling et al., 1995; Dlugokencky et al., 2009; Keenan et al., 2016; Nisbet et al., 2019). The study by Satar et al. (2016) at Beromünster, Switzerland explained that the short-term spikes were possibly related to emissions from agricultural activities, while the longer lasting peaks were because of air mass transport and mixing.

It is well established that the human activities are mainly responsible for the recent rapid CH₄ growth rates and anomalies. The analysis from Emissions Database for Global Atmospheric Research (EDGAR) showed the CH₄ emission by per sector in China (Fig. S8) (Crippa et al., 2019). During the observing period, the waste, the oil and natural gas and open burning continuously emitted large amount of CH₄ into the air. After 2000, the CH₄ emission from solid fuel increased greatly in China. After 2003, the CH₄ emitted from rice cultivation also increased continuously (Fig. S8). The increased emissions from these sectors may greatly contribute to the CH₄ increase at WLG, as well as the other regions in China. In addition, the recent studies revealed that China’s coal sector may have dominated the clearly positive trend in recent years, which contributed the highest proportion of the anthropogenic CH₄ emissions (~33%) (Janssens-Maenhout et al., 2019; Miller et al., 2019). In 2010-2015, China’s coal production increased obviously (from 3400 to 4000 million metric tons), but emissions trends of CH₄ by rice, agriculture, ruminants, waste, and oil/gas have grown slightly and even remained flat (EIA, USA). The isotopic evidence suggests that the significant increase of biogenic emissions was the dominant factor of CH₄ rise, especially in the tropical wetlands with strong rainfall anomalies, or the agricultural sources such as rice paddies and ruminants, fossil fuel emissions have not been the main cause (Nisbet et
The study by Chen et al. (2013) illustrated that the warming (0.2 °C per decade) in the Tibetan Plateau resulted in substantial emission of CH$_4$ due to the permafrost thawing and glaciers melting. However, up to now, the specific causes of such distinct variability around the years, e.g., the spikes or near-zero CH$_4$ growth rates, are not yet determined.

### 4.3.3 Annual growth rate in Qinghai-Tibetan Plateau

Although similar annual growth rates were found among the City Regions (CR), the Tibet Plateau (TP) and total regional records (Total) in the entire observing period (1994-2016) (Fig. 11), significant differences were found in short-term periods (Fig. S3). In 2013-2016 (Table 4), the TP showed larger growth rate than that in CR, implying stronger CH$_4$ source in the Tibetan Plateau in recent years. The seasonal amplitude in the Tibetan Plateau was continuously increasing, which also revealed that the Tibetan Plateau was intensively affected by strong regional sources. Without air mass transport from the city regions, the significantly increased annual growth rate (TR) in 2008-2012 (10.1 ± 0.1 ppb yr$^{-1}$) and 2013-2016 (6.3 ± 0.1 ppb yr$^{-1}$) (Fig. S5 and Table 5) suggested that there were possibly other strong CH$_4$ sources around WLG not from cities.

Northern India and eastern China were obviously the largest two source regions of CH$_4$ at WLG (Fig. S9) (Crippa et al., 2019). Since the Tibetan Plateau was coincidently trapped in the middle of the largest increased source areas, the atmospheric CH$_4$ at WLG was very likely dominated by long-distance transport from these two regions.

Although CH$_4$ emissions increased slowly during 1994-2002, and even negative trend appeared in southeast China (Fig. S9), significantly increased emissions appeared in both southeast and southwest Asia after 2007. The rapidly increased CH$_4$ would probably make it difficult to meet the goals of carbon emission reduction in the future. Especially on the scenario of quick increasing CH$_4$ on the Qinghai-Tibetan Plateau due to the emission from two largest source regions. In view of the integrated eco-environmental change processes and unique topography in the Qinghai-Tibetan
Plateau, it may provide us one of the last precious regions to study global climate changes (Chen et al., 2013). The anomalously year to year fluctuations of atmospheric CH$_4$ in Tibetan Plateau were unquestionably a warning or alarm to the world, and the unprecedented annual growth rate might be a dangerous signal to global climate change.

5 Conclusion

The atmospheric CH$_4$ at Mt.Waliguan increased continuously during 1994-2017. Although near-zero and even negative growth appeared in some particular periods, e.g., 1999-2000, and 2004-2006, the overall trend of CH$_4$ was increased rapidly, especially in recent decade. Obvious diurnal cycle was found with the peak at noon and a trough at late afternoon. Due to the unique geophysical locations and transport pathway, the seasonal averages of CH$_4$ at WLG displayed an opposite trend with sites in the northern hemisphere, with summer maximum and spring minimum. Large amount of air masses was from west and northwest regions of WLG, which accompanied with higher CH$_4$ mole fractions than that from city regions. The Northern India possibly became a strong source of CH$_4$ to WLG rather than city regions before.

As time goes by, the temporal patterns (e.g., seasonal amplitude), the annual variations, the long-term trends or potential source distribution of CH$_4$ at WLG are all changing. Thus, the long-term verification is extremely important to accurately understand CH$_4$ variations. The case study in Qinghai-Tibetan Plateau revealed unprecedented annual growth rates of CH$_4$. In recent years, the Tibetan Plateau even showed larger growth rate than that in city regions. Tibetan Plateau was with the highest average altitude and was almost impervious to strong human activities. There is no doubt that the anomalously variation and the unprecedented annual growth rate of atmospheric CH$_4$ in this region might be a dangerous signal to global climate change.
Data availability. The gridded meteorological data (2004-2017) from NOAA-ARL was available at ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/. The data from MLO, JFJ, MNM station was downloaded from World Data Centre for Greenhouse Gases (WDCGG) at https://gaw.kishou.go.jp/. The MBL data was available at ftp://aftp.cmdl.noaa.gov/data/trace_gases/CH4/flask/surface/. The geographical distribution of annual emission data by Emissions Database for Global Atmospheric Research (EDGAR) was from website https://edgar.jrc.ec.europa.eu/overview.php?v=50_GHG.

Author contributions. SL, SF and ZF designed the research. SL performed the data processing with assistance of SF and MG. The station were monitored, maintained ML and PL, and they collected, preprocessed, and provided the hourly observational dataset. SL and SF finished the manuscript with contributions from all the co-authors.

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

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Table 1. The statistics for cluster analysis result for both CH₄ and CO at WLG station. The clusters from urban areas are highlighted with face bold.

| Cluster Number | Average CH₄ mole fraction |
|----------------|--------------------------|
| Spring         |                          |
| 1              | 1853.4 ± 2.7             |
| 2              | 1852.6 ± 3.4             |
| 3              | 1877.6 ± 2.5             |
| 4              | 1850.5 ± 2.2             |
| 5              | 1860.8 ± 1.5             |
| Summer         |                          |
| 1              | 1869.9 ± 1.2             |
| 2              | 1878.5 ± 2.6             |
| 3              | 1866.3 ± 2.6             |
| 4              | 1857.8 ± 2.4             |
| 5              | 1876.3 ± 5.1             |
| Autumn         |                          |
| 1              | 1870.1 ± 3.7             |
| 2              | 1868.8 ± 1.3             |
| 3              | 1873.6 ± 1.6             |
| 4              | 1865.2 ± 3.6             |
| Winter         |                          |
| 1              | 1879.8 ± 2.1             |
| 2              | 1872.6 ± 3.4             |
| 3              | 1865.8 ± 1.0             |
Table 2. The statistics of filtered CH₄ data series over different periods during 1994-2017 at WLG station.

| Year       | Regional representative |                       | Local representative |                       |
|------------|-------------------------|-----------------------|----------------------|-----------------------|
|            | Hours | Percentage (%) | Mean (ppb) | Hours | Percentage (%) | Mean (ppb) |
| 1994-1997  | 6481  | 46.9          | 1801.7 ± 0.5 | 7346  | 53.1          | 1806.1 ± 0.5 |
| 1998-2002  | 5332  | 47.6          | 1832.6 ± 0.7 | 5877  | 52.4          | 1837.9 ± 0.6 |
| 2003-2007  | 12421 | 49.2          | 1832.2 ± 0.3 | 12850 | 50.8          | 1839.2 ± 0.3 |
| 2008-2012  | 11314 | 49.2          | 1856.4 ± 0.4 | 11664 | 50.8          | 1867.0 ± 0.4 |
| 2013-2017  | 10140 | 43.6          | 1894.9 ± 0.5 | 13121 | 56.4          | 1907.4 ± 0.5 |
| 1994-2017  | 45688 | 47.3          | 1847.9 ± 0.3 | 50858 | 52.7          | 1858.2 ± 0.4 |
Table 3. Yearly average CH₄ mole fractions at WLG station.

| Year | Mean (ppb) | Year | Mean (ppb) |
|------|------------|------|------------|
| 1995 | 1805.8 ± 0.1 | 2006 | 1835.6 ± 0.2 |
| 1996 | 1804.6 ± 0.2 | 2007 | 1839.9 ± 0.5 |
| 1997 | 1806.8 ± 0.2 | 2008 | 1865.9 ± 0.3 |
| 1998 | 1827.0 ± 0.1 | 2009 | 1849.1 ± 0.1 |
| 1999 | 1820.2 ± 0.1 | 2010 | 1857.9 ± 0.2 |
| 2000 | 1820.0 ± 0.2 | 2011 | 1872.6 ± 0.4 |
| 2001 | 1849.2 ± 0.4 | 2012 | 1881.2 ± 0.3 |
| 2002 | 1835.5 ± 0.2 | 2013 | 1896.3 ± 0.2 |
| 2003 | 1842.5 ± 0.3 | 2014 | 1890.4 ± 0.1 |
| 2004 | 1836.7 ± 0.1 | 2015 | 1905.6 ± 0.3 |
| 2005 | 1837.4 ± 0.1 | 2016 | 1903.8 ± 0.1 |
Table 4. Annual growth rates of atmospheric CH$_4$ in the City Regions (CR), the Tibet Plateau (TP), and original total regional records (Total) during 1994-2016 at WLG station.

|       | 1994-1997 | 1998-2002 | 2003-2007 | 2008-2012 | 2013-2016 | 1994-2016 |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| CR    | 2.8 ± 0.1 | 3.6 ± 0.2 | 5.6 ± 0.2 | 7.1 ± 0.2 | 5.5 ± 0.1 | 5.0 ± 0.1 |
| TP    | 3.4 ± 0.1 | 3.0 ± 0.2 | 6.8 ± 0.2 | 5.6 ± 0.2 | 7.3 ± 0.1 | 5.2 ± 0.1 |
| Total | 4.6 ± 0.1 | 2.6 ± 0.2 | 5.3 ± 0.2 | 7.6 ± 0.2 | 5.7 ± 0.1 | 5.1 ± 0.1 |
Table 5. The statistics of CH$_4$ data without air mass transport from city regions (TR) over different periods during 2005-2016 at WLG station.

| Transport regions | Hours | Percentage (%) | Average (ppb) | Updated growth rate (ppb yr$^{-1}$) |
|-------------------|-------|----------------|---------------|-----------------------------------|
| 2005-2007 TR      | 6922  | 77.2           | 1824.9 ± 0.2  | 2.7 ± 0.2                         |
| City              | 2041  | 22.8           | 1835.9 ± 0.5  | -                                 |
| 2008-2012 TR      | 7060  | 64.4           | 1853.7 ± 0.2  | 10.1 ± 0.1                        |
| City              | 4254  | 35.6           | 1861.0 ± 0.3  | -                                 |
| 2013-2016 TR      | 4152  | 61.6           | 1888.2 ± 0.3  | 6.3 ± 0.1                         |
| City              | 2591  | 38.4           | 1888.5 ± 0.5  | -                                 |
| 2005-2016 TR      | 18134 | 67.1           | 1850.6 ± 0.2  | 7.0 ± 0.1                         |
| City              | 8886  | 32.9           | 1863.2 ± 0.3  | -                                 |
Figure 1. Location of Mt. Waliguan WMO/GAW global station as well as other regional stations in China. The gradient color indicates altitude. The digital elevation model (DEM) was downloaded from Geospatial Data Cloud site, Computer Network Information Center, Chinese Academy of Sciences (http://www.gscloud.cn), and then processed by ArcGIS software. The China map was derived from © National basic Geomatics Center of China (http://www.ngcc.cn/ngcc/). The world map was obtained from © OpenStreetMap (https://www.openstreetmap.org/). And the other shpfile data and entire map were created by ArcGIS software.
Figure 2. Diurnal CH$_4$ cycles in different periods from 1994 to 2017 at WLG station. The lines with different colors represent various seasons. Error bars indicate the 95% confidence intervals.
Figure 3. Wind-rose distribution of average hourly CH$_4$ records from 16 horizontal wind directions over different periods in 1994-2017 at WLG station. The different colors represent the CH$_4$ data in different seasons. Error bars in all directions indicate 95% confidence intervals.
Figure 4. The polar plot of the distribution of CH₄ and CO concentration probability in different percentile ranges at WLG station. The analysis was based on the conditional probability functions (CPF) by Ashbaugh et al. (1985). The top plots show the measurements of CH₄ from 1994 to 2017. The bottom plots show the CO measurements in 2004-2017. ‘ws’ means the wind speed. The values in the bottom of each panel show the range of concentration in relevant percentile range. Gradient colors represent the levels of CPF probability in different percentile ranges.
Figure 5. Cluster analysis to the 72-h back trajectories in different seasons during 2004-2017 ending at WLG station. The (a), (b), (c) and (d) represents spring, summer, autumn and winter, respectively. The lines with different colors denote different cluster analysis results. The proportion of trajectories on each cluster is also marked.
Figure 6. Geographical distribution of weighted potential source of CH₄ in different periods over 1994-2017 at WLG station. The gradient color shows strong levels of potential source regions in different seasons, i.e. spring (a, b, c), summer (d, e, f), autumn (g, h, i) and winter (j, k, l), and different periods, i.e. 2004-2007 (a, d, g), 2008-2012 (b, e, h, k) and 2013-2017 (c, f, i, l).
Figure 7. Filtered hourly CH₄ data series from 1994 to 2017 at WLG station. The blue points with transparency represent regional events. The black points are the filtered local events. The red lines are calculated smooth values to the regional data by curve-fitting routine of Thoning et al. (1989).
Figure 8. Average seasonal variation of ΔCO/ΔCH₄ slopes in different periods over 2004-2017 at WLG station. The error bars show the standard deviation of the monthly averages. The vertical bars are the monthly numbers of data in different periods.
Figure 9. Long-term trend of $\Delta$CO/$\Delta$CH$_4$ slopes over 2004-2017 at WLG station.
Figure 10. Monthly variations of regional CH$_4$ mole fractions from 1994 to 2016 at WLG station. The ‘CR’, ‘TP’ and ‘Total’ represents the measurements from the City Regions, the Tibet Plateau and the original total regional records, respectively. The box respectively shows the 25th percentile, the median and the 75th percentile from bottom to top. The bottom and the top whisker respectively reaches the minimum and 1.5 times the IQR (interquartile range). The black points are identified as outliers. The red squares are the averages. The cyan lines are the smooth curve of averages using the method of loess (Local Polynomial Regression Fitting). The gray bands are the 95% confidence interval of smooth curve.
Figure 11. The top panel (a) shows the smooth curve and monthly values of CH$_4$ mole fraction in the City Regions (CR) and the Tibet Plateau (TP) during 1994-2016 at WLG station. The bottom panel (b) is the annual growth rates of atmospheric CH$_4$ records from CR, TP as well as the total regional time series (Total). The growth rates are calculated from the first derivative of trend curves. The smooth curve and the trend is calculated by the method of Thoning et al. (1989).
Figure 12. The seasonal cycles of atmospheric CH$_4$ observed over 1994-2017 at WMO/GAW global stations of Mauna Loa (MLO), Jungfraujoch (JFJ), Minamitorishima (MNM) and Mt.Waliguan (WLG) in the northern hemisphere. The data of other sites (except WLG) are from WDCGG. The data in the marine boundary layer (MBL) are from NOAA / ESRL lab at the similar latitude to WLG.