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Isotopic signatures of methane emission from oil and natural gas plants in southwestern China

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Abstract

Methane (CH_4) emissions to atmosphere from Chinese oil and gas (ONG) sector are subject to considerable uncertainty. The isotopic composition of CH_4 isotopes ($\delta^{13}C$) varies between emission sources, enabling the identification of changes in specific CH_4 sources. However, there are few relevant studies in China, especially at the ONG site level. We obtained CH_4 mixing ratios and isotopes from atmospheric samples collected by UAV and ground monitoring, and employed the HYSPLIT model to investigate CH_4 distribution at ONG sites in southwest China. It was found that the CH_4 isotopic signatures provide a strong basis for the emission intensity at the ONG sites. The meteorological and site conditions were identified as the most influential factors in CH_4 distribution at sites. The CH_4 from the equipment area contributed approximately a quarter of the CH_4 observed over the sites. The CH_4 source isotopic signatures ($\delta^{13}C$) of this study were heavier than those globally, indicating that they were mainly thermogenic sources. Finally, the heavier $\delta^{13}C$ of this region may lead to an overestimation emission of global CH_4 from fossil fuel sources by 3.47 Tg CH_4 yr^{-1}, and underestimation from microbial sources. This study highlights the importance of regional CH_4 isotopes, with great significance for CH_4 inventories of global sectors.

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1 Introduction

Methane (CH_4) is a major greenhouse gas (GHG) in the atmosphere, possessing a global warming potential 82.5 times greater than carbon dioxide (CO_2) over a 20-year timeline, and 29.8 times greater over a 100-year period(Ipcc, 2021). The mixing ratios of CH_4 in the atmosphere has increased by 150% since the industrial revolution, primarily driven by human activities(Hmiel et al., 2020; Saunois et al., 2016b; Tian et al., 2016; Skeie et al., 2023). The oil and natural gas (ONG) industry is one of the major contributors to anthropogenic CH_4 emissions accounting for approximately 25% of global emissions. Over the past 20 years, CH_4 emissions from the ONG industry have increased by about 23.1%, corresponding to an average annual growth rate of 1.1%(Lauvaux et al., 2022). However, some studies suggest that CH_4 emissions from fossil fuel sources are likely to be seriously underestimated(Lauvaux et al., 2022; Hmiel et al., 2020). In China, CH_4 emissions from ONG industry have been estimated to increase from 116.6 Gg in 1990 to 1124.8 Gg in 2018(Epa, 2019), but various nationwide investigations tend to be highly variable and uncertain(Zhang et al., 2014)· (Sun et al., 2022). Such discrepancy primarily arises from the scarcity of publicly available data and the accuracy of emission factors. The emission factor (EF) data used mainly come from the IPCC and its improvements, which may not accurately reflect the actual situation in China(Gao et al., 2022).

Overall, the general consensus is that the global CH_4 mixing ratios have been increasing over the past few decades(Schwietzke et al., 2016; Montzka et al., 2011; National Oceanic & Atmospheric Administration, 2024a). At present, the main controversy is the contribution sources of CH_4 (the drivers of the atmospheric CH_4 growth) and the high uncertainty of contribution (the uncertainty in CH_4 budget)(Kirschke et al., 2013; Saunois et al., 2016a; Rice et al., 2016; Tibrewal et al., 2024). The identification of CH_4 sources is essential for the estimating and reduction of CH_4 emissions.

The anthropogenic sources CH_4 accounting for about 50-65% of global CH_4 emissions come from human activities, including ONG industry, wetlands, agriculture

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(e.g., ruminants, rice cultivation), landfills, and wastewater. However, the contribution of each CH_4 source is highly uncertain(Skeie et al., 2023). The presence of greenhouse gases is attributed to a multitude of sources. These sources exhibit distinct isotopic signatures, which serve as a valuable tool for the identification and differentiation of their origins(Schwietzke et al., 2016). Stable isotope is one of the common tools to distinguish different sources of the same substance(Suzuki, 2021; Peng et al., 2024; Leitner et al., 2020; Basu et al., 2022). A number of isotope pool mixing-models have been developed to quantify source contributions(Parnell et al., 2013)·(Barthold et al., 2011), providing important constraints on the role of various anthropogenic and natural emissions to the overall greenhouse gas burden, and thereby enhancing our understanding of the complex dynamics of climate change(Zhang et al., 2022; Rigby et al., 2017). Several studies have attempted to use CH_4 isotopes for unraveling regional CH_4 emission patterns. Using the characteristics of carbon ($\delta^{13}C$) and hydrogen (δD) stable isotopic of CH_4, help distinguish between specific emitters of CH_4 from the Condamine region, Queensland, Australia (main CH_4 sources include coal seam gas related, piggery, ground and river seeps, feedlot and grazing cattle, landfill and others), the $\delta^{13}C$ and δD signatures of each CH_4 source were analyzed(Lu et al., 2021). Some researchers combined $\delta^{13}C$ with other models to separate industrial CH_4 emission sources from atmospheric(Assan et al., 2018). A recent research indicated that 85% CH_4 emissions growth from microbial sources during the period 2007 to 2016 were estimated based on $\delta^{13}C$ of CH_4 in the atmosphere(Basu et al., 2022). A study based on atmospheric $\delta^{13}C$ of CH_4 data showed that CH_4 emissions from the fossil fuel sector remained largely unchanged at the 1980s and 1990s levels, but increased significantly between 2000 and 2009(Rice et al., 2016). By analyzing $\delta^{13}C$ of CH_4, researchers suggested that a reduction in microbial CH_4 emissions in the Northern Hemisphere may have contributed to the stabilization of atmospheric CH_4 over the Millennium(Kai et al., 2011).

Global observations and researches on CH_4 source isotopic signatures from the ONG industry have been carried out and some results obtained, such as a global database of CH_4 isotopes from fossil fuels in the atmosphere has been established, according to the

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latest research results to update timely(Schwietzke et al., 2016). Other studies have been initiated at regional and urban scales, such as estimating CH_4 emissions from abandoned ONG wells in the United States, and $\delta^{13}C$ of CH_4 has been employed to distinguish the coalbed and nature gas sources(Townsend-Small et al., 2016). Another research also reported the CH_4 isotopic signatures of ONG fields in Romania, confirmed CH_4 in the region mainly from the ONG sector, and simultaneous resulted a wide range of $\delta^{13}C$ values, which indicated regional variation in CH_4 isotopes(Menoud et al., 2022). Recent advancements in UAV technology have facilitated novel approaches to monitor and quantify CH_4 emissions, particularly in localized settings(Shaw et al., 2021). For example, the airborne platform was used to monitor the CH_4 emission from UK and Dutch offshore ONG installations, to quantify and identify the sources(France et al., 2021), and UAV-based sampling systems were used to analyze greenhouse gas stable isotope(Leitner et al., 2023). Nevertheless, the relevant studies were largely concentrated in foreign countries, and a few reports have revealed the CH_4 isotopic values from Chinese ONG production regions (SI, Table S1). To date, no research has examined the site-specific isotopic signatures of CH_4 emissions within the industrial site in China. In addition, the CH_4 isotopic signatures at the site level is regulated by many factors, such as source types(Zhang and Zhu, 2008; Schoell, 1980; Liu et al., 2019), processing (e.g., purification or production of light hydrocarbon), meteorological condition, sampling method, size of the site and so on. Therefore, the isotope tools are likely to provide quantitative or semi-quantitative reference for investigating regional or site-level CH_4 emission hotspots.

In order to fulfill for the lack of site-level CH_4 emission research, this study aims to delineate the isotopic traits of CH_4 emitted from Chinese ONG industry stations, by analyzing the sources of CH_4, and judging whether there is CH_4 emission in the field stations combined with other information. Simultaneously, the database of CH_4 isotopes in China will be enriched. We conducted monitoring and sampling of CH_4 at 11 ONG sites in the central Sichuan Basin, China. We characterized the sources and isotopic signatures of CH_4 based on isotope data derived from these samples. This study's data significantly augments the CH_4 isotope database for ONG source in the central Sichuan

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Basin, effectively bridging the previously existing gaps in both surface and upper atmospheric CH_4 isotope data for these sites. Looking ahead, this expanded dataset will serve as a foundational resource for future research, enabling more comprehensive assessments of global CH_4 emissions and their sources, and potentially guiding the development of targeted mitigation strategies for the ONG industry.

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2 Method

2.1 Study sites

The study area is located in Sichuan Basin, Southwest China, where about 19 % of the country's total natural gas reserves have been discovered(The People's Government of Sichuan Province, 2024). Until 2022, the region has about 77,000 km gas pipelines(National Bureau of Statistics, 2024). Between 2013 and2023, natural gas production in this region increased from 21.31×10^9 to 59.48×10^9 m^3(Sichuan Provincial Bureau of Statistics, 2024), with an average annual growth rate of about 11%. In 2020, ONG production in Sichuan accounted for 24% of China's total ONG production (National Bureau of Statistics, 2024). We monitored CH_4 mixing ratios and sampled air for isotope measurements across 11 ONG processing or transportation stations in the central Sichuan Basin. The study region is characterized by a humid subtropical climate, with consistently warm and humid conditions throughout the year. The areas of these stations vary from 2,000 to 300,000 m^2, while the production activities also vary, including natural gas purification plants, gas gathering stations, light hydrocarbon plants, pigging stations, pressurization stations, etc. (Table 1). Most of the ONG stations are located in rural areas, surrounded by mountains, forests, farmlands, and reservoirs, and there are rivers located in the vicinity of only several sites. Paddy fields are the main farmland in this area, and rice is the main grain crop(Sichuan Provincial Department of Agriculture and Rural Affairs, 2024). For reasons of privacy and confidentiality, the specific locations and contours of the ONG stations cannot be disclosed in this paper.

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Table 1 Background information of the studied production/processing sites for oil and natural gas

Site	Type	Area (m^2)	Processing capacity (10^4 m^3/d)	Surrounding environment	Activity
MX (S1)	Purification plant	25000	445	Forests, farmland	Natural gas processing, including membrane separation, adsorption, desulfurization, dehydration and other processes
SN (S2)		113000	3000	Forests, farmland, many ponds	
DQ (S5)	Gas gathering stations	5096	115	Forests, reservoirs	Gas Collection and transportation
XBQ (S3)		9420	278	Forests, farmland	
XQ (S4)		4220	1000	Farmland, ponds	
QTCSN (S7)	Light hydrocarbon plant	6650	10	Forests, farmland	C^{3+} component of natural gas was recovered by low temperature separation process
QTCSZ (S8)		25257	30	Forests	
LHZ (S9)	Union Station	7958	2700	River	ONG centralized treatment, sewage treatment, product output
ZYZ (S11)	Supercharging station	7740	24	Farmland, ponds	Pressure and transmission
L1 (S10)	Central well station	8679	90.3	Forests, farmland, ponds	Gas Collection and transportation
XM (S6)	Pigging station	5167	630	River	

2.2 Sampling methods

From 13 April to 19 April 2023, we monitored and collected samples at 11 ONG production stations in the central Sichuan Basin, obtaining a total of 74 samples, including 28 ground samples and 46 air samples. Ground samples were collected at heights ranging from -0.5 m (0.5 m under the ground) to 2 m. Sampling locations were

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chosen in open areas of each station, including areas near pipelines and production equipment. Sampling in the area of pipelines and production equipment was performed at locations that show abnormal mixing ratios after ground monitoring, and in instances where no apparent CH_4 emission was detected, sampling was performed in the center of the pipelines and production equipment area. For large field stations (> 10,000 m^2), multiple sampling points were established, while for small field stations (< 10,000 m^2), 1-2 sampling points were established in facility areas, and the sampling time for each sample was about 45-50 seconds. The drone was launched in open positions. Air sampling was performed by an Unmanned Aerial Vehicle (UAV) equipped with an automatic sampling pump (Fig. 1). The UAV model was a DJI-T10 upgraded version, and the sampling pump model was KVP04-1.1-12V (1.25 L/min). Taking into account the altitude ranges utilized in previous studies(Kim et al., 2025; Han et al., 2024; Chen et al., 2024; Liu et al., 2021; Liu, 2018; Ali et al., 2017), along with the drone's flight endurance and sampling duration, the monitoring altitude for this study is defined, sampling heights were 50 m, 100 m, 200 m and 300 m respectively. Initially, a ground sampling site was identified, typically within the pipeline vicinity of the plant. Subsequently, a UAV equipped with an automatic sampling pump and air collection bags was lifted to altitude of 300 m above the ground sampling site. The UAV then sequentially descended to altitudes of 200, 100, and 50 m, respectively, dedicating 45 to 60 seconds at each elevation for collecting air samples. This systematic approach ensures a comprehensive and stratified sampling strategy, facilitating the assessment of atmospheric constituents at varying heights. The volume of each air sample was approximately 1 L. All sites sampled at altitude, with the exception of S1, which sampled at 200 m and 300 m, all other stations sampled at various altitudes. Air sampling and UAV cruising were synchronized. HOONPO Teflon gas bags (1L, 2L specifications) were used for gas sampling. In addition, we sampled the region near an urban park and river to analyze the region's atmospheric CH_4 mixing ratio and isotope information, collecting a total of 4 samples (2 from the riverbank, 2 from the park). We also sampled a production well (built in the 1980s) that was out of repair and had significant emissions, and the result was used as a reference for source signal analysis,

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with a total of 3 samples collected (one from the open area of the site and two from the leak). The sample list and test results are provided in (SI, Table S2).

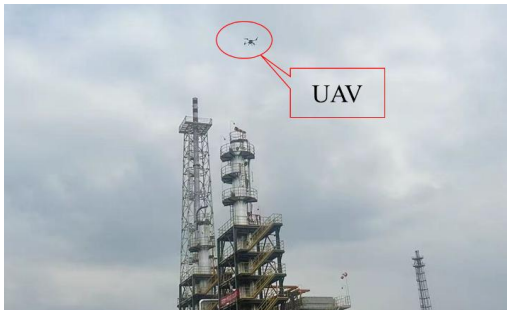

Fig. 1 UAV, automatic sampling system and sampling over the site.

The influence of meteorological conditions on the CH_4 mixing ratio and isotopes at the field station was also considered. Therefore, a portable meteorological station was deployed at each station during the sampling or monitoring periods. It was equipped with a three-dimensional ultrasonic wind speed and direction sensor (model: M307200), which recorded the wind speed (horizontal and vertical) and direction (horizontal and vertical) near the ground (3 to 10 m according to field conditions), the sampling frequency is 32 Hz with a resolution of 0.1 m/s for wind speed and 0.1° for wind direction, and the accuracy of wind direction and speed is 2° and 0.2 m/s, respectively. We also obtained air pressure, solar radiation, temperature, and relative humidity from weather stations. Since the meteorological conditions at high altitudes (50 to 300 m) cannot be monitored by instruments, we used the HYSPLIT model to test the influence of wind speed and direction on our measurements of CH_4 mixing ratios and isotopes at

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high altitudes.

2.3 Measurement methods

Gas samples were analyzed within one month after on-site sampling. Picarro G2132-i was used to detect the isotope and mixing ratio of CH_4, which is based on unique Cavity Ring-Down Spectroscopy (CRDS). The $\delta^{13}C$ detection accuracy (1-σ, 1-hour window) of the instrument is as follows: when the mixing ratio of CH_4 is greater than 1.8 ppm, the accuracy of 5-minute mean value is less than 0.8‰, when the mixing ratio of CH_4 exceeds 10 ppm, the accuracy is less than 0.4‰(Picarro, 2024). The calibration of the instrument was performed with CH_4 isotope standard gas (2.8 ppm, -68.6±0.3‰), produced by Airgas company, USA. Standard gas measurements were performed daily, before and after the start of the sample test, to correct the same-day test data (the correction parameters of CH_4 isotope and mixing ratio were approximately 1.5‰ and 0 ppm, respectively). Each gas bag sample underwent three repeatedly measurements, totaling 74 samples. For each sample measurement, analysis over 180 seconds was performed on the Picarro G2132-i CRDS, and the average of the last 120 seconds of CH_4 isotope and mixing ratio data was recorded as the sample assay value. Both CH_4 isotope and mixing ratio data are available for each test.

2.4 Calculation of source isotopic signatures

Based on the sample detection data, the method of Keeling plot method was used to determine the CH_4 source(Keeling, 1958; Pataki et al., 2003) for each field station, as shown in formula (1):

$$\delta_{(a)}=[CH_{4(b)}]\ (\delta_{(b)}-\delta_{(s)})\ \cdot 1/[CH_{4(a)}]+\delta_{(s)} \quad (1)$$

Where $\delta_{(a)}$, $\delta_{(b)}$, and $\delta_{(s)}$ represent the $\delta^{13}C$ values of the sample, the background air and the average source, respectively. $[CH_{4(a)}]$ and $[CH_{4(b)}]$ represent the CH_4 mole fractions of the sample and the background air, respectively. The intercept ($\delta_{(s)}$) of the fit line is the isotope value of the CH_4 source present in the mixed sample. In linear regression, 1/ $[CH_{4(a)}]$ and $\delta_{(a)}$ represent independent (X-axis) and dependent (Y-axis) variables, respectively. This method is suitable for carbon dioxide, methane(Thom et al., 1993), water vapor(Moreira et al., 1997), and other gases, but each gas has its

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specific considerations (Pataki et al., 2003). The gas samples from each station were collected within 30 minutes, during which the atmospheric background values (isotope and mole fraction of CH_4) did not change, fulfilling the application conditions of this method(Lu et al., 2021).

2.5 HYSPLIT model

The Hybrid Single-Particle Lagrange Integrated Trajectory (HYSPLIT) model developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory, is a widely used public platform for different atmospheric scales and supports online modules(Pereira et al., 2019; National Oceanic & Atmospheric Administration, 2024b). The model has been used to calculate the air mass transfer trajectories at different altitudes(Shan et al., 2009; Mcgowan and Clark, 2008; Stein et al., 2015). Examples of applications include meteorological analysis of ozone events(Shan et al., 2009), dust transport pathways(Mcgowan and Clark, 2008), dust storm simulation(Broomandi et al., 2017; Ashrafi et al., 2014), prediction of size distribution and mixing ratios of heavy metals in atmospheric aerosols(Chen et al., 2013) and so on. To analyze the influence of meteorological conditions on CH_4 mixing ratios and isotopes above the field station, wind direction and speed at different heights are required, which are available from the HYSPLIT model. The time resolution of the model could reach 1 hour and the height resolution was 1 meter. Backward trajectories were used in this study, to calculate 24-hour backward trajectories at ground, 50 m,100 m, 200 m, and 300 m heights over each site, respectively. The input data included the longitude and latitude of the site from field measurements and sampling time, while the output information were wind direction and speed at different heights.

2.6 Source partitioning with end-member mixing method

End-member mixing method is a common method for identifying and quantifying major sources of runoff. Several solutes have been used as tracers (typically 2-6) to determine the contribution of each water source to total runoff. The method is based on the mass balance of water and tracer, and the following assumptions: (1) the water

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solute is constant, (2) the tracer is conservative, (3) and the source solution has an extreme concentration(Bugaets et al., 2023; Barthold et al., 2011). Here, we applied it to gases, using CH_4 mixing ratios and isotopes as tracers to investigate the contribution of atmospheric background, open surface area, and facility area to high-altitude CH_4.

2.7 Statistics

Data analysis and graphing were performed using Origin 2024 software for Windows. Linear fitting was based on the principle of the Least square method, indicating the 0.95 confidence intervals. A value of $P < 0.05$ was considered significant for statistical analysis, and the fitting results are expressed as fitting mean and standard deviation. Maximum, minimum, mean, median, outliers, and 25% -75% range values were also analyzed and reported in the figures or tables.

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3 Results

3.1 Measurements of CH_4 mixing ratios and isotopes

The CH_4 mixing ratios and $\delta^{13}C$-CH_4 values from the 11 stations in this study area ranged from 1.88 to 3.66 ppm and from -48.45‰ to -30.97‰, respectively. The maximum and minimum values of CH_4 isotopes were obtained at sites S2 and S6 (H: 200 m), respectively. The variation of the CH_4 mixing ratio and isotopic values at stations S2, S4, and S7 is significantly greater than that observed at other stations (Fig. 2). The CH_4 isotope and mixing ratio of the urban samples were -46.45 ± 0.49‰ and 2.04 ± 0.07 ppm, respectively. The result of direct emissions from the production well was -15.4 ± 5.72‰ and 118.98 ± 0.52 ppm, respectively (SI, Table S2). The range of ground CH_4 isotopic values observed at the field stations in the study area was -47.98‰ to -15.40‰, with an average of -42.96 ± 6.87‰. The CH_4 mixing ratio and isotopic values in the production equipment areas of the majority of sites were higher than those in the open areas. However, there were exceptions, with some field stations displaying similar values (for example, S6 and S9). The range of air CH_4 isotopic values of the sites in the study area was -48.45 to -44.28‰, with an average value of -46.43 ±1.08‰. The ground measurements showed higher CH_4 mixing ratios and isotopic values than the air, which could be an indication of CH_4 emissions from ONG sites (Fig. 3).

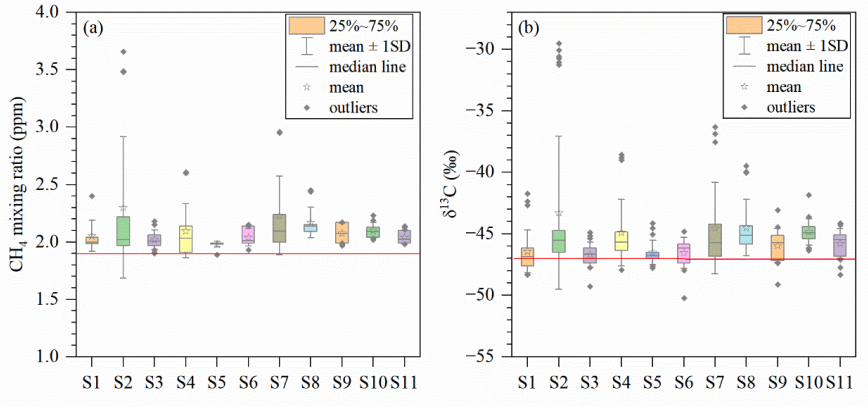

Fig. 2 Box whisker plots of CH_4 mixing ratios (a) and isotopic values (b) from the studied sites (mean, median, outliers, 25% -75% range, and 1 SD are indicated in the figures; the red lines refer to CH_4 mixing ratios (a, 1.9 ppm) and isotopic values (b, -47‰) from the atmospheric background.

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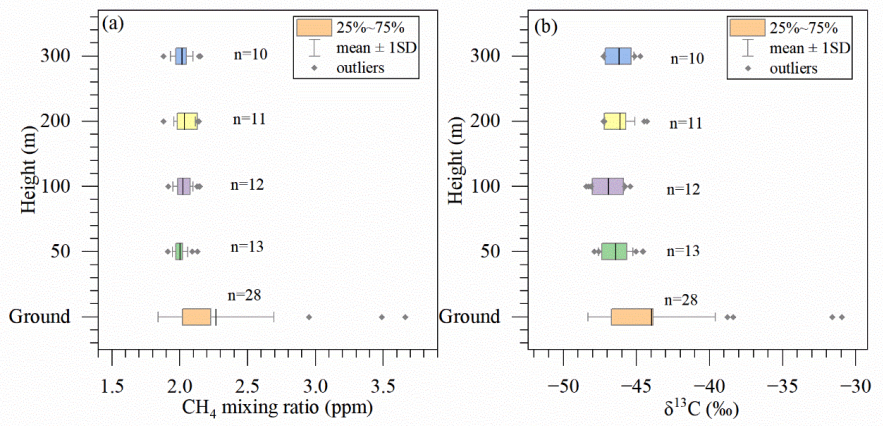

Fig. 3 Box whisker plots showing the variations of CH_4 mixing ratios (a) and isotopic values (b) at different heights (from ground to 300 m at all sites); include mean, 25% - 75% range, and 1 SD; "n" represents the number of samples.

3.2 Vertical profiles of CH_4 mixing ratios and isotopes and source partitioning

The distributional trend of the CH_4 mixing ratios and isotopes in the vertical direction differed. For instance, the mean CH_4 mixing ratios were higher at 100 m than at 50 m, yet the isotopic values ($\delta^{13}C$) were lower (Fig. 3). From the perspective of a single station, the conditions were similar yet more complex. Some stations exhibited consistent trends (S1, S3, S6, S7, S9, S11), while others displayed different trends (S2, S4, S5, S8, S10) (SI, Fig. S1). For instance, the CH_4 mixing ratio and isotopic values at 100 m and 200 m altitude of station S8 were inversely proportional. As the altitude increased from the ground to 300 m, the CH_4 isotopic values of stations S4 and S1 exhibited a decline, ranging from -45.10‰ to -47.27‰ (ground to 300 m) and from -42.27‰ to -47.92‰ (ground to 100 m), respectively (SI, Fig. S1). The CH_4 isotopic values of stations S3 and S6 initially decreased with increasing altitude and subsequently increased, reaching a minimum at 100 m altitude (-48.45‰ and -48.11‰, respectively). The variation of the CH_4 isotope vertical profile at station S8 was analogous to that observed at sites S6 and S3, with the exception that the CH_4 isotopic minimum value reached -46.18‰ at 200 m altitude. The variation of CH_4 isotopic values with altitude at station S9 was complex, exhibiting a decrease followed by an increase, which then decreased again, reaching minimum and maximum values at 50 m

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(-45.06‰) and 200 m (-44.47‰), respectively.

The end-member mixing method is a commonly employed technique for calculating isotope mixing by various sources of GHGs(Bugaets et al., 2023). In this study, we determined the contribution of CH_4 from the atmospheric background, surface, and facility areas to the air over the sites (the details and results are presented in SI part 1). The results demonstrated that the atmospheric background contributed 52.2 ± 28.9% to the total, the facility area contributed 21.9 ± 27.1%, and the ground open area contributed 25.9 ± 25.5% (Fig. 4b). The contribution of the atmospheric background initially decreased and then increased, reaching a minimum at 200 m, while the contribution of the ground and facility areas initially increased and then decreased, reaching a maximum at 100 m and 200 m, respectively (Fig. 4a). In cases where calculations are not feasible, the CH_4 emissions may be predominantly influenced by microbial activity or other local sources in the vicinity of the sites.

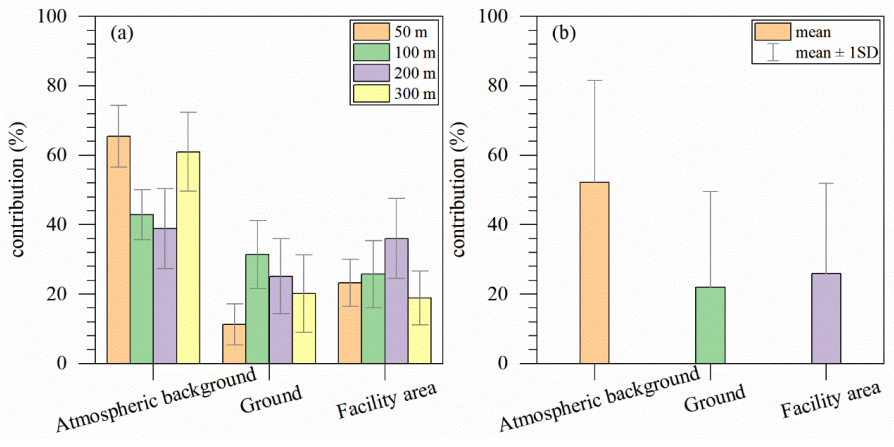

Fig. 4 The fractional contributions from ambient background, surface, and facility areas contribute to the vertical atmospheric sampling. (a) the proportion of contributions to different heights with standard error; (b) the proportion of contributions to all heights of all stations with 1SD.

3.3 Characteristics of source isotopes

The Keeling plot method was employed to determine the isotopic signatures ($\delta^{13}C$) of CH_4 sources at each station, with the results presented in Fig. 5. The range of the CH_4 source isotopic signatures varied from -50.7 ± 8.7‰ to -10.9 ± 5.5‰, indicating

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that they were mainly thermogenic sources (associated with oil production)(Menoud et al., 2022; Sherwood Lollar et al., 2002). The value of the CH_4 source signature for station S10 was -50.7‰ ± 8.7‰, which was lower than the atmospheric background value. Additionally, the data fitting for this field station was poor (R^2 = 0.03). This may be attributed to the low CH_4 emissions from the site and the primary contribution of CH_4 from microbial sources in the surrounding area (Table 1). Furthermore, the measurements of the CH_4 samples collected in urban parks and riverside revealed that the CH_4 source signature value was -35.1‰ ± 6.3‰, which was considerably higher than the atmospheric background value. It is yet to be determined whether this value can be considered representative of the atmospheric background value of the study area. Additional sample data are necessary to facilitate a more comprehensive analysis. On the other hand, the direct measurements of emission from wells indicated that source ^{13}C signature was -18.7 ± 6.3‰, which is close to the result of the sample test (-15.4 ± 5.72‰) (SI, Table S2). Globally, the range of CH_4 isotopic values from fossil fuels is -75‰ to -25‰, with a median value of -44‰(Defratyka et al., 2021). Our results fall outside this range and exhibit higher values.

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4 Discussion

4.1 Variations of CH_4 isotopic values from the atmosphere and ground

The mean values of CH_4 isotope were higher than the atmospheric background (-47.0 ±0.3‰) at all sites(Tyler, 1986), with some sites exhibiting values close to the atmospheric background (e.g., S1, S3, and S5). However, the average values of CH_4 mixing ratios were significantly higher than the atmospheric background (1.9 ppm) at all stations(Skeie et al., 2023). This indicated that CH_4 emissions occurred at all sites, with obvious leakage at most stations. On the other hand, the correlation between CH_4 mixing ratios and isotopes at the ONG sites was significant (R^2=0.90). Besides, the ground exhibited a stronger correlation (R^2=0.94) than the air (R^2=0.31) (SI, Fig. S2). These findings indicated that the CH_4 sources in the surface of the station were rather similar and derived from the ONG industry, and that CH_4 in the region has a similar genesis. This conclusion was further supported by the analogous CH_4 source isotopic signatures from most stations determined by keeling plot approach (Fig. 5). In addition, an investigation of the potential sources of CH_4 in the vicinity of the ONG sites revealed that the primary source of CH_4 at the station was from ONG, with other sources exerting a lesser impact.

However, multiple sources may be involved when looking into the relationship between mixing ratios and isotopes at each site alone (Fig. 5). The hypothesis was corroborated by isotope data. We discovered that approximately half of the ONG production stations (6 out of 11) exhibited higher ground CH_4 isotopic values ($\delta^{13}C$) than those observed in the air (S1, S3, S4, S7, S8, S10). The observed decline in isotope values can be attributed to the mixing of microbial sources of CH_4 present in the vicinity of the stations. Conversely, the remaining half of the stations (5 out of 11) displayed ground CH_4 isotopes that were either lower than or comparable to those observed in the air (S2, S5, S6, S9, S11). This discrepancy may be attributed to the uncertainty associated with the sources of CH_4 in the air, which is more sensitive to meteorological conditions. Additionally, the majority of sites exhibit elevated CH_4 mixing ratios and isotopic signatures in their pipeline and facility areas. Studies have indicated that infrastructure, including components such as dehydrators, valves, compressors, and

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pipelines, represents a significant source of CH_4 emissions from the ONG system. Infrastructure is particularly vulnerable to CH_4 leakage due to corrosion and wear(Anifowose et al., 2014; Fernandez et al., 2005; Burnham et al., 2012; Anifowose and Odubela, 2015).

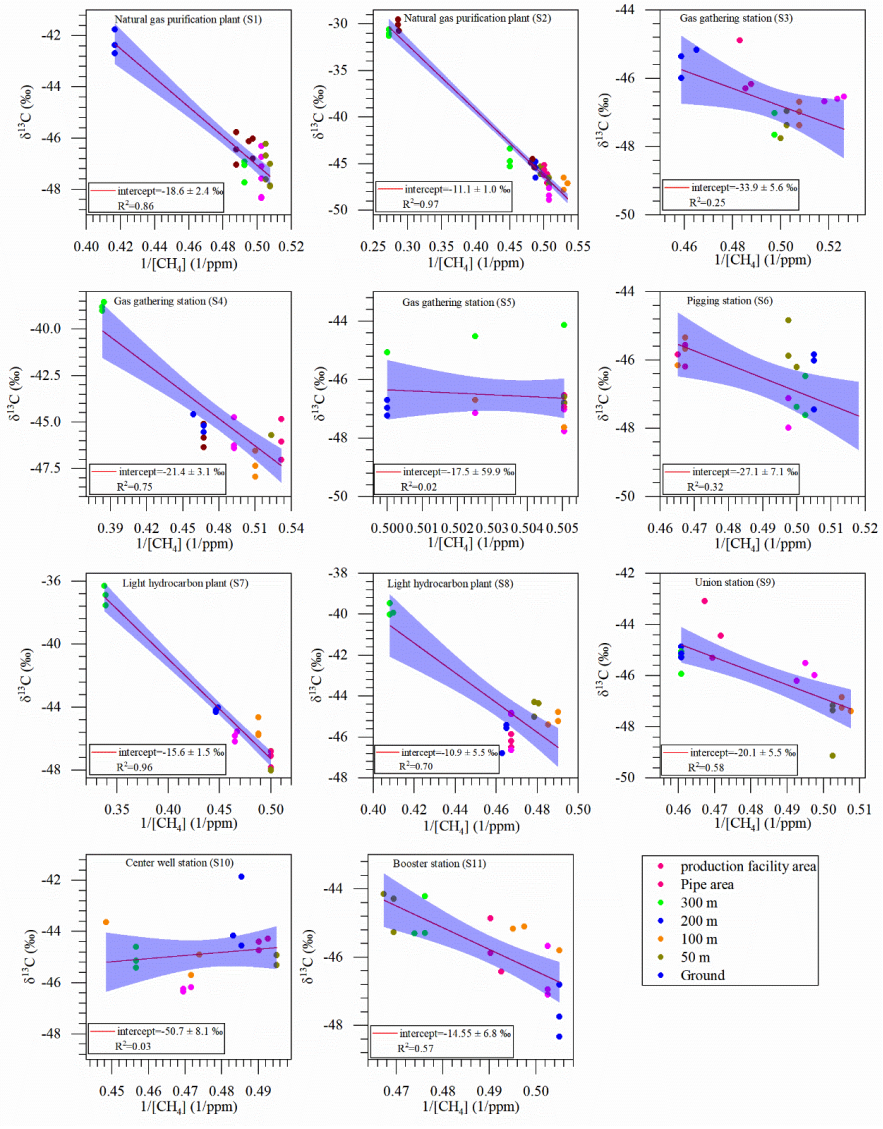

Fig. 5 The CH_4 source isotopic signatures of 11 field stations. The blue area represents the 95% confidence interval, and the red line is the result of linear regression posterior mean fit; The samples in different positions are distinguished by different colors. The intercept and R^2 are given, which means the source isotope signal value and the fitting

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degree, respectively.

4.2 Factors of drone-based isotope measurements in the atmosphere

Significant variability was evident in the CH_4 mixing ratios and isotopic signatures at the stations, with notable discrepancies observed at varying altitudes. This inconsistency is likely attributable to a number of factors, including the presence of additional CH_4 sources in the vicinity and the influence of meteorological conditions(Kavitha and Nair, 2016). An examination of the site's environment revealed that the area was predominantly forested, with agricultural land (paddy fields), water bodies, and human settlements also present. Paddy fields and ponds have been identified as the primary microbial sources of CH_4, characterized by lighter isotopes(Minami and Neue, 1994; Wang et al., 2023; Vizza et al., 2022). The influence of meteorological conditions is significant and complex, and challenging to analyze. Wind direction and speed were obtained using the HYSPLIT model to assist with the analysis (due to privacy considerations, the specific locations cannot be disclosed in this work, only the data can be provided, SI, Table S3). Integration of the HYSPLIT model data with that obtained from the meteorological station indicates that the results produced by HYSPLIT were credible (SI, Fig. S3). The correlation analysis between wind speed and CH_4 isotope results revealed an exponential relationship with an R-squared value of 0.33 (SI, Fig. S4). This indicates that as wind speed increases, the impact of CH_4 diffusion and dilution becomes more significant. Wind direction plays a role in the uncertainty of CH_4 distribution, as it has a significant influence on CH_4 transport near the surface, resulting in a non-uniform distribution of CH_4 and typically higher mixing ratios downwind from the emission source. Furthermore, upwind CH_4 sources can have a notable impact on CH_4 levels over the station. The utilization of HYSPLIT model serves a crucial function in this regard (SI, Fig. S5 for a detailed example of S7 site). To illustrate, the presence of a large wetland upwind can result in air masses transporting microbial CH_4, consequently affecting the CH_4 mixing ratios and isotopes above the station.

Moreover, the conditions at the station are among the primary determinants of the

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results, encompassing factors such as the size of the sites, the treatment processes employed, the treatment capacity, and the timing and location of sampling. A larger site is likely to produce a great quantity of CH_4 emissions(Omara et al., 2016) and accumulate CH_4 from a wider area, thereby exerting a more significant influence on the air's CH_4 content. A correlation was observed between the area and the isotopes. It is noteworthy that the correlation is enhanced when the site area was less than 10,000 m^2 (SI, Fig. S6). This may be attributed to the fact that larger site areas encompass a wider array of factors, which can exert a more significant influence. By contrast, the treatment processes that involve physical chemistry may exert isotope fractionation effects that affect CH_4 isotopes ($\delta^{13}C$), and the general heavier isotopes of this study may be influenced by the treatment processes. The intermittent nature of emissions from the site facilities introduces an element of uncertainty with regard to the sampling time and locations(Omara et al., 2016). The results of the Principal Component Analysis (PCA) demonstrated a weak relationship among wind direction, wind speed and isotopes, and a strong correlation between the size and capacity of the sites with CH_4 isotopes (SI, Fig. S7).

4.3 Global source isotopic signatures of ONG-derived CH_4

Previous studies have investigated the characteristics of CH_4 isotopes in Chinese ONG production regions, mainly in the Sichuan Basin, Xinjiang, Northeastern China, and the Ordos Basin. Based on previous work, the reported values of CH_4 isotopes cover a wide range, from -54.9% to -17.4‰ (SI, Table S1). In general, the origin of natural gas can be divided into two major categories: biogenic and abiogenic gas(Sherwood Lollar et al., 2002; Dai et al., 2005), of which biogenic gases include “coal-type” and “oil-type” gases(Liu et al., 2019; Dai et al., 1985; Dai et al., 1992; Xu, 1994). Studies have suggested that CH_4 of different origin carries distinct isotopic characteristics(Cai et al., 2013; Huang et al., 2017; Wang et al., 2018; Zhang et al., 2018; Zou et al., 2007; Zhu et al., 2014). This study is situated in the central region of the Sichuan Basin, where previous research on CH_4 isotopes has predominantly concentrated on large-scale statistical analyses. To date, no studies have specifically focused on the isotopic

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characteristics of CH_4 emanating from ONG industrial sites in this area. The Sichuan Basin has a complex geological environment and many gas-production layers, such as Cambrian, Ordovician, Carboniferous, Jurassic, etc., and CH_4 from different layers with various isotopic characteristics(Zhang et al., 2018; Cai et al., 2013). In comparison to the findings of other researchers on CH_4 isotopes in the Sichuan Basin (SI, Table S1), our results of ^{13}C-CH_4 isotope signatures spanned more widely and also appeared to be heavier. In another study, Menoud et al.(Menoud et al., 2022) examined isotopic signatures of CH_4 from an ONG extraction plant in Romania. Their methodology aligns closely with ours, and their findings indicate a range of $\delta^{13}C$ values from –67.8 ± 1.2 ‰ to –22.4 ± 0.04 ‰. Generally, our results showed heavier isotopes source signatures, exceeding the global mean of fossil fuel CH_4 isotope (-44.0 ± 0.7‰)(Schwietzke et al., 2016). This discrepancy can be attributed to a number of factors, including geographical differences(Menoud et al., 2022), the treatment processing of natural gas, and the size of samples. A comparison of the CH_4 isotopic signatures from the global ONG system(Menoud et al., 2022; Lopez et al., 2017; Hoheisel et al., 2019; Defratyka et al., 2021; Kang et al., 2014; Jenden et al., 1993) is presented in Fig. 6. The $\delta^{13}C$ of CH_4 was found to be lighter in the United States and Canada, but heavier in China. Regional variations in $\delta^{13}C$ values were observed, even within the same region, with fluctuations occurring. Our results exhibited a significantly heavier $\delta^{13}C$ than those of other studies. This was attributed to differences in the origin of CH_4, with geographical differences playing a prominent role(Zhang and Zhu, 2008; Wang et al., 2018; Defratyka et al., 2021; Schoell, 1980).

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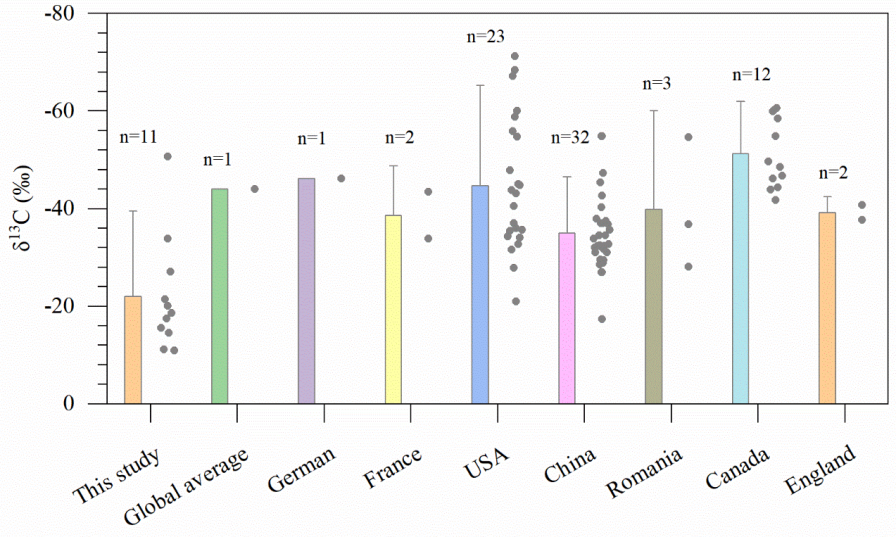

Fig. 6 An overview of global isotopic signals of CH_4 emitted from ONG industry or geo-thermal sources; data from both literature and this study are included. The right side of the box chart is the data point, the number of data points is also shown at the top of the box chart, and carry on the error analysis. "n" represents the number of data points.

The $\delta^{13}C$ of CH_4 represents a valuable indicator for constraining and estimating CH_4 emissions particularly from anthropogenic sources of the globe(Milkov et al., 2020). As a sum-up, the mean $\delta^{13}C$ signatures of CH_4 sources as indicated from measurements of atmospheric background integrated the collective contributions from various sources of CH_4 (SI, Fig. S8). Hence, with updated isotopic signatures for specific sources such as ONG industry, the previous conclusions on global contribution/flux of CH_4 from ONG industry may need to be revised(Schwietzke et al., 2016). In comparison with previous studies, the $\delta^{13}C$ values from ONG industry in our work (-21.95‰ based on 11 stations) are significantly higher, especially different from the global flux-weighted averaged by Schwietzke et al.(Schwietzke et al., 2016). By incorporation of flux contribution from Chinese ONG industry, isotope signatures as well as global datasets utilized in the previous work(Schwietzke et al., 2016), we conducted a sensitivity analysis, examining the effect on diverse source contributions (in flux) when updated the $\delta^{13}C$-CH_4 from Chinese ONG industry (SI, part 2 for details). Our finding suggests

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that, our field observation of isotope signature from China would elevate global fossil fuel-derived CH_4 isotopes signature by about 0.5‰; as a consequence, the new result would lead to a smaller contribution from global ONG industry (corresponds to an overestimation of emissions by 3.47 Tg CH_4 yr^{-1}) but a larger contribution from microbial sources. This findings is consistent with some recent research findings, such as Chandra et al.(Chandra et al., 2024), who reported that CH_4 emissions decreased in fossil fuel sources, while increasing in microbial sources during 1990-2020. In Australia, CH_4 emissions from agricultural ponds (microbial sources) were underestimated in national greenhouse gas inventories(Malerba et al., 2022). Overall, the decline of global mean CH4 isotopic signals seem to slightly speed up in recent years, likely supporting the importance of microbial emissions. Previous studies have identified potential avenues for reducing CH_4 leakage in the ONG industry, including improvements in technology, equipment, and management practices(Us Environmental Protection Agency, 2012; China National Petroleum Corporation, 2023), this may provide an insight into the overestimation of CH_4 emissions from ONG sources.

4.4 Feasibility and limitations

Atmosphere CH_4 isotopic research has shown its power in distinguishing between microbial and fossil sources of global atmospheric CH_4 trends(Basu et al., 2022; Bruhwiler et al., 2017). However, due to scarcity of observational evidence of various CH_4 source signatures, large uncertainties still exist for such estimations. The objective of our research was to distinguish sources of CH_4 as well as to quantify CH_4 leakage strength at site-level, providing basic but convincing data for constraining CH_4 sources. With both ground- and air-based approaches, our study has demonstrated the feasibility of our work in studying the characteristics of CH_4 sources and their influencing factors at ONG stations in SW China. Nevertheless, it is necessary to point out, that the impact of meteorological conditions and site conditions on the dampening/masking of CH_4 isotope signatures in the atmosphere may be significant. Therefore, the reconciliation between ground and atmospheric measurements as well as source partitioning remain to be further validated, given more sampling coverage both spatially and temporally. In

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addition, more sampling at different locations or different ONG plants will be greatly beneficial to the constraints on CH_4 source isotope signature from fossil fuel industry in China.

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5 Summary

The objective of this study is to differentiate CH_4 sources and examine the $\delta^{13}C$ isotopic characteristics at locations where gas samples were collected from ONG stations in the central Sichuan Basin, China. The characteristics of CH_4 isotopes were analyzed on the ground, in the air, and with regard to the vertical variations of CH_4 isotopes. Coupled with an analysis of the surrounding environment of the stations, we reached the conclusion that the primary source of CH_4 at the ONG stations is emissions from production facilities. Furthermore, CH_4 on the ground at the majority of sites is more significantly influenced by the ONG source, while CH4 in the air is more affected by meteorological conditions. Additionally, the vertical variation of CH4 isotopes is complex and changeable, and is affected by several factors, including meteorological conditions, station size, sample size, and other factors. The isotopic values of CH_4 from various sites were also analyzed to determine the sources of the gas. The results showed that the isotopic values of CH_4 from the ONG ranged from -50.7 ± 8.7‰ to -10.9 ± 5.5‰, indicating a heavy $\delta^{13}C$ of fossil fuel. In comparison with the CH_4 source isotopic values from the ONG globally, the results of this study revealed heavier isotopic signatures. This study contributes to the global CH_4 isotope database from the ONG, and addresses a gap in CH_4 isotope research at the site level in China. The primary factors influencing the CH_4 isotope at field stations are the station's intrinsic characteristics and the meteorological conditions present, as evidenced by the PCA analysis. A weighted calculation on a global scale based on the results of this study suggests that CH_4 emissions from microbial sources may be underestimated, while those from fossil fuel sources may be overestimated. It is our contention that an investigation into the isotopic characteristics of CH_4 at the site will prove invaluable in distinguishing between the various sources of CH_4 and accounting for emissions.

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Author contributions

D. Chen and Y. Liu conceptualized the study, with guidance from L. Yu. D. Chen and Y. Liu conducted the field observation and sample analysis, with the help from Ze. Niu, A, Wang and X. Pang. Y. Huang contributed data for the global literature analysis. D. Chen, Y. Liu and L. Yu wrote the manuscript together. All coauthors reviewed and contributed to the revision and finalization of the manuscript.

Competing interests

The authors declare no competing interests.

Data availability

All the data published in this work could be accessed upon request from the corresponding author.

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References

Ali, H., Odeh, M., Odeh, A., Abou-ElNour, A. A., and Tarique, M.: Unmanned Aerial Vehicular System for Greenhouse Gas Measurement and Automatic Landing, Netw. Protoc. Algorithms, 9, 56-76, 2017.

Anifowose, B. and Odubela, M.: Methane emissions from oil and gas transport facilities – exploring innovative ways to mitigate environmental consequences, Journal of Cleaner Production, 92, 121-133, 2015.

Anifowose, B., Lawler, D., van der Horst, D., and Chapman, L.: Evaluating interdiction of oil pipelines at river crossings using Environmental Impact Assessments, Area, 46, 4-17, 2014.

Ashrafi, K., Shafiepour-Motlagh, M., Aslemand, A., and Ghader, S.: Dust storm simulation over Iran using HYSPLIT, Journal of environmental health science and engineering, 12, 1-9, 2014.

Assan, S., Vogel, F. R., Gros, V., Baudic, A., Staufer, J., and Ciais, P.: Can we separate industrial CH_4 emission sources from atmospheric observations? - A test case for carbon isotopes, PMF and enhanced APCA, Atmospheric Environment, 187, 317-327, 2018.

Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H.-G., and Breuer, L.: How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis, Water Resources Research, 47, 2011.

Basu, S., Lan, X., Dlugokencky, E., Michel, S., Schwietzke, S., Miller, J. B., Bruhwiler, L., Oh, Y., Tans, P. P., and Apadula, F.: Estimating emissions of methane consistent with atmospheric measurements of methane and $\delta\ ^{13}C$ of methane, Atmospheric Chemistry and Physics Discussions, 2022, 1-38, 2022.

Broomandi, P., Dabir, B., Bonakdarpour, B., and Rashidi, Y.: Identification of the sources of dust storms in the City of Ahvaz by HYSPLIT, Pollution, 3, 341-348, 2017.

Bruhwiler, L. M., Basu, S., Bergamaschi, P., Bousquet, P., Dlugokencky, E., Houweling, S., Ishizawa, M., Kim, H.-S., Locatelli, R., Maksyutov, S., Montzka, S., Pandey, S., Patra, P. K., Petron, G., Saunois, M., Sweeney, C., Schwietzke, S., Tans, P., and Weatherhead, E. C.: U.S. CH_4 emissions from oil and gas production: Have recent large increases been detected?, Journal of Geophysical Research: Atmospheres, 122, 4070-4083, 2017.

Bugaets, A., Gartsman, B., Gubareva, T., Lupakov, S., Kalugin, A., Shamov, V., and Gonchukov, L.: Comparing the Runoff Decompositions of Small Experimental Catchments: End-Member Mixing Analysis (EMMA) vs. Hydrological Modelling, Water, 15, 752, 2023.

Burnham, A., Han, J., Clark, C. E., Wang, M., Dunn, J. B., and Palou-Rivera, I.: Life-cycle greenhouse gas emissions of shale gas, natural gas, coal, and petroleum, Environmental science & technology, 46, 619-627, 2012.

Cai, C., Zhang, C., He, H., and Tang, Y.: Carbon isotope fractionation during methane-dominated TSR in East Sichuan Basin gasfields, China: A review, Marine and Petroleum Geology, 48, 100-110, 2013.

Chandra, N., Patra, P. K., Fujita, R., Höglund-Isaksson, L., Umezawa, T., Goto, D., Morimoto, S., Vaughn, B. H., and Röckmann, T.: Methane emissions decreased in fossil fuel exploitation and sustainably increased in microbial source sectors during 1990–2020, Communications Earth & Environment, 5, 147, 2024.

Chen, B., Stein, A. F., Maldonado, P. G., Sanchez de la Campa, A. M., Gonzalez-Castanedo, Y., Castell, N., and de la Rosa, J. D.: Size distribution and concentrations of heavy metals in atmospheric

https://doi.org/10.5194/egusphere-2025-377
Preprint. Discussion started: 5 March 2025

aerosols originating from industrial emissions as predicted by the HYSPLIT model, Atmospheric Environment, 71, 234-244, 2013.

Chen, L., Pang, X., Wu, Z., Huang, R., Hu, J., Liu, Y., Zhou, L., Zhou, J., and Wang, Z.: Unmanned aerial vehicles equipped with sensor packages to study spatiotemporal variations of air pollutants in industry parks, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 382, 20230314, doi:10.1098/rsta.2023.0314, 2024.

"Intelligent" control of methane emission by digital module in southwest oil and gas field: http://news.cnpc.com.cn/system/2023/12/22/030121011.shtml, last

Dai, J., Pei, X., and Qi, H.: Natural gas geology in China, Petroleum Publication, 42-46, 1992.

Dai, J., Qi, H., and Song, Y.: Primary discussion of some parameters for identification of coal-and oil-type gases, Acta Petrolei Sinica, 6, 31-38, 1985.

Dai, J., Yang, S., Chen, H., and Shen, X.: Geochemistry and occurrence of inorganic gas accumulations in Chinese sedimentary basins, Organic Geochemistry, 36, 1664-1688, 2005.

Defratyka, S. M., Paris, J.-D., Yver-Kwok, C., Fernandez, J. M., Korben, P., and Bousquet, P.: Mapping Urban Methane Sources in Paris, France, Environmental Science & Technology, 55, 8583-8591, 2021.

Non-CO_2 Greenhouse Gas Emission Projections & Mitigation: https://www.epa.gov/global-mitigation-non-co2-greenhouse-gases, last

Fernandez, R., Petrusak, R., Robinson, D., and Zavadil, D.: Cost-Effective Methane Emissions Reductions for Small and Midsize Natural Gas Producers, Journal of Petroleum Technology, 57, 34-42, 2005.

France, J. L., Bateson, P., Dominutti, P., Allen, G., Andrews, S., Bauguitte, S., Coleman, M., Lachlan-Cope, T., Fisher, R. E., and Huang, L.: Facility level measurement of offshore oil and gas installations from a medium-sized airborne platform: method development for quantification and source identification of methane emissions, Atmospheric Measurement Techniques, 14, 71-88, 2021.

Gao, J., Guan, C., and Zhang, B.: Why are methane emissions from China's oil & natural gas systems still unclear? A review of current bottom-up inventories, Science of The Total Environment, 807, 151076, 2022.

Han, T., Xie, C., Yang, Y., Zhang, Y., Huang, Y., Liu, Y., Chen, K., Sun, H., Zhou, J., Liu, C., Guo, J., Wu, Z., and Li, S.-M.: Spatial mapping of greenhouse gases using a UAV monitoring platform over a megacity in China, Science of The Total Environment, 951, 175428, https://doi.org/10.1016/j.scitotenv.2024.175428, 2024.

Hmiel, B., Petrenko, V. V., Dyonisius, M. N., Buizert, C., Smith, A. M., Place, P. F., Harth, C., Beaudette, R., Hua, Q., Yang, B., Vimont, I., Michel, S. E., Severinghaus, J. P., Etheridge, D., Bromley, T., Schmitt, J., Faïn, X., Weiss, R. F., and Dlugokencky, E.: Preindustrial $^{14}CH_4$ indicates greater anthropogenic fossil CH4 emissions, Nature, 578, 409-412, 2020.

Hoheisel, A., Yeman, C., Dinger, F., Eckhardt, H., and Schmidt, M.: An improved method for mobile characterisation of δ13CH4 source signatures and its application in Germany, Atmos. Meas. Tech., 12, 1123-1139, 2019.

Huang, S., Feng, Z., Gu, T., Gong, D., Peng, W., and Yuan, M.: Multiple origins of the Paleogene natural gases and effects of secondary alteration in Liaohe Basin, northeast China: Insights from the molecular and stable isotopic compositions, International Journal of Coal Geology, 172, 134-148, 2017.

IPCC: Climate Chang 2021 The Physical Science Basis, 1017, 2021.

https://doi.org/10.5194/egusphere-2025-377
Preprint. Discussion started: 5 March 2025

Jenden, P. D., Drazan, D. J., and Kaplan, I. R.: Mixing of Thermogenic Natural Gases in Northern Appalachian Basin1, AAPG Bulletin, 77, 980-998, 1993.

Kai, F. M., Tyler, S. C., Randerson, J. T., and Blake, D. R.: Reduced methane growth rate explained by decreased Northern Hemisphere microbial sources, Nature, 476, 194-197, 2011.

Kang, M., Kanno, C. M., Reid, M. C., Zhang, X., Mauzerall, D. L., Celia, M. A., Chen, Y., and Onstott, T. C.: Direct measurements of methane emissions from abandoned oil and gas wells in Pennsylvania, Proceedings of the National Academy of Sciences, 111, 18173-18177, 2014.

Kavitha, M. and Nair, P. R.: Non-homogeneous vertical distribution of methane over Indian region using surface, aircraft and satellite based data, Atmospheric Environment, 141, 174-185, 2016.

Keeling, C. D.: The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas, Geochimica et Cosmochimica Acta, 13, 322-334, 1958.

Kim, H., Kim, K. T., Jeong, S., Lee, Y. S., Zhao, X., and Kim, J. Y.: Enhancing Uncrewed Aerial Vehicle Techniques for Monitoring Greenhouse Gas Plumes at Point Sources, Atmospheric Environment, 342, 120924, https://doi.org/10.1016/j.atmosenv.2024.120924, 2025.

Kirschke, S., Bousquet, P., Ciais, P., Saunois, M., Canadell, J. G., Dlugokencky, E. J., Bergamaschi, P., Bergmann, D., Blake, D. R., Bruhwiler, L., Cameron-Smith, P., Castaldi, S., Chevallier, F., Feng, L., Fraser, A., Heimann, M., Hodson, E. L., Houweling, S., Josse, B., Fraser, P. J., Krummel, P. B., Lamarque, J.-F., Langenfelds, R. L., Le Quéré, C., Naik, V., O'Doherty, S., Palmer, P. I., Pison, I., Plummer, D., Poulter, B., Prinn, R. G., Rigby, M., Ringeval, B., Santini, M., Schmidt, M., Shindell, D. T., Simpson, I. J., Spahni, R., Steele, L. P., Strode, S. A., Sudo, K., Szopa, S., van der Werf, G. R., Voulgarakis, A., van Weele, M., Weiss, R. F., Williams, J. E., and Zeng, G.: Three decades of global methane sources and sinks, Nature Geoscience, 6, 813-823, 2013.

Lauvaux, T., Giron, C., Mazzolini, M., d'Aspremont, A., Duren, R., Cusworth, D., Shindell, D., and Ciais, P.: Global assessment of oil and gas methane ultra-emitters, Science, 375, 557-561, 2022.

Leitner, S., Hood-Nowotny, R., and Watzinger, A.: Successive and automated stable isotope analysis of CO_2, CH_4 and N_2O paving the way for unmanned aerial vehicle-based sampling, Rapid Communications in Mass Spectrometry, 34, e8929, 2020.

Leitner, S., Feichtinger, W., Mayer, S., Mayer, F., Krompetz, D., Hood-Nowotny, R., and Watzinger, A.: UAV-based sampling systems to analyse greenhouse gases and volatile organic compounds encompassing compound-specific stable isotope analysis, Atmospheric Measurement Techniques, 16, 513-527, 2023.

Liu, Q., Wu, X., Wang, X., Jin, Z., Zhu, D., Meng, Q., Huang, S., Liu, J., and Fu, Q.: Carbon and hydrogen isotopes of methane, ethane, and propane: A review of genetic identification of natural gas, Earth-Science Reviews, 190, 247-272, 2019.

Liu, S.: Development of a UAV-based system to monitor air quality over an oil field, Montana Tech of The University of Montana, 2018.

Liu, S., Yang, X., and Zhou, X.: Development of a low-cost UAV-based system for CH_4 monitoring over oil fields, Environmental Technology, 42, 3154-3163, 10.1080/09593330.2020.1724199, 2021.

Lopez, M., Sherwood, O. A., Dlugokencky, E. J., Kessler, R., Giroux, L., and Worthy, D. E. J.: Isotopic signatures of anthropogenic CH_4 sources in Alberta, Canada, Atmospheric Environment, 164, 280-288, 2017.

Lu, X., Harris, S. J., Fisher, R. E., France, J. L., Nisbet, E. G., Lowry, D., Röckmann, T., van der Veen, C., Menoud, M., Schwietzke, S., and Kelly, B. F. J.: Isotopic signatures of major methane sources in the coal seam gas fields and adjacent agricultural districts, Queensland, Australia, Atmos. Chem.

https://doi.org/10.5194/egusphere-2025-377
Preprint. Discussion started: 5 March 2025

Phys., 21, 10527-10555, 2021.
Malerba, M. E., de Kluyver, T., Wright, N., Schuster, L., and Macreadie, P. I.: Methane emissions from agricultural ponds are underestimated in national greenhouse gas inventories, Communications Earth & Environment, 3, 306, 2022.
McGowan, H. and Clark, A.: Identification of dust transport pathways from Lake Eyre, Australia using Hysplit, Atmospheric Environment, 42, 6915-6925, 2008.
Menoud, M., van der Veen, C., Maazallahi, H., Hensen, A., Velzeboer, I., van den Bulk, P., Delre, A., Korben, P., Schwietzke, S., Ardelean, M., Calcan, A., Etiope, G., Baciu, C., Scheutz, C., Schmidt, M., and Röckmann, T.: CH_4 isotopic signatures of emissions from oil and gas extraction sites in Romania, Elementa: Science of the Anthropocene, 10, 2022.
Milkov, A. V., Schwietzke, S., Allen, G., Sherwood, O. A., and Etiope, G.: Using global isotopic data to constrain the role of shale gas production in recent increases in atmospheric methane, Scientific Reports, 10, 4199, 2020.
Minami, K. and Neue, H.-U.: Rice paddies as a methane source, Climatic change, 27, 13-26, 1994.
Montzka, S. A., Dlugokencky, E. J., and Butler, J. H.: Non-CO_2 greenhouse gases and climate change, Nature, 476, 43-50, 2011.
Moreira, M., Sternberg, L., Martinelli, L., Victoria, R., Barbosa, E., Bonates, L., and Nepstad, D.: Contribution of transpiration to forest ambient vapour based on isotopic measurements, Global Change Biology, 3, 439-450, 1997.
National data: https://tjj.sc.gov.cn/scstjj/c111701/common_list.shtml, last
Global Monitoring Laboratory: https://gml.noaa.gov/dv/data/, last
HYSPLIT Trajectory Model: https://www.ready.noaa.gov/hypub-bin/trajasrc.pl, last
Omara, M., Sullivan, M. R., Li, X., Subramanian, R., Robinson, A. L., and Presto, A. A.: Methane emissions from conventional and unconventional natural gas production sites in the Marcellus Shale Basin, Environmental science & technology, 50, 2099-2107, 2016.
Parnell, A. C., Phillips, D. L., Bearhop, S., Semmens, B. X., Ward, E. J., Moore, J. W., Jackson, A. L., Grey, J., Kelly, D. J., and Inger, R.: Bayesian stable isotope mixing models, Environmetrics, 24, 387-399, 2013.
Pataki, D. E., Ehleringer, J. R., Flanagan, L. B., Yakir, D., Bowling, D. R., Still, C. J., Buchmann, N., Kaplan, J. O., and Berry, J. A.: The application and interpretation of Keeling plots in terrestrial carbon cycle research, Global Biogeochemical Cycles, 17, 2003.
Peng, L., Ti, C., Yin, B., Dong, W., Li, M., Tao, L., and Yan, X.: Traceability of atmospheric ammonia in a suburban area of the Beijing-Tianjin-Hebei region, Science of The Total Environment, 907, 167935, 2024.
Pereira, A. P. M. F., Rodrigues, L. A. d. C., Santos, E. A. d., Cardoso, T. A. d. O., and Cohen, S. C.: CBRN events management and the use of the Hysplit model: an integrative literature review, Saúde em Debate, 43, 925-938, 2019.
G2132-i Isotope Analyzer: https://www.picarro.com/environmental/products/g2132i_isotope_analyzer, last
Rice, A. L., Butenhoff, C. L., Teama, D. G., Röger, F. H., Khalil, M. A. K., and Rasmussen, R. A.: Atmospheric methane isotopic record favors fossil sources flat in 1980s and 1990s with recent increase, Proceedings of the National Academy of Sciences, 113, 10791-10796, 2016.
Rigby, M., Montzka, S. A., Prinn, R. G., White, J. W., Young, D., O'doherty, S., Lunt, M. F., Ganesan, A. L., Manning, A. J., and Simmonds, P. G.: Role of atmospheric oxidation in recent methane

https://doi.org/10.5194/egusphere-2025-377
Preprint. Discussion started: 5 March 2025

growth, Proceedings of the National Academy of Sciences, 114, 5373-5377, 2017.
Saunois, M., Jackson, R. B., Bousquet, P., Poulter, B., and Canadell, J. G.: The growing role of methane in anthropogenic climate change, Environmental Research Letters, 11, 120207, 2016a.
Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Covey, K., Curry, C., Frankenberg, C., Gedney, N., Höglund-Isaksson, L., Ishizawa, M., Ito, A., Joos, F., Kim, H. S., Kleinen, T., Krummel, P., Lamarque, J. F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K. C., Marshall, J., Melton, J. R., Morino, I., Naik, V., O'Doherty, S., Parmentier, F. J. W., Patra, P. K., Peng, C., Peng, S., Peters, G. P., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W. J., Saito, M., Santini, M., Schroeder, R., Simpson, I. J., Spahni, R., Steele, P., Takizawa, A., Thornton, B. F., Tian, H., Tohjima, Y., Viovy, N., Voulgarakis, A., van Weele, M., van der Werf, G. R., Weiss, R., Wiedinmyer, C., Wilton, D. J., Wiltshire, A., Worthy, D., Wunch, D., Xu, X., Yoshida, Y., Zhang, B., Zhang, Z., and Zhu, Q.: The global methane budget 2000–2012, Earth Syst. Sci. Data, 8, 697-751, 2016b.
Schoell, M.: The hydrogen and carbon isotopic composition of methane from natural gases of various origins, Geochimica et Cosmochimica Acta, 44, 649-661, 1980.
Schwietzke, S., Sherwood, O. A., Bruhwiler, L. M. P., Miller, J. B., Etiope, G., Dlugokencky, E. J., Michel, S. E., Arling, V. A., Vaughn, B. H., White, J. W. C., and Tans, P. P.: Upward revision of global fossil fuel methane emissions based on isotope database, Nature, 538, 88-91, 2016.
Shan, W., Yin, Y., Lu, H., and Liang, S.: A meteorological analysis of ozone episodes using HYSPLIT model and surface data, Atmospheric Research, 93, 767-776, 2009.
Shaw, J. T., Shah, A., Yong, H., and Allen, G.: Methods for quantifying methane emissions using unmanned aerial vehicles: A review, Philosophical Transactions of the Royal Society A, 379, 20200450, 2021.
Sherwood Lollar, B., Westgate, T., Ward, J., Slater, G., and Lacrampe-Couloume, G.: Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs, Nature, 416, 522-524, 2002.
2023 the statistical bulletin of national economic and social development of Sichuan province: https://tjj.sc.gov.cn/scstjj/c111701/common_list.shtml, last
Scientific and technological paths and policy suggestions for reducing greenhouse gas emissions from paddy fields in our province: https://nynct.sc.gov.cn/nynct/c110427/2021/9/3/2e13faeab72e4608bb5ef0ea1aa345d7.shtml, last
Skeie, R. B., Hodnebrog, Ø., and Myhre, G.: Trends in atmospheric methane concentrations since 1990 were driven and modified by anthropogenic emissions, Communications Earth & Environment, 4, 317, 2023.
Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.: NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System, Bulletin of the American Meteorological Society, 96, 2059-2077, 2015.
Sun, S., Ma, L., and Li, Z.: A Source-Level Estimation and Uncertainty Analysis of Methane Emission in China's Oil and Natural Gas Sector, 2022.
Suzuki, Y.: Achieving food authenticity and traceability using an analytical method focusing on stable isotope analysis, Analytical Sciences, 37, 189-199, 2021.

https://doi.org/10.5194/egusphere-2025-377
Preprint. Discussion started: 5 March 2025

Energy Resources: https://www.sc.gov.cn/10462/10778/10876/2021/1/4/abbdfe3e4cb943d885236f623361caf7.shtml#:~:text=%E6%B2%B9%E6%B0%94%E8%B5%84%E6%BA%90%E4%BB%A5%E5%A4%A9%E7%84%B6%E6%B0%94,%E5%8C%BA%E3%80%81%E5%B7%9D%E4%B8%9C%E5%8C%97%E7%89%87%E5%8C%BA%E3%80%82, last

Thom, M., Bösinger, R., Schmidt, M., and Levin, I.: The regional budget of atmospheric methane of a highly populated area, Chemosphere, 26, 143-160, 1993.

Tian, H., Lu, C., Ciais, P., Michalak, A. M., Canadell, J. G., Saikawa, E., Huntzinger, D. N., Gurney, K. R., Sitch, S., Zhang, B., Yang, J., Bousquet, P., Bruhwiler, L., Chen, G., Dlugokencky, E., Friedlingstein, P., Melillo, J., Pan, S., Poulter, B., Prinn, R., Saunois, M., Schwalm, C. R., and Wofsy, S. C.: The terrestrial biosphere as a net source of greenhouse gases to the atmosphere, Nature, 531, 225-228, 2016.

Tibrewal, K., Ciais, P., Saunois, M., Martinez, A., Lin, X., Thanwerdas, J., Deng, Z., Chevallier, F., Giron, C., and Albergel, C.: Assessment of methane emissions from oil, gas and coal sectors across inventories and atmospheric inversions, Communications Earth & Environment, 5, 26, 2024.

Townsend-Small, A., Ferrara, T. W., Lyon, D. R., Fries, A. E., and Lamb, B. K.: Emissions of coalbed and natural gas methane from abandoned oil and gas wells in the United States, Geophysical Research Letters, 43, 2283-2290, 2016.

Tyler, S. C.: Stable carbon isotope ratios in atmospheric methane and some of its sources, Journal of Geophysical Research: Atmospheres, 91, 13232-13238, 1986.

Summary Report: Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990–2030: https://nepis.epa.gov/Exe/ZyPDF.cgi/P100FE8H.PDF?Dockey=P100FE8H.PDF, last

Vizza, C., Jones, S. E., Hart, J. A., West, W. E., and Lamberti, G. A.: Pond methane dynamics, from microbial communities to ecosystem budget, during summer in Alaska, Limnology and Oceanography, 67, 450-467, 2022.

Wang, J., Ciais, P., Smith, P., Yan, X., Kuzyakov, Y., Liu, S., Li, T., and Zou, J.: The role of rice cultivation in changes in atmospheric methane concentration and the Global Methane Pledge, Global Change Biology, 29, 2776-2789, 2023.

Wang, Y., Chen, J., Pang, X., Zhang, B., Chen, Z., Zhang, G., Luo, G., and He, L.: Origin of deep sour natural gas in the Ordovician carbonate reservoir of the Tazhong Uplift, Tarim Basin, northwest China: Insights from gas geochemistry and formation water, Marine and Petroleum Geology, 91, 532-549, 2018.

Xu, Y.: Genetic theories of natural gases and their application, 1994.

Zhang, B., Chen, G. Q., Li, J. S., and Tao, L.: Methane emissions of energy activities in China 1980–2007, Renewable and Sustainable Energy Reviews, 29, 11-21, 2014.

Zhang, S. and Zhu, G.: Natural gas origins of large and medium-scale gas fields in China sedimentary basins, Science in China Series D: Earth Sciences, 51, 1-13, 2008.

Zhang, S., He, K., Hu, G., Mi, J., Ma, Q., Liu, K., and Tang, Y.: Unique chemical and isotopic characteristics and origins of natural gases in the Paleozoic marine formations in the Sichuan Basin, SW China: Isotope fractionation of deep and high mature carbonate reservoir gases, Marine and Petroleum Geology, 89, 68-82, 2018.

Zhang, Z., Poulter, B., Knox, S., Stavert, A., McNicol, G., Fluet-Chouinard, E., Feinberg, A., Zhao, Y., Bousquet, P., and Canadell, J. G.: Anthropogenic emission is the main contributor to the rise of atmospheric methane during 1993–2017, National science review, 9, nwab200, 2022.

https://doi.org/10.5194/egusphere-2025-377
Preprint. Discussion started: 5 March 2025

848 Zhu, G., Wang, Z., Dai, J., and Su, J.: Natural gas constituent and carbon isotopic composition in
849 petroliferous basins, China, Journal of Asian Earth Sciences, 80, 1-17, 2014.
850 Zou, Y.-R., Cai, Y., Zhang, C., Zhang, X., and Peng, P. a.: Variations of natural gas carbon isotope-type
851 curves and their interpretation – A case study, Organic Geochemistry, 38, 1398-1415, 2007.
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