1 Seasonal variation of methane microseepage in the Dawangi oilfield (China): a 2 possible climatic control 3 4 Yujia Zhao<sup>1</sup>, Guojian Wang<sup>2</sup>, Giuseppe Etiope<sup>3,4</sup>, Yong wang<sup>5</sup>, Zhenzhen Zhu<sup>1</sup>, Chunhui Wang<sup>1</sup>, Xufeng, Chen<sup>1</sup>, Junhong Tang<sup>1</sup> 5 6 7 8 <sup>1</sup>College of Materials Science and Environmental Engineering, Hangzhou Dianzi University, 9 Hangzhou, China 10 <sup>2</sup>Wuxi Research Institute of Petroleum Geology, Research Institute of Petroleum Exploration and 11 Production, SINOPEC, Wuxi, China 12 <sup>3</sup>Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy 13 <sup>4</sup>Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, 14 15 Romania <sup>5</sup>Department of Kela Oil and Gas Development, PetroChina Tarim Oilfield Company, Korla, 16 17 Xinjiang, China Corresponding author: Junhong Tang (tang\_jhjh@163.com) 18 †College of Materials Science and Environmental Engineering, Hangzhou Dianzi University, 19 Hangzhou, China 20 21 22 **Key Points:** 23 Microseepage of thermogenic gas over the Dawanqi oilfield is confirmed by molecular 24 and isotopic hydrocarbon data in 4-m deep boreholes. 25 Contrarily to previous observations in other petroleum basins, methane fluxes to the 26 atmosphere are higher in summer and lower in winter due to relevant ice thickness in the 27 soil. 28 Methanotrophic consumption and the ice-snow barrier effect compete in the 29 establishment of the seasonal microseepage pattern; microseepage may increase in future 30 milder winters due to regional climatic warming. 31 32

#### **Abstract**

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

Natural gas microseepage in petroleum-bearing sedimentary basins is an important complement to geophysical methods in oil-gas exploration and a natural source of methane (CH<sub>4</sub>) for the atmosphere. Microseepage, typically occurring in correspondence with petroleum fields throughout the world, is generally lower in summer, due to temperature-driven methanotrophic consumption, and higher in winter. The global estimates of microseepage methane emission have, however, relatively high uncertainties because of limited amounts of flux data, leading to poor knowledge of the spatial distribution and temporal variability of the gas emission factors. We studied the seasonal variation of microseepage flux to the atmosphere from a petroleum field in China (the Dawanqi oilfield), through methane flux measurements performed in summer 2014, winter 2015 and summer 2019. Winter data refer to frozen soil conditions, with snow cover and ice thickness in the soil exceeding 60 cm. Gas concentration (CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2+</sub> alkanes) and stable C isotopic composition of CH<sub>4</sub> and CO<sub>2</sub> in shallow (4 m deep) boreholes confirmed the existence of thermogenic gas seepage. Methane microseepage is higher in summer and lower or nil in winter. This seasonal trend is opposite to what was observed in areas where winter soil is not or poorly frozen. Our data suggest that seasonal microseepage variation may not be univocal worldwide, being strongly dependent on the presence of ice and snow cover in winter. The regional increase of temperature due to climate change, already demonstrated for the Tarim Basin over the last 50 years, could, in the future, reduce winter ice and enhance annual methane emission to the atmosphere.

5354

55

**Keywords**: Microseepage, methane, petroleum fields, seasonal variations, iced soil

5657

#### 1 Introduction

59 60

61

62

63

64

58

Microseepage of methane (CH<sub>4</sub>) on the Earth's surface is an important geochemical proxy of subsurface petroleum reservoirs and source rocks (Price, 1986; Klusman & Saaed, 1996; Saunders et al., 1999; Brown, 2000; Kvenvolden & Rogers, 2005; Xiao et al., 2019) and a natural source of methane for the atmosphere (Etiope et al., 2009; Etiope & Klusman, 2010; Etiope, 2015; Tang et al., 2017; Etiope & Schwietzke, 2019). Microseepage is likely the most

```
important geological source of methane, globally estimated to be in the order of 10-24 Tg yr<sup>-1</sup>,
65
     followed by macro-seepage emissions such as mud volcanoes, gas-oil seeps and submarine seeps
66
     (Etiope & Klusman, 2010; Etiope et al., 2019; Etiope & Schwietzke, 2019). Many studies show
67
     that (a) hydrocarbon microseepage dominantly occurs in correspondence with petroleum fields
68
     (mostly gas fields), and in particular along the faulted boundaries of the reservoirs (Macgregor,
69
     1993; Ciotoli et al., 2020), and (b) that the gas flux to the atmosphere is higher in winter and
70
     lower in summer, in relation to temperature-driven methanotrophic consumption (Klusman,
71
     2003; Etiope & Klusman, 2010). Methane flux data are however available only from a few
72
     petroleum provinces (mostly in central United States, Italy, Romania and China) and their
73
     seasonal variation is scarcely known. The actual global area of microseepage is, then, only
74
     theoretically predictable and the emission factors, which are essential for bottom-up emission
75
     estimates, have relatively high uncertainty (Etiope & Schwietzke, 2019; Saunois et al., 2020). In
76
     particular, there are no sufficient data showing the effect of ice content in the soil in winter.
77
     Although methanotrophic consumption is lower in winter, leading to enhanced methane release
78
     to the atmosphere, in some regions the presence of ice may reduce the gas exhalation (as
79
80
     observed in permafrost regions; e.g., O'Connor et al., 2010), inverting the seasonal trend.
     The oil field of Dawangi, in the Tarim Basin (China), offered the possibility to investigate the
81
82
     seasonal changes of microseepage in conditions of highly frozen soil, as in typical extreme desert
     climates: the Tarim Basin has January mean temperatures of -10 to -20 °C (Chen et al., 2007).
83
84
     Microseepage in the summer season (summer 2014) in the Dawanqi area was already
     investigated by Tang et al. (2017). Seepage was found to be strictly correlated with faults and
85
     with the occurrence of subsurface gas-oil pools related to the Dawanqi petroleum system (Tang
86
     et al., 2017).
87
     In this work, we show new microseepage flux data acquired in winter 2015 and summer 2019,
88
     along the same transects investigated in 2014. Winter data refer to frozen soil conditions, with
89
     snow cover and ice thickness in the soil exceeding 60 cm. The concentration of methane, heavier
90
     alkanes (ethane, propane, butane, and pentane) and carbon dioxide (CO<sub>2</sub>) in the ground, and the
91
     stable C isotopic compositions of CH<sub>4</sub> and CO<sub>2</sub> in summer, at depths down to about 4 m, were
92
     also analyzed to assess the microseepage mechanism. The Tarim Basin is experiencing regional
93
     warming related to climate change (mean annual temperature increased of about 1 °C over the
94
```

past 50 years; Chen et al., 2007), and our multi-seasonal study can predict the effect of this warming on methane microseepage in future milder winters.

# 2 Environmental and geological setting of the Dawanqi oilfield

The Dawanqi oilfield is located in the western part of the Kuqa-Baicheng depression, Tarim Basin (Figure 1). The region is characterized by an arid climate, low land productivity and severe soil salinization, resulting in rare vegetation and no biological methanogenic production near the surface. The dry soil, type "Gobi" (Luo et al., 2014), is generally a net sink of atmospheric methane. The average annual temperature is 10.6-11.5 °C; monthly mean temperature ranges from 20 to 30 °C in July and -10 to -20 °C in January (Chen et al., 2007). The snow cover, averagely lasts from 71 to 120 days and is homogeneously distributed with a thickness of 10-15 cm (Ding et al., 2018). The frozen soil reaches depths of about 90 cm (Fu et al., 2013; Hu et al., 2014). In the winter 2015, we observed ice thickness in the soil exceeding 60 cm; the temperature ranged from -14 °C to -10 °C and the atmospheric pressure was  $8.96 \times 10^4$  -  $9 \times 10^4$  Pa.

Discontinuous aquifers occur at a depth > 4.2 m. The geology of the Dawanqi oilfield was described in detail in previous papers (e.g., Tang et al., 2017). Here, we highlight that the area is highly faulted and fractured (dominated by the Tuzimazha fault system), hydrocarbon reservoirs are relatively shallow (170 to 700 m) in Quaternary to Neogene sandstones, while oil and gas are generated in Triassic and Jurassic coal-bearing formations (Zhao et al., 2003; Kuang et al., 2003; Kuang & Jin, 2005; Yang et al., 2006). Gas reservoirs have at least 89 vol% of thermogenic CH<sub>4</sub> ( $\delta^{13}$ C: -18 to -38 % VPDB), with C<sub>2+</sub> alkanes (~8 vol%), N<sub>2</sub> (2 vol%) and CO<sub>2</sub> (0.5 vol%) (Wang et al., 2012).

3 Methods

*3.1 Field work* 

- 124 3.1.1 Ground gas sampling
- Ten locations were selected for installation of tubing for nested soil gas sampling, nine in the
- proximity of fault systems or in correspondence with reservoirs, and one in a control area,
- outside the petroleum field. Sampling tubes were installed at depths of 0.3, 0.6, 0.9, 1.2, 1.5, 1.8,
- 2.1, 2.4, 2.7 m, 3 m (some at 3.5 m and 4 m; Fig. 2a). Groundwater was encountered at 4.2 m at
- some locations, and in these cases gas samples were preferably collected at maximum 3 m. The
- sampling layer was composed of sand and were sealed using bentonite, preventing gas exchange
- at different depths. High density polyethylene tubing (0.64 cm OD, 0.32 cm ID) was inserted in
- each sampling layer (Fig. 2b). The polyethylene tubing was closed at the top with a rubber pad,
- which is wrapped with vacuum sealant tape at the junction of the gas sampling tube. This
- arrangement allows sampling with a syringe. Ground gas was purged from the probe using a
- syringe after 10 days. Then the gas samples were drawn and injected into a 500 ml glass vial
- filled with saturated brine. In total, 116 gas samples were collected in summer 2016 and 2019,
- and sent to the laboratory for molecular and stable C composition (CH<sub>4</sub>, CO<sub>2</sub>) analyses.
- 3.1.2 Microseepage methane flux measurements
- For this work we used data of methane flux measurements performed in August 2014 (51)
- points), along three transects (MT1, MT2 and MT3) crossing the main reservoirs and faults (data
- published in Tang et al. 2017) and carried out new measurements, along the same transects in
- January 2015 (42 points) and August 2019 (31 points), as illustrated in Fig 3. In January 2015
- the investigated area was homogeneously covered by snow (about 10-15 cm thick). As in 2014,
- 2015 and 2019 CH<sub>4</sub> flux measurements were performed using a portable laser-based gas analyzer
- (LGR915-0011; detection limit of 5 ppbv CH<sub>4</sub>, 1σ precision of 0.6 ppbv) combined with a closed
- accumulation chamber (radius of 37 cm and height of 12 cm; Fig. 3).
- The chamber was inserted into the soil to a depth of about 5 cm, so that internal net volume was
- $3\times10^4$  cm<sup>3</sup> (during winter measurements the snow cover inside the chamber was removed). Gas
- 150 Flux was then calculated by using a linear regression of gas concentration buildup in the
- chamber, as typically performed for closed chambers. Each measurement was based on gas
- accumulation times of about 20 min. Methodological and calculation details, and further
- references, are reported in Tang et al. (2007) and Tang et al. (2017). Sampling interval along

each transect varied from 50 to 300 m, depending on the availability of suitable ground 154 conditions for installation of the closed chamber. As a control and for comparison, measurements 155 were also taken in an area located outside the petroleum field, approximately 50 km from the 156 field boundary. 157 158 3.2 Laboratory analyses 159 160 The concentrations of methane, ethane, propane, n-butane, i-butane, n-pentane, i-pentane and 161 CO<sub>2</sub> in the gas samples were analyzed by Perkin-Elmer model Auto system XL (FID/TCD) gas chromatograph with flame ionization detection, which was calibrated by using standards of 2.04 162 ppmv CH<sub>4</sub>, 1.01 ppmv C<sub>2</sub>H<sub>6</sub>, 1.05 ppmv C<sub>3</sub>H<sub>9</sub> (provided by Dalian Special Gases Corporation 163 Limited, China) before and after each batch of measurements. The chromatograph used alumina 164 column (Al<sub>2</sub>O<sub>3</sub> PLOT, 50m×0.53mm) and operated isothermally at 120 °C; N<sub>2</sub> was the carrier 165 gas (flow of 30 mL/min); the FID detector operated at 180 °C. The values of hydrocarbons were 166 determined with a precision of 0.01 ppmv. 167 The stable C isotopic composition of CH<sub>4</sub> and CO<sub>2</sub> were determined by gas chromatography-168 mass spectrometry, based on MAT-253 isotope mass spectrometer by Thermo Finnigan. The GC 169 used a Porapak QCP7551 capillary column (27.5m×0.32mm×10 m) and He as carrier gas (flow 170 of 1.8 mL/min). CH<sub>4</sub> is oxidised to CO<sub>2</sub> in combustion furnace and the isotopic composition of 171 the  $CO_2$  is analysed by isotope-ratio mass spectrometry. The  $\delta^{13}C$  values were determined with a 172 precision of 0.4‰ (n=10). Chinese national carbonate standard GBW04405 with known isotopic 173 values was used for isotope calibration. The stable C isotopic compositions are reported using 174 notation per mill (‰) relative to VPDB (Vienna Pee Dee Belemnite). 175 176 177 178 4 Results 179 4.1. Gas concentration profiles in the ground 180 CH<sub>4</sub> concentration in the ground (Fig. 5) increases with depth, in all sites located within the 181

petroleum field, from near atmospheric values at 0.3 m, to more than 30,000 ppmv at the depth

of 3 m (profile 545-13; Fig. 5). The control site, outside the field, did not provide any significant

gas increase with depth, with  $CH_4$  always around 2 ppmv. Within the petroleum field area,  $\delta^{13}C$ -

182

183

- 185 CH<sub>4</sub> increased from values near the atmospheric level (-44 to -46 %) at 0.3 m, to values around -
- 186 20 % below 1.5 m. From 1 to 4 m, the CH<sub>4</sub> isotopic composition is quite stable ( $\delta^{13}$ C within -20
- and -30 ‰), but it decreases progressively and rapidly towards the surface.
- The  $C_1/C_{2+}$  ratio (Fig. 6) also increases with depth, which implies progressive, relative decrease
- of CH<sub>4</sub> towards the surface (as shown in Figure 5). C<sub>2+</sub> gases are higher (see Table S2 in
- Supporting Information) at the 545-13 site (at the fault intersection), where also CH<sub>4</sub> is higher.
- 191 CO<sub>2</sub> concentration also increases with depth, up to 10,100 ppmv, although with wider
- oscillations (Fig. 7). Its stable C isotope composition does not change significantly below 1 m,
- with  $\delta^{13}$ C-CO<sub>2</sub> values around -16 to -22 %, and increases reaching the atmospheric value (about
- -9 ‰) near the surface. A slight, less pronounced CO<sub>2</sub> increase (up to 2000 ppmv) is observed
- also in the control site.
- Overall, the hydrocarbon data confirm the existence of thermogenic gas seepage from depth, as
- recorded in the oil-gas migration literature (Zhang et al., 1998; Hou & Su, 2001). The seeping
- gas has however higher  $C_1/(C_2+C_3)$  ratio compared to reservoir (Fig. 8): this is typical of gas
- seepage and is generally interpreted as due to molecular segregation during upward migration
- 200 (Etiope et al. 2009). The increase of CO<sub>2</sub> with depth could, partially, be also due to gas seepage,
- as the Dawangi reservoirs host 0.5 vol.% CO<sub>2</sub>. Additional CO<sub>2</sub> may derive from aguifer
- 202 degassing (including CH<sub>4</sub> oxidation).
- 203 The data at the shallower depths (< 1 m) suggest contamination of atmospheric air. This could be
- due to air leakage in the shallowest tubing, a less effective removal of air from the pipes before
- sampling, or flow of air into the soil due to atmospheric pumping, typically induced by
- barometric pressure and wind changes (e.g., Wyatt et al. 1995).
- 208 4.2 Methane flux

- Methane microseepage flux was measured along the three transects MT1, MT2 and MT3, both in
- January 2015 and August 2019, confirming the seepage potential of the area studied in August
- 2014 and discussed in Tang et al. (2017). Descriptive statistics of the flux data are summarized in
- Table 1 and the individual values along the three transects are shown in Figures 9, 10 and 11 (all
- data are available in the Supporting Information Table S1). The data clearly show that summer
- fluxes (both in 2014 and 2019) are systematically higher than the winter ones. Fig. 12 shows the
- 215 microseepage CH<sub>4</sub> histogram distribution in the two seasons. The methane flux in summer

(median value 0.49 mg m<sup>-2</sup> d<sup>-1</sup>; mean value 13.87 mg m<sup>-2</sup> d<sup>-1</sup>, including both 2014 and 2019 data) is mostly distributed between 0 and 5 mg m<sup>-2</sup> d<sup>-1</sup>, which is consistent with the global pattern of microseepage values (Etiope & Klusman, 2010). Summer fluxes reach orders of 10<sup>2</sup> mg m<sup>-2</sup> d<sup>-1</sup>, and positive are in 76.8 % of the cases. The highest values were observed near major faults (the highest value of 329.9 mg m<sup>-2</sup> d<sup>-1</sup> at point 554-11 is located over the intersection of two faults). Winter fluxes are mostly negative (81.4 % of the January 2015 cases), and not exceeding 0.53 mg m<sup>-2</sup> d<sup>-1</sup>. Where the measurements were taken exactly at the same point (42 cases), the summer-winter difference ranges from -1.41 to 329.9 mg m<sup>-2</sup> d<sup>-1</sup> (vertical lines in Figs. 9 to 11).

224225

216

217

218

219

220

221

222

223

#### **5 Discussion and conclusions**

226227228

229

230

231

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

The ground gas profiles clearly demonstrated the existence of thermogenic gas seepage in correspondence with the Dawanqi oilfield. The seepage is higher in the proximity of the fault systems, consistent with numerous seepage studies and models (Etiope, 2015; Ciotoli et al., 2020). The profiles from 4 m to 1 m, characterized by the absence of significant CH<sub>4</sub> isotopic fractionation compared to reservoir gas, suggest that seepage is likely driven by advective process (gas migration driven by pressure gradients), as considered in the crustal degassing literature (Etiope & Martinelli, 2002; Etiope, 2015). The  $\delta^{13}$ C-CH<sub>4</sub> values at depth >1.5 m are consistent with those measured in the deeper Neogene reservoirs (Tang et al., 2017). Near the surface, however,  $\delta^{13}$ C-CH<sub>4</sub> and  $\delta^{13}$ C-CO<sub>2</sub> may slightly increase and decrease, respectively, due to methanotrophic oxidation (Whiticar & Faber, 1986; Phelps et al., 1989; Benstead & King, 1997). The  $\delta^{13}$ C-CH<sub>4</sub> values at the soil-atmosphere interface (i.e. the isotopic value of methane actually entering the atmosphere and measured within the chamber) was reported in Tang et al., (2017): methane accumulating in the chamber is generally more enriched in <sup>13</sup>C than atmospheric air, with δ<sup>13</sup>C-CH<sub>4</sub> values (measured in 17 points) ranging from -46.3 ‰ to -30.7 ‰; the values increase with the flux, reflecting the input and dilution in the chamber of the thermogenic gas from the reservoir ( $\delta^{13}$ C: -18 to -38 % VPDB; Fig.8) with atmospheric air  $(\delta^{13}C \sim -47 \% VPDB)$ . The gas microseepage flux is then controlled by near-surface soil conditions, which change seasonally. The fluxes are higher in summer and lower in winter. This trend is opposite to the one typically observed in areas with less extreme climatic conditions. It is generally considered,

249

250

251

252

253

254

255

256

257

258

259

260

261

262

263

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

in fact, that microseepage is lower in summer, compared to winter, because of the higher methanotrophic consumption (Klusman et al., 2000; Etiope & Klusman, 2010). However, Klusman, (2003) reported variable patterns over a petroleum field in Colorado (Rangely): the fluxes in the winter 2001/2002 were higher than in summer 2001 (as expected because of the methanotrophic consumption variability), but the fluxes in winter 2000/2001 were lower than those in summer 2001. This suggests that not all winters lead to higher microseepage. A similar winter seepage decrease is observed at the Dawanqi oilfield. The Dawanqi area is characterized by extreme climatic conditions in winter, with abundant snow covers (about 10-15 cm of snow were observed in our winter measurements in 2015) and significant ice thickness in the soil (reaching depths of about 90 cm; Fu et al., 2013; Hu et al., 2014). The higher winter fluxes reported by Klusman, (2003) were actually reported in less cold climatic conditions, with reduced presence of snow and ice (thickness not exceeding 60 cm; Klusman, 2003). It is likely, then, that significant ice thickness and snow cover act as a barrier for microseepage, and this effect prevails on the one (in opposite direction) of the lower methanotrophic consumption (Wu et al., 2014). Methanotrophic consumption seems to occurs also in presence of snow and ice, as also observed by Klusman (2003). We also note that the methane fluxes in summer (Figs. 9-11) are consistent with the order of magnitude of the local theoretical microseepage derived by a global gridding, process-based and statistical, model (Etiope et al., 2019): the microseepage grid cells in correspondence with the Dawanqi oilfield have mostly theoretical (modeled) fluxes in the range of  $0.01-12 \text{ mg m}^{-2} \text{ d}^{-1}$ . Overall, our data suggest that seasonal variations of microseepage are not the same everywhere, as they depend on the specific winter climate conditions: the lower methanotrophic consumption (leading to higher fluxes) and the ice-snow barrier effect (leading to lower fluxes) seem to compete in the establishment of the seasonal pattern. This pattern is expected to be "normal" (mostly controlled by methanotrophic activity) in temperate and not extreme winter climatic regions, and "inverse" in extremely cold regions, as the Dawanqi region. The Tarim Basin is experiencing climatic warming, as observed over the last 50 years, with an average temperature increase of 1 °C (Chen et al., 2007). This implies that, if warming will continue in the future, winters may become milder and the presence of ice in the soil may decrease. If so, it is expected that winter methane seepage will tend to increase, in a process similar to that observed in permafrost and sub-arctic regions (Anisimov & Reneva, 2006;

- O'Connor et al., 2010b; Masyagina & Menyailo, 2020; Anthony et al., 2020). Further
- 280 microseepage measurements in the Dawanqi area shall be performed in the next winters to
- monitor and confirm the possible climate control of microseepage methane exhalations. A more
- careful investigation, including modeling, on microseepage mechanisms (advection vs diffusion)
- and methane oxidation in iced and ice-free soil, will be essential to improve process-based
- 284 models for global emission estimates.

286

## Acknowledgments

- 287 This work was supported by the Joint Funds of the National Natural Science Foundation of
- 288 China (grants U2003101) and National Natural Science Foundation of China (grants 41872126
- and 41373121). Thanks to Mr. Suo Xiaodong (Bureau of Geophysical Prospecting INC., China
- National Petroleum Corporation) for his guidance on petroleum geology of the Dawanqi field.

291

292293

294

295

296

297

298

299

300

301

302 303

304 305

306

307

308

309

310

### References

- Anisimov, O., & Reneva, S. (2006). Permafrost and Changing Climate: The Russian Perspective. *AMBIO: A Journal of the Human Environment*, 35(4), 169–175. https://doi.org/10.1579/0044-7447(2006)35[169:PACCTR]2.0.CO;2
  - Anthony, K., Lindgren, P., Hanke, P., Engram, M., Anthony, P., Daanen, R., et al. (2020). Decadal-scale hotspot methane ebullition within lakes following abrupt permafrost thaw. *Environmental Research Letters*. https://doi.org/10.1088/1748-9326/abc848
  - Benstead, J., & King, G. (1997). Response of methanotrophic activity in forest soil to methane availability. *FEMS Microbiology Ecology*, 23(4), 333–340. https://doi.org/10.1111/j.1574-6941.1997.tb00414.x
  - Brown, A. (2000). Evaluation of Possible Gas Microseepage Mechanisms. *AAPG Bulletin*, 84(11), 1775–1789. https://doi.org/10.1306/8626C389-173B-11D7-8645000102C1865D
  - Chen, Y., Li, W., Xu, C., & Hao, X. (2007). Effects of climate change on water resources in Tarim River Basin, Northwest China. *Journal of Environmental Sciences*, 19(4), 488–493. https://doi.org/10.1016/S1001-0742(07)60082-5
- Ciotoli, G., Procesi, M., Etiope, G., Fracassi, U., & Ventura, G. (2020). Influence of tectonics on global scale distribution of geological methane emissions. *Nature Communications*, 11(1), 2305. https://doi.org/10.1038/s41467-020-16229-1
- Ding, Y., Li, Y., Li, L., Yao, N., Hu, W., & Yang, D. (2018). Spatiotemporal variations of snow characteristics in Xinjiang, China over 1961–2013 | Request PDF. *Nordic Hydrology*, 49(5–6), 1578–1593. https://doi.org/10.2166/nh.2017.035
- Etiope, G. (2015). *Natural Gas Seepage: The Earth's Hydrocarbon Degassing*. Springer, Switzerland. https://doi.org/10.1007/978-3-319-14601-0
- Etiope, G., & Klusman, R. W. (2010). Microseepage in drylands: Flux and implications in the global atmospheric source/sink budget of methane. *Global and Planetary Change*, 72(4), 265–274. https://doi.org/10.1016/j.gloplacha.2010.01.002
- Etiope, G., & Martinelli, G. (2002). Migration of carrier and trace gases in the geosphere: an overview. *Physics of the Earth and Planetary Interiors*, 129(3), 185–204. https://doi.org/10.1016/S0031-9201(01)00292-8
- Etiope, G., & Schwietzke, S. (2019). Global geological methane emissions: An update of top-down and bottom-up estimates. *Elementa-Science of the Anthropocene*, 7, 1–9. https://doi.org/10.1525/elementa.383

- Etiope, G., Ciotoli, G., Schwietzke, S., & Schoell, M. (2019). Gridded maps of geological methane emissions and their isotopic signature. *Earth System Science Data*, *11*(1), 1–22. https://doi.org/10.5194/essd-11-1-2019
- Etiope, G, Feyzullayev, A., & Baciu, C. L. (2009). Terrestrial methane seeps and mud volcanoes: A global perspective of gas origin. *Marine and Petroleum Geology*, 26(3), 333–344. https://doi.org/10.1016/j.marpetgeo.2008.03.001
- Fu, C., Dan, L., Wu, J., & Wei, R. (2013). Variation and Abrupt Change of Maximum Depth of Frozen Soil over Xinjiang Under the Background of Global Warming, 1961-2005. *Journal of Glaciology and Geocryology*, 35(06), 1410–1418.
- Hou, W., & Su, J. (2001). The evidence and characteristics of vertical micro-migration of upper pool's hydrocarbons in northern Tarim Basin (in Chinese). *Xinjiang Petroleum Geology*, (06), 465-468+452–453.

334

335

336

337

338

339

340

341

342

343

344

345

346 347

348

349

350

351

352

353

354 355

356

357

358 359

360

361

362

363

364

365

366

367

- Hu, L., Wu, P., Liang, C., & Zhang, W. (2014). Analyzing the effect of snow cover in spring and winter and air temperature on frozen ground depth in Xinjiang. *Glaciology and Geocryology*, 36(01), 48–54.
- Klusman, R. W. (2003). Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, Colorado, USA. *Applied Geochemistry*, *18*(12), 1825–1838. https://doi.org/10.1016/s0883-2927(03)00108-2
- Klusman, R. W., & Saaed, M. A. (1996). Comparison of Light Hydrocarbon Microseepage Mechanisms, 157–168.
- Klusman, R. W., Leopold, M. E., & LeRoy, M. P. (2000). Seasonal variation in methane fluxes from sedimentary basins to the atmosphere: Results from chamber measurements and modeling of transport from deep sources. *Journal of Geophysical Research: Atmospheres*, 105(D20), 24661–24670. https://doi.org/10.1029/2000JD900407
- Kuang, H., & Jin, G. (2005). Reservoir characteristic and evalution of the Kangcun formation in the Dawanqi oilfield Tarim Basin (in Chinese). *Geomechanics*, (01), 81–89.
- Kuang, H., Niu, S., & Chen, X. (2003). The diagenetic characteristics and its controlling factors of the Kangcun formation in the Dawanqi oilfield, the Tarim Basin (in Chinese). *Geoscience*, 17(02), 211–216.
- Kvenvolden, K. A., & Rogers, B. W. (2005). Gaia's breath—global methane exhalations. *Marine and Petroleum Geology*, 22(4), 579–590. https://doi.org/10.1016/j.marpetgeo.2004.08.004
- Luo, W., Dong, Z., Qian, G., Feng, M., Lu, J., Wang, M., et al. (2014). Geochemical compositions of surface sediment from Gobi Desert in northern China and its sedimentary significance (in Chinese). *Journal of Desert Research*, 34(06), 1441–1453.
- Macgregor, D. S. (1993). Relationships between seepage, tectonics and subsurface petroleum reserves. *Marine and Petroleum Geology*, *10*(6), 606–619. https://doi.org/10.1016/0264-8172(93)90063-X
- Masyagina, O. V., & Menyailo, O. V. (2020). The impact of permafrost on carbon dioxide and methane fluxes in Siberia: A meta-analysis. *Environmental Research*, 182, 109096. https://doi.org/10.1016/j.envres.2019.109096
- Milkov, A. V., & Etiope, G. (2018). Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples. *Organic Geochemistry*, 125, 109–120. https://doi.org/10.1016/j.orggeochem.2018.09.002
- O'Connor, F. M., Boucher, O., Gedney, N., Jones, C. D., Folberth, G. A., Coppell, R., et al. (2010a). Possible role of wetlands, permafrost, and methane hydrates in the methane cycle under future climate change: A review. *Reviews of Geophysics*, 48(4). https://doi.org/10.1029/2010RG000326
- Phelps, T. J., Raione, E. G., White, D. C., & Fliermans, C. B. (1989). Microbial activities in deep subsurface environments. *Geomicrobiology Journal*, 7(1–2), 79–91. https://doi.org/10.1080/01490458909377851
- Price, L. C. (1986). A critical overview and proposed working model of surface geochemical exploration. *Unconventional Methods in Exploration for Petroleum and Natural Gas IV*, 245–309.
- Rusticucci, M., Brönnimann, S., Charabi, Y., Dentener, F., Easterling, D., Soden, B., et al. (2014). IPCC (2013), Climate Change 2013, in The Physical Science Basis, Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, WMO/UNEP, Cambridge (pp. 159–254).
- Saunders, D. F., Burson, K. R., & Thompson, C. K. (1999). Model for Hydrocarbon Microseepage and Related
   Near-Surface Alterations. *AAPG Bulletin*, *83*(1), 170–185. https://doi.org/10.1306/00AA9A34-1730-11D7-8645000102C1865D
- Saunois, M., Stavert, A. R., Poulter, B., Bousquet, P., Canadell, J. G., Jackson, R. B., et al. (2020). The Global Methane Budget 2000–2017. *Earth System Science Data*, 12(3), 1561–1623. https://doi.org/10.5194/essd-12-1561-2020
- Tang, J., Bao, Z., Xiang, W., & Gou, Q. (2007). Daily Variation of Natural Emission of Methane to the Atmosphere and Source Identification in the Luntai Fault Region of the Yakela Condensed Oil/Gas Field in the Tarim

- 378 Basin, Xinjiang, China. *Acta Geologica Sinica English Edition*, 81(5), 771–778. 379 https://doi.org/10.1111/j.1755-6724.2007.tb01001.x
- Tang, J., Xu, Y., Wang, G. J., Etiope, G., Han, W., Yao, Z., & Huang, J. (2017). Microseepage of methane to the atmosphere from the Dawanqi oil-gas field, Tarim Basin, China. *Journal of Geophysical Research-Atmospheres*, 122(8), 4353–4363. https://doi.org/10.1002/2016jd026385

  Wang, Q., Bao, J., Xie, Z., & Wang, S. (2012). Geochemical characteristics and genesis of natural gas in the
  - Wang, Q., Bao, J., Xie, Z., & Wang, S. (2012). Geochemical characteristics and genesis of natural gas in the Dawanqi oilfield (in Chinese). *Journal of Yangtze University(Natural Science Edition)*, 9(08), 28–31.
  - Whiticar, M. J., & Faber, E. (1986). Methane oxidation in sediment and water column environments—Isotope evidence. *Organic Geochemistry*, 10(4), 759–768. https://doi.org/10.1016/S0146-6380(86)80013-4
  - Wu, X., Brueggemann, N., Butterbach-Bahl, K., Fu, B., & Liu, G. (2014). Snow cover and soil moisture controls of freeze-thaw-related soil gas fluxes from a typical semi-arid grassland soil: a laboratory experiment. *Biology and Fertility of Soils*, 50(2), 295–306. https://doi.org/10.1007/s00374-013-0853-z
  - Wyatt, J. M., & Knowles, C. J. (1995). Microbial degradation of acrylonitrile waste effluents: the degradation of effluents and condensates from the manufacture of acrylonitrile. *International Biodeterioration & Biodegradation*, 35(1), 227–248. https://doi.org/10.1016/0964-8305(95)00031-Y
  - Xiao, C., Wu, X., Wang, D., & Zhu, Y. (2019). Oil-gas information extraction and prospective area prediction based on hydrocarbon microseepage theory: A case study of Salamat Basin in Central Africa (in Chinese). *Remote Sensing for Land & Resources*, 31(04), 120–127.
  - Yang, X., Che, C., Yang, S., & Zhao, D. (2006). Reservoir types and distribution regularities in the Dawanqi oilfield (in Chinese). *West China Petrol. Geosci*, (01), 41–44.
  - Zhang, B., Zhu, H., & Wang, R. (1998). Vertical micro-migration characteristics of deep hydrocarbon gas in the north part of Tarim Basin (in Chinese). *Natural Gas Industry*, (01), 39-42+7–8.
  - Zhao, M., Song, Y., Liu, S., & Qin, S. (2003). The diffusion influence on gas pool: Dawanqi oilfield as an example (in Chinese). *Natural Gas Geoscience*, (05), 393–397.

# Figure captions

384

385

386

387 388

389

390

391

392

393

394

395

396

397

398

399

400

401

402 403

404

405

406

410

412

415

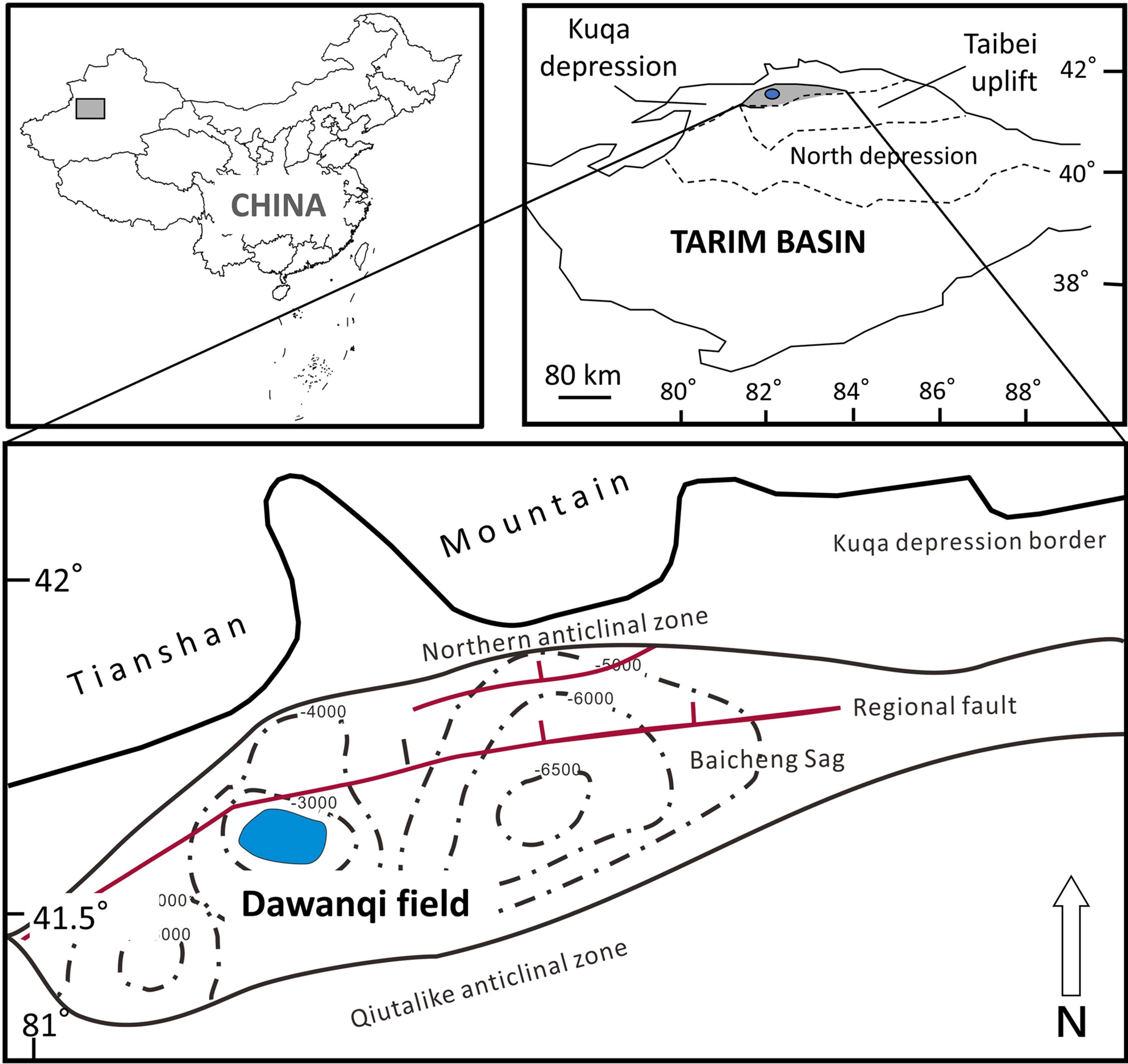
421

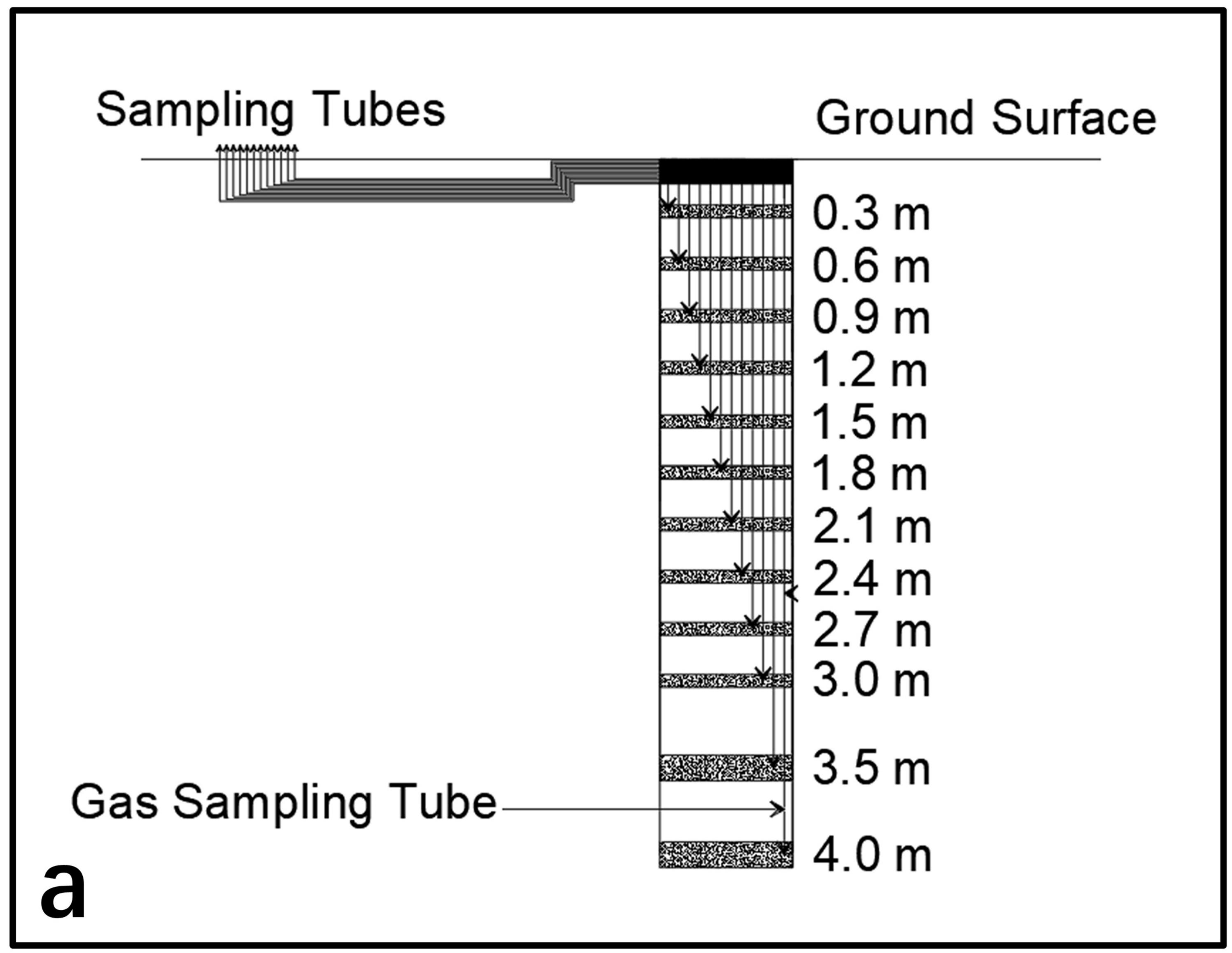
- Figure 1. Location of Dawanqi oilfield. The main tectonic units and fault systems of the Kuqa depression (northern sector of Tarim Basin) are shown (redrawn from Tang et al. 2017). The dashed lines are the isolines (m) for the top of the Baicheng Sag structure.
- Figure 2. Sketch of gas sampling tubes in the ground (a); installation of tubes in a borehole (b).
- Figure 3. Gas flux measurements using the closed-chamber method with portable gas analyzer, in summer (a) and winter (b).
- Figure 4. Gas flux measurement locations at the Dawanqi oilfield. MT1, MT2 and MT3 are the measurements transects (see also Table S1). Red lines are fault and fracture systems identified by geophysical prospections (see Tang et al. 2017). Stars are the boreholes for ground gas profile.
- Grey circles are oil wells. Triangles (August 2014), diamonds (January 2015) and squares (August 2019) are the measurement sites of each measurement campaign.
- Figure 5. Methane concentration (a) and stable C isotope composition (b) profiles versus depth, in the 4-meter boreholes. All measurements were taken in summer season.

425	<b>Figure 6.</b> C <sub>1</sub> /C <sub>2+</sub> profiles in the 4-meter boreholes. All measurements were taken in summer
426 427	season.
428 429	<b>Figure 7.</b> CO <sub>2</sub> concentration (a) and stable C isotope composition (b) profiles in the 4-meter holes. All measurements were taken in summer season.
430	
431 432 433	<b>Figure 8.</b> $\delta^{13}$ C-CH <sub>4</sub> vs C <sub>1</sub> /(C <sub>2</sub> +C <sub>3</sub> ) diagram for gas samples collected in six ground boreholes compared to Dawanqi oil-gas reservoir (reservoir data after Wang et al., 2012). CR: CO reduction, F: methyl-type fermentation, SM: Secondary microbial, LMT: late mature
434 435	thermogenic gas, OA: oil-associated thermogenic gas. Genetic zonation after Milkov & Etiope (2018).
436	
437 438	<b>Figure 9.</b> Methane microseepage flux data along transect MT1. Vertical lines highlight the flux difference between summer and winter where measurements were performed at the same point.
439	
440 441	<b>Figure 10.</b> Methane microseepage flux data along transect MT2. Vertical lines as in Fig. 5.
442 443	<b>Figure 11.</b> Methane microseepage flux data along transect MT3. Vertical lines as in Fig. 5.
444 445	Figure 12. Histogram of microseepage flux data in summer (a) and winter (b)
446	
447	
448	Table caption
449	<b>Table 1.</b> Descriptive statistics of CH <sub>4</sub> microseepage flux (mg m <sup>-2</sup> d <sup>-1</sup> )
450	

**Table 1** Descriptive statistics of CH<sub>4</sub> microseepage flux (mg m<sup>-2</sup> d<sup>-1</sup>)

Flux (mg·m <sup>-2</sup> ·d <sup>-1</sup> )				
Parameter	summer	winter		
Mean	13.87	-0.24		
Median	0.49	-0.28		
Min	-1.41	-1.05		
Max	329.9	0.53		
Std.dev	50.94	0.33		

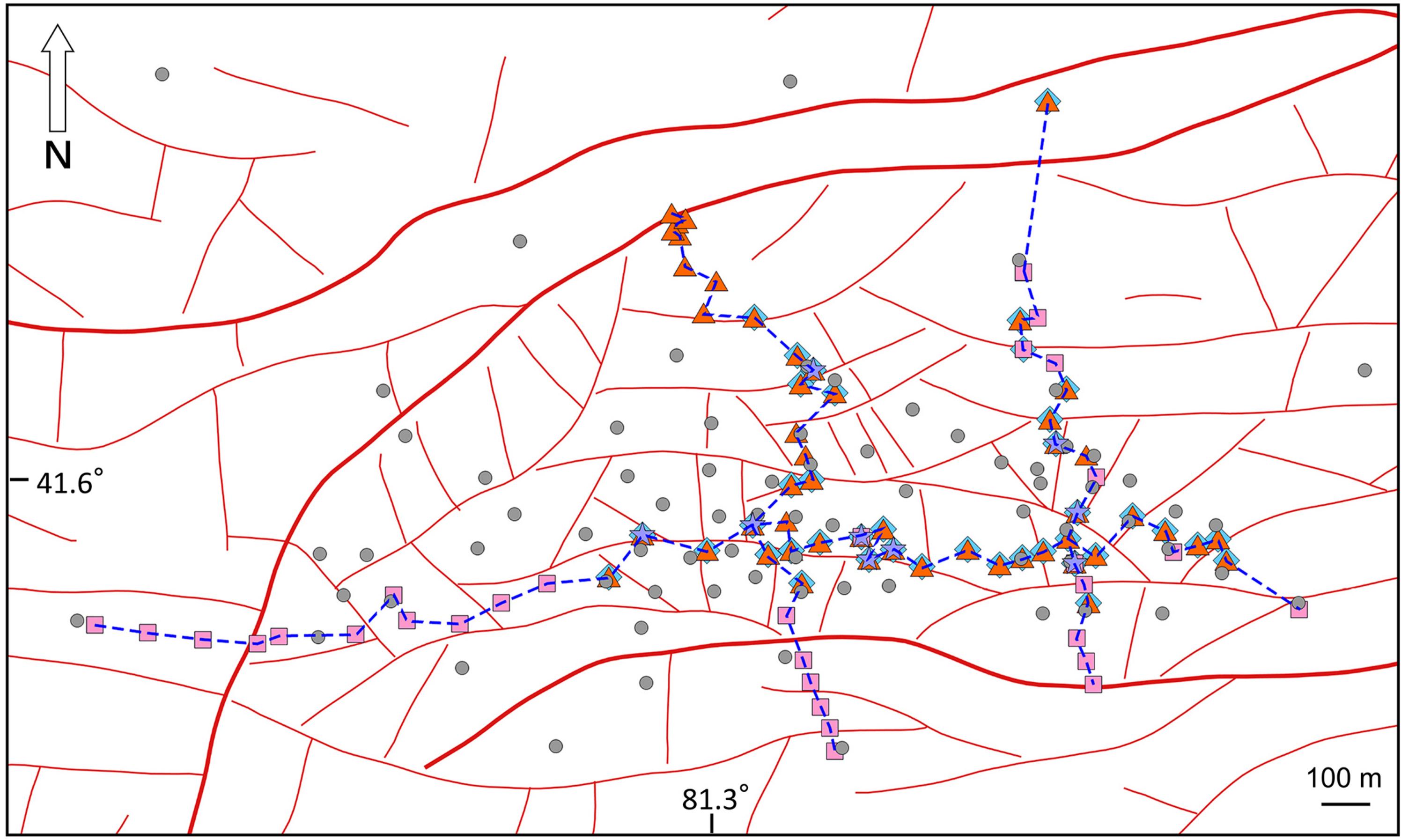












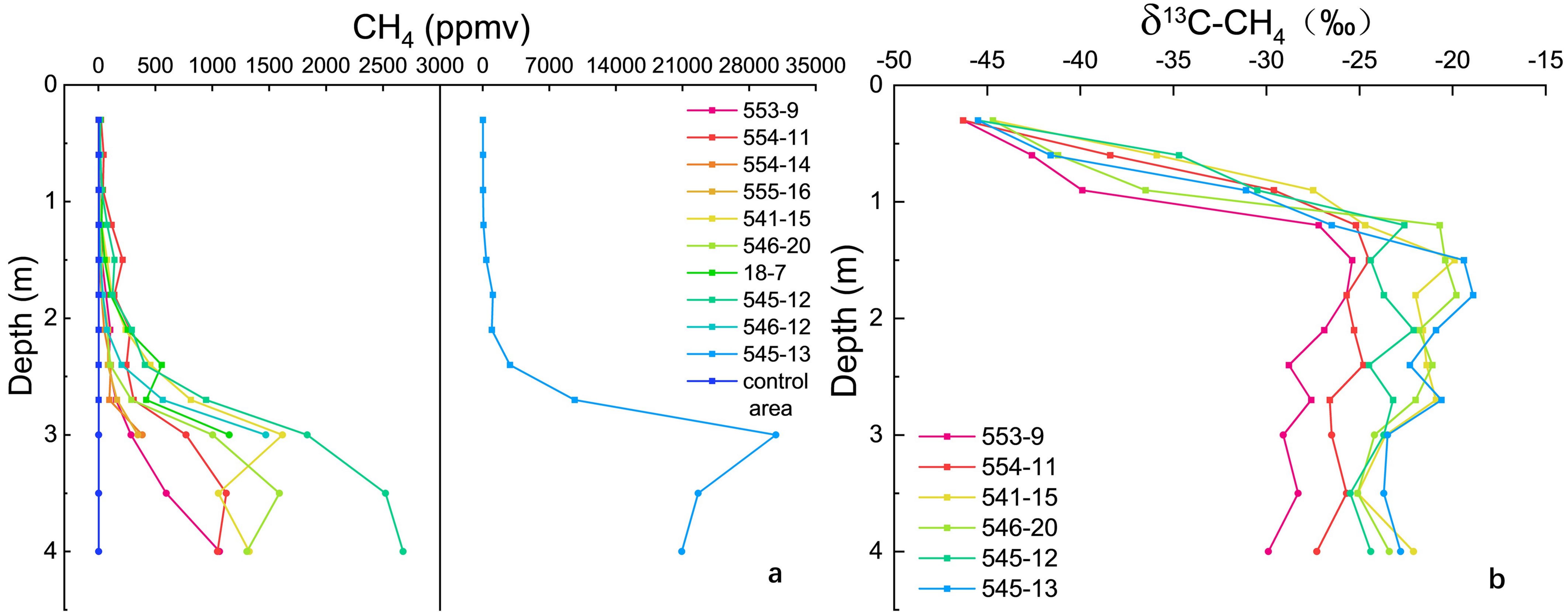
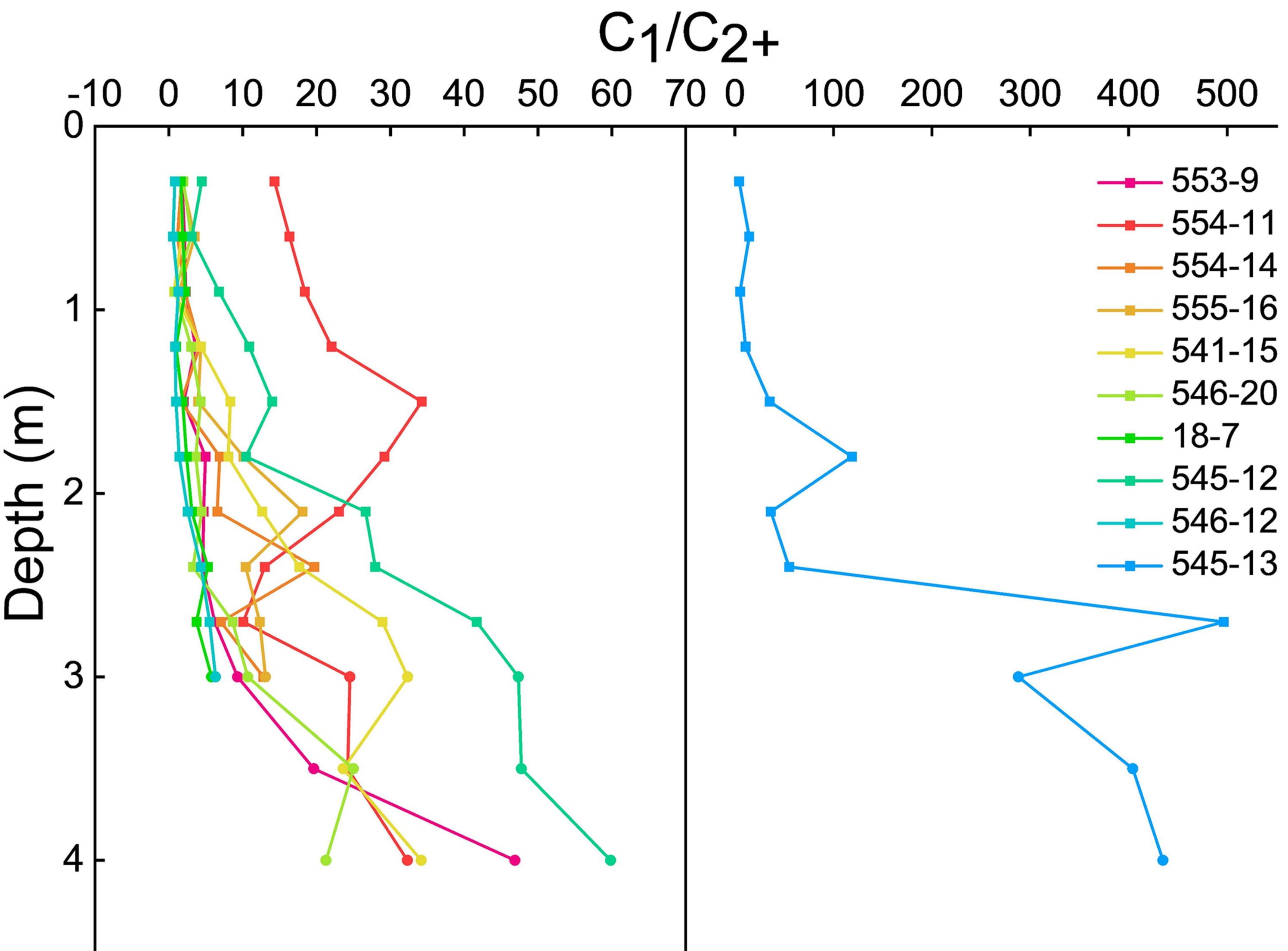


Figure	6.
--------	----



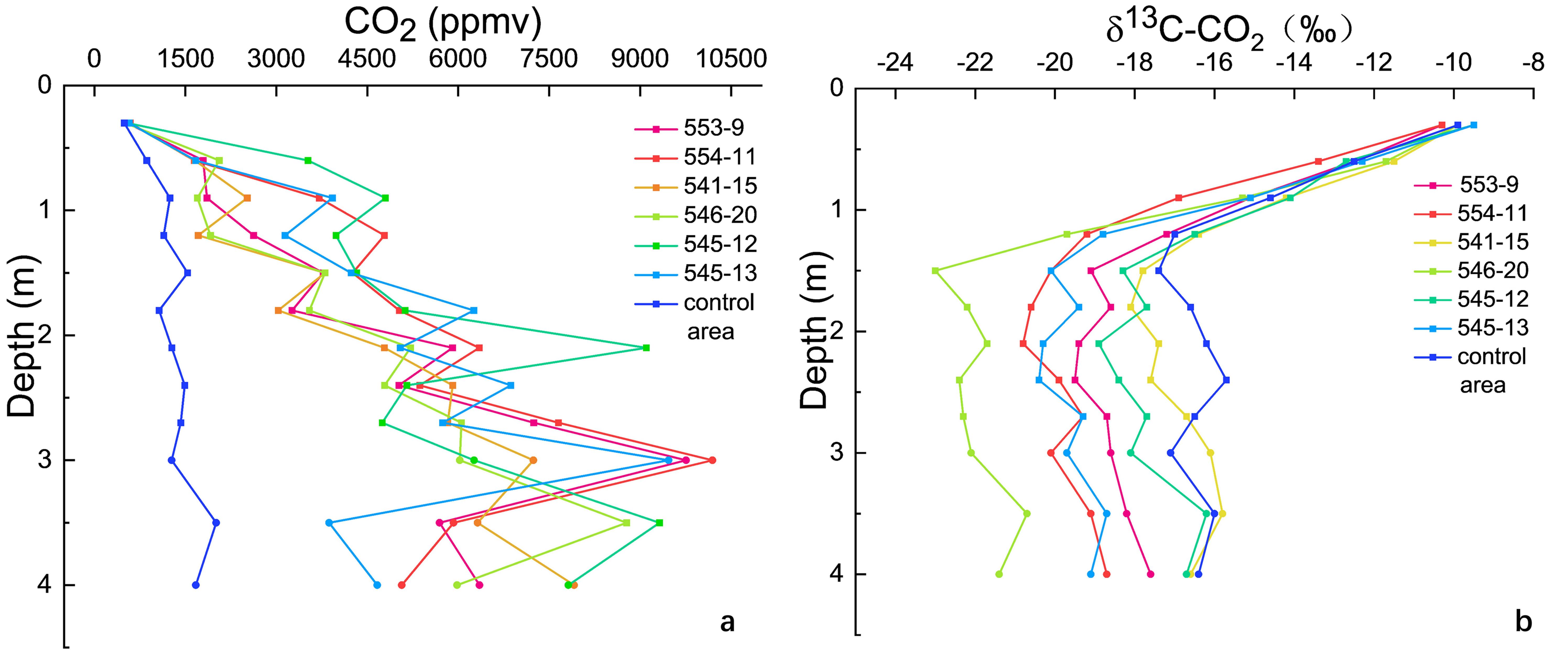


Figure 8.	•
-----------	---

