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Greenhouse gas emissions from oilfield-produced water in Shengli Oilfield, Eastern China

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ABSTRACT

Greenhouse gas (GHG) emissions from oil and gas systems are an important component of the GHG emission inventory. To assess the carbon emissions from oilfield-produced water under atmospheric conditions correctly, *in situ* detection and simulation experiments were developed to study the natural release of GHG into the atmosphere in the Shengli Oilfield, the second largest oilfield in China. The results showed that methane (CH₄) and carbon dioxide (CO₂) were the primary gases released naturally from the oilfield-produced water. The atmospheric temperature and release time played important roles in determining the CH₄ and CO₂ emissions under atmospheric conditions. Higher temperatures enhanced the carbon emissions. The emissions of both CH₄ and CO₂ from oilfield-produced water were highest at 27°C and lowest at 3°C. The bulk of CH₄ and CO₂ was released from the oilfield-produced water during the first release period, 0–2 hr, for each temperature, with a maximum average emission rate of 0.415 g CH₄/(m³·hr) and 3.934 g CO₂/(m³·hr), respectively. Then the carbon emissions at other time periods gradually decreased with the extension of time. The higher solubility of CO₂ in water than CH₄ results in a higher emission rate of CH₄ than CO₂ over the same release duration. The simulation proved that oilfield-produced water is one of the potential emission sources that should be given great attention in oil and gas systems.

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Introduction

CH₄ and CO₂, the most well-known greenhouse gases (GHGs), are highly associated with global climate change (Glagolev et al., 2008; Rodhe, 1990; Xu et al., 1999). CH₄ contributes more than 20% to global warming and is receiving increased attention. The International Panel on Climate Change (IPCC) reported that on a 100-year time horizon, CH₄ emissions are more potent than CO₂ in terms of global warming potential, because its emissions have 25 times more impact on the

atmosphere than CO₂ on a mass basis (Griggs and Noguer, 2002; IEA, 2008). CH₄ and CO₂ emissions from oil and natural gas systems are important sources in GHG inventories, and their relative roles are anticipated to increase in the future (IPCC, 2000; Reilly et al., 2003; EPA, 2006a). In 2006, the Environmental Protection Agency (EPA) estimated that fugitive CH₄ emissions from the oil and gas sector were approximately 130 million tons of CO₂-eq in total, which accounts for approximately 2% of the total GHG emissions in the USA (EPA, 2008). These fugitive emissions of CH₄ are

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generated from disparate sources located throughout the main processes: production, processing, transmission, distribution, and storage processes (EPA, 2006b). As the oil and gas system is large, diverse and complex, and there are numerous types of emission sources, a few poorly known sources have been ignored (Dedikov et al., 1999). Thus assessing the accessible sources is conducive to minimizing the uncertainty of carbon emission values, and reducing these possibly insufficiently considered sources (Guan et al., 2012; Sinton and Fridley, 2000; Streets et al., 2001).

Wastewater, which includes human and industrial wastewater, is listed as one of the CH₄ emission sources in the IPCC Guidelines for National GHG Inventories (IPCC, 2006). As is well known, formation water is an important medium in the process of natural gas and liquid petroleum migration underground (Dhima et al., 1998). Natural gas could be enriched in underground aquifers, and the solubility of natural gas is higher than liquid petroleum in water at reservoir temperature and pressure (Gao et al., 2012). When the formation water is produced at the surface, most gases are released from the water as the temperature and pressure decrease. Thus, formation water has the potential for carbon emissions from an environmental aspect when it is produced at the surface (IPCC, 2006). China is one of the world's major oil producers, and forty-one large- to medium-sized oilfields have been discovered in China (Jin, 2008). With the exploration and development of the oilfields, the amount of oilfield-produced wastewater is increasing. Chen et al. (2014) confirmed by experiment the existence of carbon emissions from gas-field-produced water at atmospheric temperature and pressure. The concentration of CH₄ is generally over 90% in gas fields, but is generally 60%–90% in oilfields. Thus, there is little known about the carbon emissions from large

amounts of oilfield-produced water under atmospheric conditions. Scientists have always taken seriously the natural gas dissolved in and exsolved from underground formation water, but have seemed to ignore the contributions to the atmosphere by the gases released from oilfield-produced water as a by-product of the oil extraction process from subsurface geological formations (Weschenfelder et al., 2015). No scientific literature has presented the carbon emissions from oilfield-produced water under atmospheric conditions until now.

Most Chinese giant oilfields are distributed in the sags rich in oil and gas. Shengli Oilfield, located in Dongying Sag of the Bohai Bay Basin (Fig. 1), is the second largest oilfield in China. After several decades of development, it has entered the mid-and-late part stages. The moisture content of crude oil has increased by up to 90% in the Shengli Oilfield, as a mass of water has been injected back into the wells. When the large quantity of formation water was drained during the extraction of crude oil and natural gas, most of the gases were released from the water as the temperature and pressure decreased quickly. Before the water reached the well mouth, three phases (oil, gas and water) were separated by an oil-gas-water separator. Most of the gas was released, except for a small quantity of gas that remained in the water after it rose to the surface. However, the quantity of produced water has now reached, on average, tens of thousands of cubic meters a day in the Shengli Oilfield. The fugitive emissions of CH₄ and CO₂ from the oil and gas system are an important component of the GHG emission inventory (IPCC, 2006). It is also of scientific importance to assess the possible contribution of GHGs released from oilfield-produced water into the atmosphere and to reduce the uncertainty of estimating carbon emissions in oil and gas systems. Shengli Oilfield is believed

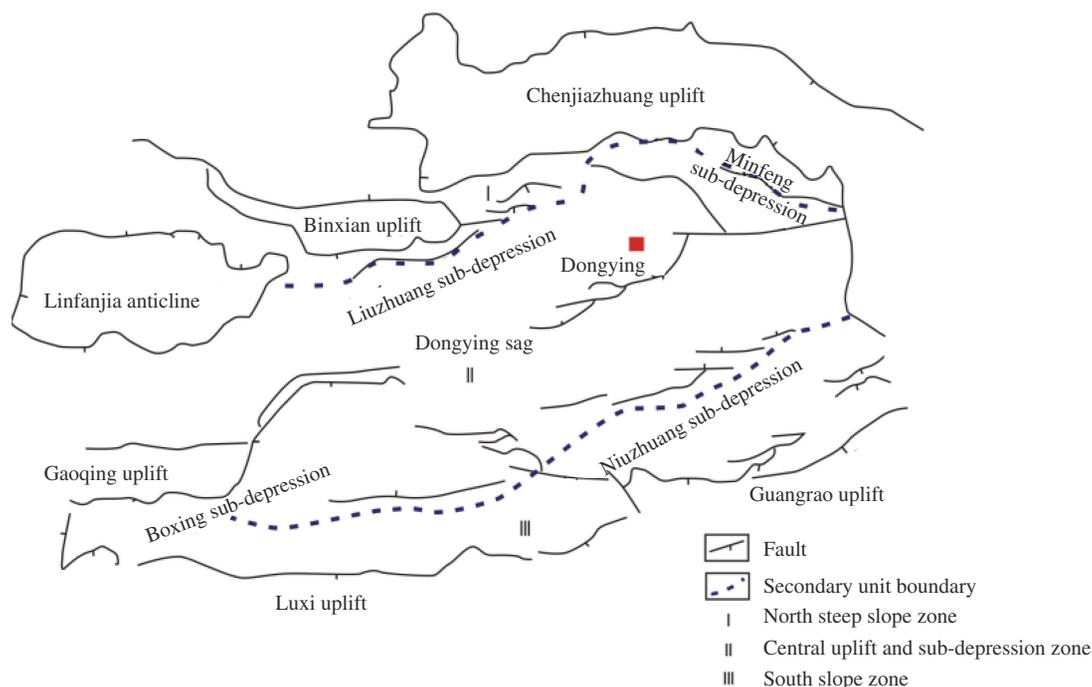


Fig. 1 – Dongying Sag and its secondary structural units, modified from the work by Zhang et al. (2014).

to be a representative region to study whether the huge amounts of oilfield-produced water are a potential greenhouse gas emission source in the oil and gas system. *In situ* detection and modeling experiments were performed on the carbon emissions from the oilfield-produced water.

1. Methods and materials

1.1. Sample distribution

Dongying Sag, a third-class structure unit of the Bohai Bay Basin, is a typical hydrocarbon-rich sag, with large amounts of oil and gas originating from the source rock of the Shahejie Formation (Guo et al., 2012). The strata have experienced a boom in hydrocarbon generation, leading to a formation pressure increase (Yuan et al., 2015; Zhang et al., 2012). The formation overpressure system is developed below 2200 m, and the frequency of the drilling overpressure interval and the overpressure intensity increase with depth. In particular, at 2900–3800 m, the overpressure is as much as 36 MPa, and the pressure coefficient ranges as high as 2.0. The formation water is of a deep and closed CaCl₂ type and its salinity is 2.3–335.5 g/L with an average of 64.8 g/L. The abundance of CH₄ and CO₂ varies from 60.5% to 94.7% and from 1.0% to 7.0% by volume, respectively, and for the gas mixture (0.22%–23.9% ethane +0.08%–26.7% propane +0.04%–36.5% C₄). These gas composition data are actual measurements from 29 wells in the Shahejie Formation.

The water samples were obtained directly from the drainpipe after the three oil, gas and water phases were separated by an oil–gas–water separator before they reached the well mouth. The sampling bottles were sealed immediately after being filled with water, then submerged in an ice-water mixture for the gases to dissolve thoroughly in the oilfield-produced water. Air samples were collected above the water tanks and at the union station.

1.2. *In situ* detection

The oilfield-produced water flows into the water tanks after the formation water is produced at the surface. The volume of water tanks at the union station of Shengli Oilfield is 4000 m³. The roof is 17.7 m high, the diameter of the tank is 17 m and the vent valves on the roof are 0.5 m wide. CH₄ and CO₂ concentration detectors with a range of 0–5000 ppm and an accuracy of 1 ppm were used to detect both the CH₄ and CO₂ emissions from the vent valves on the roof and from the air at the union station. Air samples in the vent valves on the water tank and at the union station were also collected for component analysis.

1.3. Emission experiment

A simulated mini-water tank (30 L) was applied to study GHG emissions (Fig. 2). The test tank was strictly scaled in equal proportion according to the real size of a water tank in the oilfield. The tank, whose roof was a gentle curved surface, had a cylindrical shape with an internal diameter and length of 0.33 and 0.35 m, respectively. The mini-tank was made with

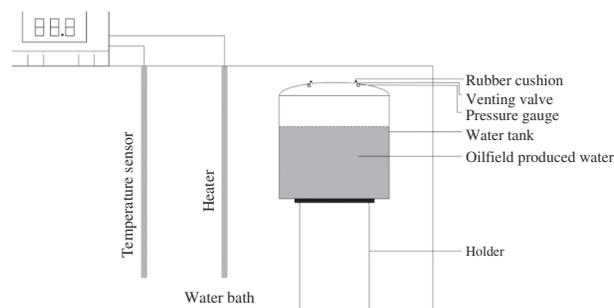


Fig. 2 – Schematic diagram of experimental system for oilfield-produced water.

an organic glass material to ensure even heating of the sample and improve the sample's sensitivity to the water 20 L bath temperature simultaneously. Oilfield-produced water was stored in the mini-tank, and the remaining 10 L of headspace was filled with fresh air to provide enough space for CH₄ and CO₂ emissions. The vent valves were sealed with rubber septa to prevent air exchange, and two pressure gauges were mounted below the two venting valves to detect whether the pressure was maintained at atmospheric pressure. If the pressure exceeded atmospheric pressure, as a result of the gases released from the oilfield-produced water, then the experimental conditions were not qualified. The water tank was immersed in a constant-temperature water bath, which was controlled and maintained at the desired temperature by a temperature controller.

We collected water samples from the oilfield union station in July, when the atmospheric temperature was 27°C. A temperature of 27°C was adopted as the first experimental temperature because July has the highest temperature during the year, with an average temperature of 26.6°C in the study region. The second experimental temperature was 13°C, which is the average annual temperature in the study region. In addition, we chose 3°C, the average temperature in the coldest month of January, to detect the quantity of GHGs released under the low temperature condition. Because of the high water output, oilfield-produced water stays at the surface for up to 12 hr until it is re-injected into the reservoir with the aim of enhancing oil recovery. Along with the process of producing oil, most gases are released from the formation water as the temperature and pressure decreases quickly, thus the first CH₄ and CO₂ concentrations were monitored after the gases had been released for 2 hr at different temperatures. Therefore, the target time was set within a range of 0–12 hr, with 2 hr as an interval to monitor the release variation. Gas samples of 200 mL were taken via a syringe through a rubber septum at each measurement time at 2, 4, 6, 8, 10, and 12 hr, and then placed into aluminum foil bags for gas analysis. The rubber septum was then removed from the vent valves and fresh air was redrawn for the test analysis in the next time period. All samples were measured in triplicate.

1.4. Analysis method

Gas concentrations in the gas samples were analyzed at the Lanzhou Geological Institute of the Chinese Academy of

Table 1 – CH₄ and CO₂ concentration analysis (units: ppm).

Sampling	Vent valves		Union station	
	CH ₄	CO ₂	CH ₄	CO ₂
SL-1	0	499	3	467
SL-2	0	515	5	485
SL-3	0	502	4	475
SL-4	0	477	4	473
SL-5	0	554	6	494
SL-6	0	521	3	462

Sciences using a MAT271 mass spectrometer and GC-5890 A gas chromatograph (FID). The working conditions of the mass spectrometer were as follows: ion source, EI; discrimination ratio, 3000; and emission current, 0.200 mA. The working conditions of the chromatograph were set as: HP-PLOTQ column (50 m × 0.32 mm × 0.25 μm), N₂ (99.999%) as load gas, and FID detector with a temperature of 260°C. By treating the non-hydrocarbon data of the mass spectrometer and hydrocarbon data of the chromatography with a normalization treatment, the final data were obtained. The relative standard deviation of the non-hydrocarbons was no more than 0.01%, and the relative standard deviation of the hydrocarbons was less than 0.2%.

2. Results

2.1. In situ measurement

CH₄ and CO₂ concentrations were detected several times at vent valves on the water tank with the CH₄ and CO₂ detectors, respectively. Ranges of CH₄ concentration were below 2 ppm and CO₂ concentrations were under 500 ppm. Six groups of air samples at the venting valves were evaluated, on the water tank and in the union station. Deducting the background concentration, only CO₂ was detected from the air samples at the vent valves, with a concentration of 477–554 ppm. CH₄ and CO₂ concentrations were both detected in the air samples collected at the union station. The concentration of CO₂ was 462–494 ppm and the concentration of CH₄ was between 3 and 6 ppm (Table 1).

The water tank sits approximately 17.7 m above the ground, where the wind speed is almost 2 m/sec. The molecular mass of CH₄ is less than air, thus CH₄ will dissipate quickly if it is released, but the molecular mass of CO₂ is heavier and, therefore, it does not dissipate as easily. As a

result, CH₄ is difficult to detect and CO₂ is easier. The detected CH₄ concentration was almost at a background concentration level, whereas the detected CO₂ concentration was higher than background concentration levels, demonstrating that there were CO₂ emissions from the water tank. Additionally, as it was windless on the ground at the union station, both the CH₄ and CO₂ concentrations were detected. The CO₂ concentration at the union station was lower than that in the water tank, which clearly showed that the vent valves were potential CO₂ emission sources. Additionally, there are many pieces of equipment and oil and gas pipes at the union station. We measured all of the potential leak points from each pipe's flange, valve core, joints etc., using a CH₄ concentration detector, and found that there were several CH₄ leaks. Thus, it is obvious that there was a CO₂ release from the oilfield-produced water, which is therefore an atmospheric CO₂ emission source in the oil-gas system. It is uncertain whether oilfield-produced water is a CH₄ emission source, owing to the multiple emission sources in the union station. Therefore, the following data were needed.

2.2. CH₄ emissions

The data (Table 2) of 12-hr simulations at each temperature from the mini-water tank were used to analyze the emissions of GHGs from the produced water. The results clearly showed that there were CH₄ emissions during each interval (0–2, 2–4, 4–6, 6–8, 8–10, and 10–12 hr) over the 12 hr period (Fig. 3). The oilfield-produced water in the tank had the highest CH₄ emissions at 27°C under atmospheric conditions. It was approximately twice as much as at 3°C, and in between at 13°C. At each temperature, the water in the first time period from 0 to 2 hr was the largest emitter. With the extension of time, the emissions declined.

2.3. CO₂ emissions

The measurement (Table 2) of the natural release of CO₂ from the oilfield-produced water in the mini-water tank at 6 intervals over 12 hr (0–2, 2–4, 4–6, 6–8, 8–10, and 10–12 hr) is shown in Fig. 3. Comparing the conditions at 3, 13 and 27°C, most of CO₂ was released at 27°C, followed by 13 and 3°C. The main CO₂ emission period was the first 0–2 hr at the three aforementioned temperatures. In 2–4 hr, all emissions quickly declined. Then, the emissions gradually declined in other time periods. Over 0–12 hr, higher temperatures led to higher CO₂ emissions under atmospheric conditions.

Table 2 – Average emission rates of CH₄ and CO₂ at different durations (units: g/(m³.hr)).

Sampling time (hr)	Average emission rates of CH ₄			Average emission rates of CO ₂		
	ST-1	ST-2	ST-3	ST-1	ST-2	ST-3
	5°C	13°C	27°C	5°C	13°C	27°C
0–2	0.179 ± 0.02	0.257 ± 0.02	0.415 ± 0.01	2.012 ± 0.12	3.080 ± 0.24	3.934 ± 0.24
2–4	0.085 ± 0.02	0.107 ± 0.01	0.184 ± 0.02	0.869 ± 0.05	1.058 ± 0.10	1.388 ± 0.13
4–6	0.050 ± 0.02	0.094 ± 0.02	0.122 ± 0.01	0.826 ± 0.05	0.941 ± 0.09	1.236 ± 0.10
6–8	0.044 ± 0.02	0.092 ± 0.01	0.088 ± 0.01	0.643 ± 0.05	0.745 ± 0.04	1.015 ± 0.02
8–10	0.047 ± 0.01	0.035 ± 0.01	0.040 ± 0.00	0.265 ± 0.04	0.431 ± 0.01	0.637 ± 0.02
10–12	0.030 ± 0.00	0.034 ± 0.00	0.024 ± 0.00	0.241 ± 0.03	0.402 ± 0.08	0.613 ± 0.04

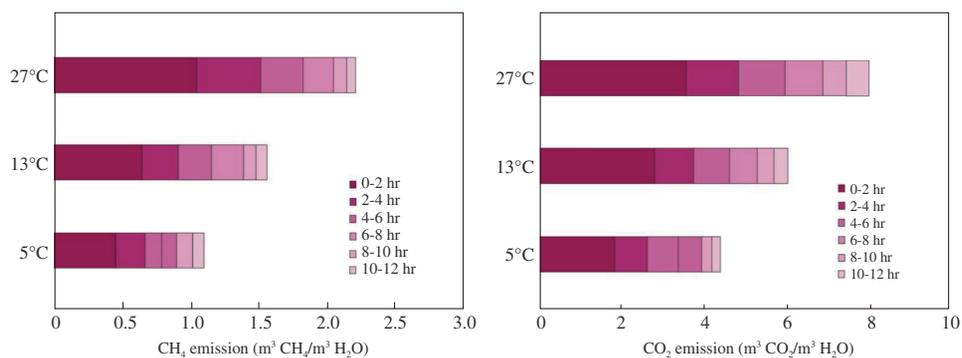


Fig. 3 – CH₄ and CO₂ emissions from oilfield-produced water for different time periods.

3. Discussion

3.1. Gases changes under different geologic environments

Natural gas is dissolved in formation water in gas-and-oil-containing basins. Temperature, pressure, natural gas content and salinity are the primary controlling factors of the solubility of natural gas in formation water (Barker, 1987; Dhima et al., 1998; Diamond and Akinfiev, 2003). High pressure has an important influence on the solubility of gases in formation water. The solubility of natural gas in high-pressure formations is several or tens of times greater than the content of 1–5 m³ CH₄/m³ H₂O at normal temperature and pressure (Zhang, 1995; Pang et al., 2000). Chen et al. (2014) performed a study to compare GHG emissions from gas-field-produced water arising from a high pressure and normal pressure formation. The results showed that the produced water from higher pressure formations released more GHG emissions under atmospheric conditions. If the formation pressure is the same, the solubility will increase with increasing temperature when the temperature is above 80°C, and decrease with an increase in temperature when the temperature is below 80°C, under complex geological conditions (Hao and Zhang, 1993; Yuan et al., 2008). When the pressure is below 5 MPa, it might be the case that solubility decreases with an increase in temperature (Hao and Zhang, 1993). However, no previous studies have demonstrated these results from an environmental perspective. In our study, the simulations not only proved the previous

inference but also made up for gaps in gas emission data under low pressure.

Natural gas is a hydrocarbon gas mixture, primarily composed of CH₄ but also a small amount of low carbon paraffin hydrocarbons and some non-hydrocarbon gases, such as CO₂, nitrogen, etc. The solubility of hydrocarbon gases decreases with increasing carbon number in the formation water, where the solubility follows the order of CO₂ > N₂ > C₁ > C₂ > C₃ > C₄ (McAuliffe, 1979). When produced-water is at a stable equilibrium status under the conditions of atmospheric pressure and temperature, the solubility of natural gas in produced-water obeys Henry's law and follows the order of CO₂ > C₄ > C₃ > C₂ > C₁ > N₂ (Olofsson et al., 1984; Jacquemin et al., 2006), which is greatly different from that of *in situ* formation water. From the foregoing discussion, CO₂ is more liable to dissolve both in produced-water and formation water. According to simulation experiment results, Dhima et al. (1999) held that the Henry constant for both dissolved CO₂ and CH₄ at low-temperature and pressure is far above than at high temperature and pressure. Comparing the two conditions, the range of increase of the Henry constant of CO₂ is larger than that of CH₄ when the temperature and pressure decrease, which means the amount of CO₂ released would be higher than CH₄ from oilfield produced-water. Natural gas with a high CH₄ and CO₂ content dissolved in formation water could produce more carbon emissions when it is produced at the surface. The reservoirs typically contain wet gases in oilfields and will produce fewer carbon emissions than those in gas fields (Chen et al., 2014). However, oilfields, given their increasing numbers and

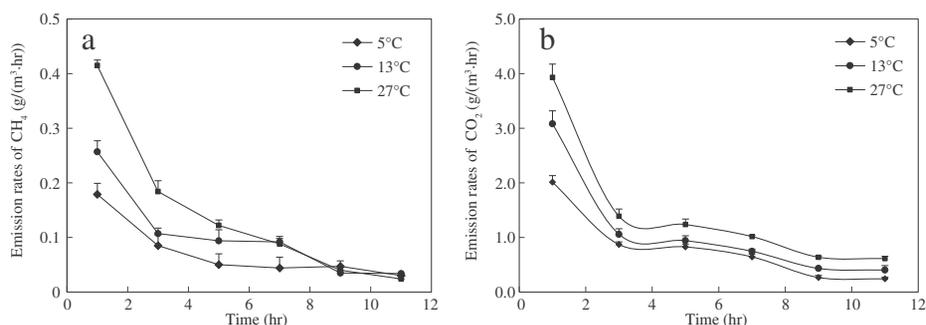


Fig. 4 – Emission rate shift of CH₄ and CO₂ emissions from oilfield-produced water at different time periods.

subsequent surge in water produced, have more potential to be important carbon emission sources in the oil and gas system.

The formation salinity, as a contributing factor, has less of an impact than the temperature and pressure underground. Generally, solubility will increase with the reduction of salinity (Barker, 1987), but the salinity has a large effect on the solubility under high-pressure conditions, and in contrast, the solubility is less affected by the salinity under low-pressure conditions. Additionally, hydrocarbon-degrading bacteria and methanogens in the indigenous microorganism community are two important factors in the production of CH₄ and CO₂ (Dahle et al., 2008; Grabowski et al., 2005). Methanogens are grown under strictly anaerobic conditions and the produced water stays on the surface for less than 12 hr before being re-injected into the reservoir at the union stations in Shengli Oilfield. Thus, the effect of microbes was ignored in this study. Finally, based on the above analyses, the atmospheric temperature and release time are significant contributors to the carbon emissions' impact on the environment, when the formation water is produced at the surface.

3.2. GHG changes with temperature

Temperature is one of the primary controlling factors of the solubility of natural gas in formation water (Fu et al., 1996; Sultanov et al., 1972; Zhang et al., 2012). When the formation water became oilfield-produced water, variations in GHG emissions were detected for the mini-water tank, with the highest average temperature (27°C) occurring in July, the lowest average temperature (3°C) occurring in January, and the average annual temperature (13°C) under atmospheric conditions in the study area. Variations of CH₄ and CO₂ emissions over 12 hr showed similar patterns at different release periods (Fig. 4) and increased with the increase in temperature, from 3 to 27°C (Fig. 3). Both of the highest CH₄ and CO₂ emission rates occurred in the first emission period 0–2 hr, at 27°C. In the first three time intervals of 0–6 hr, almost all of the CH₄ emission rates were higher at the three temperatures. CH₄ emission rates were significantly and positively correlated with temperature in 0–2 hr ($R = 0.999$, $p < 0.001$) (Table 3); then the correlation decreased with time. For the emissions at 8–10 and 10–12 hr, CH₄ emission rates correlated negatively with temperature. CO₂ emission rates correlated positively with temperature in all time periods.

The CH₄ emission rate declined more quickly at 27°C than at 13 and 3°C (Fig. 4), which clearly proved that the higher the temperature, the faster the CH₄ was released. The CO₂ emission rates declined smoothly in the five time intervals between 2 and 12 hr at the three temperatures (Fig. 4). McAuliffe's (1979) study found that the lower the carbon number of a hydrocarbon, the

Table 4 – Results from regression analyses (R) of CH₄ and CO₂ emission rates with time (t) at different temperatures.

Parameter	3°C	13°C	27°C
R_{CH_4-t}	-0.833 **	-0.870 **	-0.897 **
R_{CO_2-t}	-0.895 **	-0.826 **	-0.817 **

** $p < 0.01$.

higher its solubility in water, and the solubility of CO₂ is higher than for hydrocarbons. CH₄ solubility in water is determined by temperature and pressure (Bonham, 1978) and is more sensitive to temperature than CO₂ under atmospheric conditions. As a whole, more CH₄ and CO₂ emissions were produced from oilfield-produced water at 27°C than at 13 and 3°C (Fig. 3). Trends for emissions can be generalized i.e., higher temperature enhances carbon emissions. Thus, there will be more carbon emissions from oilfield-produced water in the summer and fewer carbon emissions in the winter.

3.3. GHG changes with time

Both of the highest CH₄ and CO₂ emission rates occurred in the first emission interval 0–2 hr, whereas the emission rates decreased greatly from 0 to 2 to 2–4 hr. Then, succeeding emission rates varied slowly. CH₄ and CO₂ emission rates correlated negatively with time at the same temperature ($p < 0.01$) (Table 4). The higher the temperature, the more significantly negative was the linear correlation between the release time and the CH₄ emission rate. However, the lower the temperature, the more significantly negative was the linear correlation between release time and the CO₂ emission rate. For the same time period and temperature, CH₄ is released more quickly than CO₂ owing to its relatively lower solubility. At 0–12 hr, CH₄ emissions were nearly complete. Nevertheless, CO₂ emissions continued with time, according to the CH₄ and CO₂ emission curves. Overall, before the produced water was re-injected into the formation, most of the CH₄ and CO₂ had been released to the atmosphere and formed carbon emissions in the oil and gas system.

4. Conclusions

GHG emissions are expected to grow as natural gas and oil consumption increases in a business-as-usual scenario, owing to the increase in global energy demand. By simulation, oilfield-produced water was determined to be one of the potential emitters of GHGs in oil and gas systems. More oilfield-produced water results in more emissions of CH₄ and

Table 3 – Results from regression analyses (R) of CH₄ and CO₂ emission rates with temperatures (T) at each time duration.

Parameter	0–2 hr	2–4 hr	4–6 hr	6–8 hr	8–10 hr	10–12 hr
R_{CH_4-T}	0.999 ***	0.984 **	0.951 **	0.759 *	-0.549 *	-0.697 *
R_{CO_2-T}	0.976 **	1.00 ***	0.995 **	0.981 **	0.995 **	0.995 **

*** $p < 0.001$.

** $p < 0.01$.

* $p < 0.05$.

CO₂, both of which are primary greenhouse gases. High pressure and an abundant gas source results in more water-soluble gas accumulation underground, which will release more carbon emissions into the atmosphere than when it is produced at the surface. As temperature and pressure quickly declined, most of the gases had already been released, although a small amount of gases remained in the water. Atmospheric temperature and release time are the primary controlling factors of CH₄ and CO₂ emissions from oilfield-produced water in the atmospheric environment. High temperature enhances the emissions of CH₄ and CO₂ from oilfield-produced water under atmospheric conditions. Over the entire time period (12 hr), the total emissions of CH₄ and CO₂ at 27°C were 1.746 and 17.646 g/m³, respectively. The ratio of the cumulative CH₄ emissions to the total CH₄ emissions was obviously higher than for CO₂, accounting for 47.5%, 68.6%, 82.6%, 92.7%, 97.3%, respectively, corresponding to different time points (2, 4, 6, 8, and 10 hr) at 27°C, which indicated that the release of CH₄ was faster than CO₂ over the whole time period since CH₄ is more sensitive to temperature. Nevertheless, the emission rate of CH₄ is still lower than CO₂ owing to its much lower solubility in the formation water, resulting in low exsolved gas content from produced-water when temperature and pressure declined, and the highest emission rates of CH₄ and CO₂ were 0.415 and 3.934 g/(m³·hr), both of which occurred during the first 2 hr at 27°C, and then their emission rates decreased remarkably in the next emission interval of 2–4 hr. Emissions at other time intervals released gradually with the extension of time. Thus the exsolved gas content controlled by the solubility was the primary factor influencing the emission rates during the simulation time once the temperature and pressure decreased. In conclusion, there will be more carbon emissions from oilfield-produced water in the summer than in the winter. A higher atmospheric temperature contributes to CH₄ emissions, and the warming caused by increased CH₄ emissions will itself release more CH₄, thus forcing the temperature to rise faster than predicted. Therefore, large amounts of produced water in oilfields would result in a large amount of carbon emissions. Precisely estimating the emissions from oilfield-produced water contributes to minimizing the uncertainty regarding the strengths of poorly known sources, as well as the uncertainty of carbon emission values in oil and gas systems; therefore the carbon emissions fostered by oilfield-produced water should not be ignored by the oil-gas sectors.

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REFERENCES

Barker, C., 1987. Development of abnormal and subnormal pressures in reservoirs containing bacterially generated gas. *AAPG Bull.* 71 (11), 1404–1413.

- Bonham, L.C., 1978. Solubility of methane in water at elevated temperatures and pressures: Geologic notes. *AAPG Bull.* 62 (12), 2478–2481.
- Chen, G.J., Yang, W., Fang, X., Zhong, J.A., Zhang, Z.N., Wang, Z.D., 2014. Greenhouse gases (GHG) emissions from gas field water in southern gas field, Sichuan Basin, China. *Water Air Soil Pollut.* 225 (4), 1902.
- Dahle, H., Garshol, F., Madsen, M., Birkeland, N.K., 2008. Microbial community structure analysis of produced water from a high-temperature North Sea oil-field. *Antonie Van Leeuwenhoek* 93 (1–2), 37–49.
- Dedikov, J.V., Akopova, G.S., Gladkaja, N.G., Piotrovskij, A.S., Markellov, V.A., Salichov, S.S., et al., 1999. Estimating methane releases from natural gas production and transmission in Russia. *Atmos. Environ.* 33 (20), 3291–3299.
- Dhima, A., De Hemptinne, J.C., Moracchini, G., 1998. Solubility of light hydrocarbons and their mixtures in pure water under high pressure. *Fluid Phase Equilib.* 145 (1), 129–150.
- Dhima, A., De Hemptinne, J.C., Jose, J., 1999. Solubility of hydrocarbons and CO₂ mixtures in water under high pressure. *Ind. Eng. Chem. Res.* 38 (8), 3144–3161.
- Diamond, L.W., Akinfiev, N.N., 2003. Solubility of CO₂ in water from –1.5 to 100°C and from 0.1 to 100 MPa: Evaluation of literature data and thermodynamic modelling. *Fluid Phase Equilib.* 208 (1–2), 265–290.
- EPA, 2008. Inventory of U.S. greenhouse gas Emissions and sinks: 1990–2006. US Environmental Protection Agency, Washington D.C.
- EPA (Environmental Protection Agency), 2006a. Global anthropogenic non-CO₂ greenhouse gas emissions: 1990–2020. Office of Atmospheric Programs Climate Change Division, US Environmental Protection Agency, Washington D.C.
- EPA (Environmental Protection Agency), 2006b. Global mitigation of non-CO₂ greenhouse gases. US Environmental Protection Agency, Washington D.C.
- Fu, X.T., Wang, Z.P., Lu, S.F., 1996. Mechanisms and solubility equations of gas dissolving in water. *Sci. China: Chem.* 39 (5), 500–508.
- Gao, G., Huang, Z.L., Huang, B.J., Yuan, J., Tong, C.X., 2012. The solution and exsolution characteristics of natural gas components in water at high temperature and pressure and their geological meaning. *Pet. Sci.* 9 (1), 25–30.
- Glagolev, M.V., Golovatskaya, E.A., Shnyrev, N.A., 2008. Greenhouse gas emission in West Siberia. *Contemp. Probl. Ecol.* 1 (1), 136–146.
- Grabowski, A., Nercessian, O., Fayolle, F., Blanchet, D., Jeanthon, C., 2005. Microbial diversity in production waters of a low-temperature biodegraded oil reservoir. *FEMS Microbiol. Ecol.* 54 (3), 427–443.
- Griggs, D.J., Noguer, M., 2002. Climate change 2001: the scientific basis. Contribution of working group I to the third assessment report of the intergovernmental panel on climate change. *Weather* 57 (8), 267–269.
- Guan, D.B., Liu, Z., Geng, Y., Lindner, S., Hubacek, K., 2012. The gigatonne gap in China's carbon dioxide inventories. *Nat. Clim. Chang.* 2 (9), 672–675.
- Guo, X.W., Liu, K.Y., He, S., Song, G.Q., Wang, Y.S., Hao, X.F., et al., 2012. Petroleum generation and charge history of the northern Dongying Depression, Bohai Bay basin, China: Insight from integrated fluid inclusion analysis and basin modelling. *Mar. Pet. Geol.* 32 (1), 21–35.
- Hao, S.S., Zhang, Z.Y., 1993. The characteristic of the solubility of natural gas in formation waters and its geological significance. *Acta Petrol. Sin.* 14 (2), 12–22.
- IEA (International Energy Agency), 2008. Energy technology perspectives. IEA, Paris.
- IPCC (Intergovernmental Panel on Climate Change), 2000. Good practice guidance and uncertainty management in national greenhouse gas inventories. IGES, Japan.

- IPCC (Intergovernmental Panel on Climate Change), 2006. IPCC guidelines for national greenhouse gas inventories. IGES, Japan.
- Jacquemin, J., Gomes, M.F.C., Husson, P., Majer, V., 2006. Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric. *J. Chem. Thermodyn.* 38 (4), 490–502.
- Jin, Z.J., 2008. Distribution and structures of large and medium oil–gas fields in China. *Xinjiang Pet. Geol.* 29 (3), 385–388.
- McAuliffe, C.D., 1979. Oil and gas migration: Chemical and physical constraints. *AAPG Bull.* 63 (5), 761–781.
- Olofsson, G., Oshodj, A.A., Qvarnström, E., Wadsö, I., 1984. Calorimetric measurements on slightly soluble gases in water enthalpies of solution of helium, neon, argon, krypton, xenon, methane, ethane, propane, *n*-butane, and oxygen at 288.15, 298.15, and 308.15 K. *J. Chem. Thermodyn.* 16 (11), 1041–1052.
- Pang, X.Q., Jiang, Z.X., Li, J.Q., Zhou, R.N., 2000. Geologic thresholds in the process of forming oil and gas reservoir and their functions of controlling petroleum. *J. Univ. Pet.* 24 (4), 53–57.
- Reilly, J.M., Jacoby, H.D., Prinn, R.G., 2003. Multi-gas contributors to global climate change: Climate impacts and mitigation costs of non-CO₂ gases. Pew Center on Global Climate Change, Arlington, VA.
- Rodhe, H., 1990. A comparison of the contribution of various gases to the greenhouse-effect. *Science* 248 (4960), 1217–1219.
- Sinton, J.E., Fridley, D.G., 2000. What goes up: Recent trends in China's energy consumption. *Energy Policy* 28 (10), 671–687.
- Streets, D.G., Jiang, K.J., Hu, X.L., Sinton, J.E., Zhang, X.Q., Xu, D.Q., et al., 2001. Recent reductions in China's greenhouse gas emissions. *Science* 294 (5548), 1835–1837.
- Sultanov, R.C., Skripka, V.G., Namiot, A., 1972. Solubility of methane in water at high temperatures and pressures. *AAPG Bull.* 17 (5), 6–7.
- Weschenfelder, S.E., Mello, A.C.C., Borges, C.P., Campos, J.C., 2015. Oilfield produced water treatment by ceramic membranes: Preliminary process cost estimation. *Desalination* 360, 81–86.
- Xu, X.H., Wang, D.H., Jiang, H., Shi, H.X., 1999. Study on greenhouse gas emissions in Jiangsu province. *Water Air Soil Pollut.* 109 (1–4), 293–301.
- Yuan, H.F., Xu, G.S., Liu, S.G., Wang, G.Z., 2008. Paleo-temperature evolution and water soluble gas in Sinian reservoir, Anpingdian–Gaoshiti structural zone, Central Sichuan Basin. *J. China Univ. Geosci.* 19 (6), 707–714.
- Yuan, G.H., Gluyas, J., Cao, Y.C., Oxtoby, N.H., Jia, Z.Z., Wang, Y.Z., et al., 2015. Diagenesis and reservoir quality evolution of the Eocene sandstones in the northern Dongying Sag, Bohai Bay Basin, East China. *Mar. Pet. Geol.* 62, 77–89.
- Zhang, Z.S., 1995. A primary study on water-soluble gas. *Nat. Gas Geosci.* 6 (5), 29–34.
- Zhang, S.W., Zhang, L.Y., Bao, Y.S., Li, X.Y., Liu, Q., Li, J.Y., et al., 2012. Formation fluid characteristics and hydrocarbon accumulation in the Dongying Sag, Shengli Oilfield. *Pet. Explor. Dev.* 39 (4), 423–435.
- Zhang, Q., Zhu, X.M., Steel, R.J., Zhong, D.K., 2014. Variation and mechanisms of clastic reservoir quality in the Paleogene Shahejie Formation of the Dongying Sag, Bohai Bay Basin, China. *Pet. Sci.* 11 (2), 200–210.