

Distribution characteristics of methane in the water column and sea-to-air flux in “Haima” cold seep, South China Sea[#]

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ABSTRACT

Methane (CH₄) is a powerful greenhouse gas with a stronger greenhouse effect than carbon dioxide. The ocean is the largest CH₄ reservoir in the world and plays an important role in adjusting climate change. Water column CH₄ distribution and sea-to-air in the marine CH₄ seeping areas are crucial to finger the ultimate fate of marine CH₄. In this research, we investigated the distribution of dissolved CH₄ and environmental factors in the water column, and calculated the sea-to-air flux in the “Haima” cold seep area. The results showed that the surface dissolved CH₄ concentration ranged from 0.50 to 53.20 nM, and the sea-to-air flux was 38.56 μmol/m²/d. Compared with previous studies, it was higher than that on the general ocean surface but lower than that in the estuary area. In addition, the vertical distribution showed that the CH₄ concentration in the surface layer was lower than that in the bottom layer, and the maximum value appeared at about 150 m. By PCA analysis, it can be found that SO₄²⁻ and TOC were important factors affecting the dissolved CH₄ concentration. In conclusion, understanding the CH₄ emissions in cold seep areas is of great significance for coping with global warming.

Keywords: methane distribution; “Haima” cold seep; air-sea flux; environmental factor; climate change

1. INTRODUCTION

Methane (CH₄) is a powerful greenhouse gas. Under the background of global warming, people are increasingly aware of the seriousness of the greenhouse effect caused by CH₄. According to the fifth assessment report of the Intergovernmental Panel on Climate Change (IPCC), the global warming potential of CH₄ is 20–40 times that of carbon dioxide on average in a 100-year period [1]. At present, the atmospheric CH₄

concentration has reached the maximum value since records, and the contribution rate to global warming is about 30%. The United Nations Climate Change Conference (COP26) promised that the CH₄ emission in 2030 need be 30% less than that in 2020 [2, 3]. Therefore, the control of CH₄ emissions plays an important role in mitigating climate change.

Although CH₄ in the atmosphere mainly comes from human activities, the ocean is the largest CH₄ reservoir in the world. It is estimated that there is 3×10¹⁵ m³ CH₄, which is equivalent to 1500 GtC in the global ocean [4]. When the dissolved CH₄ in the surface seawater is supersaturated, CH₄ escaping from the seawater is one of the important sources of atmospheric CH₄ [5]. The negative feedback generated by it is incalculable. It is estimated that the CH₄ released from the seafloor accounts for 5–10% of the current global atmospheric input [1, 6]. Meanwhile, there have been large-scale CH₄ release events in history, so the release of CH₄ from the ocean cannot be ignored. Although the observation of dissolved CH₄ in seawater began in the mid-1950s [7]. In recent years, due to the sharp increase of activities such as the input of terrestrial rivers, oil and gas field exploitation, land reclamation, and mariculture, the sources and sinks of dissolved CH₄ in the marine are diversified, and its concentration and sea-air exchange flux show a new feature of more intense spatio-temporal evolution, and its contribution to atmospheric CH₄ continue to increase [5, 8]. Therefore, scholars have made a lot of observations on dissolved CH₄ in estuaries, open seas, and continental shelves [9-12].

The major sources of dissolved CH₄ in the ocean are terrestrial inputs, sediment emissions (including geological sources), and biological metabolism [13]. The cold seep is a special geological phenomenon that the fluid rich in CH₄ and other hydrocarbons overflows from

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the seafloor sediment interface, it is an important source of CH₄ entering the seawater column and atmosphere, and plays an important role in the marine carbon cycle and deep-sea ecosystem [14]. When CH₄ leaks from the seafloor to the ocean, although the majority (about 80%–90%) of CH₄ is removed by anaerobic methane oxidation (AOM) on the sediment surface, some CH₄ still will continue to migrate upward and dissolve in seawater [7]. CH₄ dissolved in seawater undergoes an oxidation reaction to generate carbon dioxide, which may accelerate ocean acidification [15]. Therefore, accurate quantification of the generation, dissolution, migration, and discharge of CH₄ from seafloor cold seeps is crucial for assessing its impact on the global CH₄ budget and climate change.

The South China Sea (SCS) covers an area of 3.5×10^6 km² and has an average depth of 1200 m. It is the largest marginal sea in the world, meanwhile, it is a prospective area of gas hydrate, and a large number of geological evidence related to cold seep activity have been found, such as pockmarks, mud volcanoes, carbonate crusts, and cold seep biomes. However, there are few studies on CH₄ distribution, sea-to-air flux, and its driver factors in the cold seep of SCS.

The objective of this research is to study the vertical distribution of CH₄ in the water column of the “Haima” cold seep area, explore the environmental factors that may affect the distribution of dissolved CH₄, and estimate the sea-to-air flux of CH₄ in the “Haima” cold seep area. It is hoped that this study can enhance our understanding of the contribution of the region to global marine CH₄ emissions.

2. MATERIALS AND METHODS

2.1 Study area and sample testing

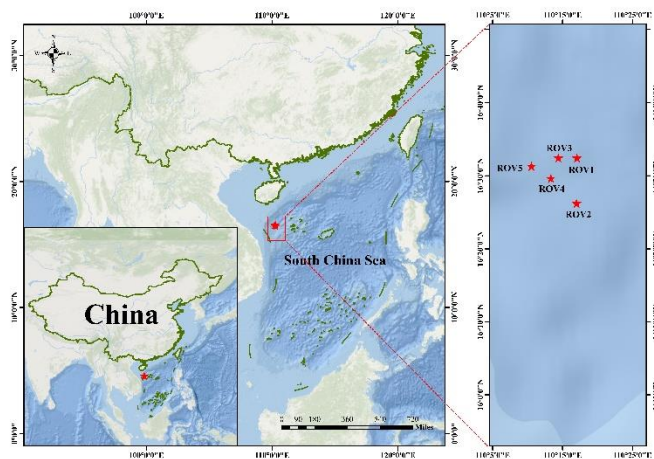


Fig. 1 Study area and sampling locations. (The based map is derived from the ArcGIS online)

“Haima” cold seep (16°43’ N, 110 °28’ E) has an area of 350 km² with a depth of 1350–1430 m in the southwestern part of Qiongdongnan Basin, which is a typical large active cold seep area found in China. Its terrain is relatively gentle, with a gentle slope of about 0.2° that gradually deepens from southwest to northeast. This scientific investigation was conducted in the “Haima” cold seep area in May 2021 by the Scientific Research Vessel “HAIYANG DIZHI LIUHAO”. Geological and habitat characteristics were surveyed by the submersible ROV “Haima”. The five seepage stations were named ROV1, ROV2, ROV3, ROV4, and ROV5, respectively. The detail locations were displayed in Fig. 1. At the surface sediment of ROV1, a lot of CH₄ bubbles were discovered, meanwhile, many mussels, white clam mactras, anemones, brittle stars, and other organisms were found as well, moreover, there are also some small pieces of carbonate rocks in the sediment; At ROV2, there was no CH₄ bubble leakage, but pipe worms, mussels, anemones, and other organisms were discovered. At the same time, there were large carbonate rocks that are more abundant than ROV1. In addition, no CH₄ bubble leakage was found in ROV3, but white attachments like bacterial mats were found on the surface of the sediment, and there were some white clam mactras and anemones; However, no cold seep signs were found in ROV4 and ROV5, therefore, we think they are the general seafloor.

In this study, sampling depths were set at ten discrete depths (i.e., 25 m, 50 m, 85 m, 150 m, 200 m, 400 m, 600 m, 800 m, 1000 m, and 1350 m). Water samples were collected from the water columns above the five seepage sites using a conductivity-temperature-depth rosette system (CTD). The geochemical parameters of water samples were measured at the scene. The CH₄ concentrations, temperature, dissolved oxygen (DO), salinity, and pH were analyzed by CTD sensors in real-time. Total organic carbon (TOC) and Inorganic carbon (IC) were determined by a TOC-L analyzer (TOC-L, Shimadzu, Japan). An automatic nutrition analyzer (LACHAT QUITCHEM 8500 S2, HACH, USA) was applied to measure the NO₃⁻. Sulfate (SO₄²⁻) was measured by ion chromatography (Aquion, ThermoFisher).

2.2 Saturation and sea-to-air flux calculations

The saturation (R, %) and sea-to-air flux (F, μmol/m²/d) of the CH₄ were estimated using the following equations:

$$R = C_{obs} / C_{eq} \times 100\% \quad (1)$$

$$F = k_w \times (C_{obs} - C_{eq}) \quad (2)$$

where C_{obs} is the observed concentration of dissolved CH_4 ; C_{eq} is the air-equilibrated seawater CH_4 concentration, which was calculated for the *in situ* temperatures and salinities using the solubility data of [16]. The atmospheric CH_4 mixing ratio was 1.89 ppm in 2021 from the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) Global Monitoring Division *in situ* program was used to calculate C_{eq} . k_w (cm/h) is the gas transfer velocity, which is a function of wind speed and the Schmidt number (Sc), we used the updated relationship $k_w = 0.251 \times U^2 \times (Sc/660)^{-0.5}$ to compute k_w in this study [17], the average squared wind speed was 5.4 m/s from the National Centers for Environmental Prediction (NCEP) Reanalysis data from the NOAA ESRL (<http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.surface.html>).

2.3 Statistical analysis

Principal component analysis (PCA) is a multivariate statistical analysis technique in which a set of correlated variables is transformed into a new set of mutually uncorrelated or orthogonal variables. It can effectively reduce the dimensions of variables, simplify multiple measured variables into fewer variables, and help us to reveal the insignificant relationship between different variables. In this study, PCA was used to estimate the relationship between CH_4 concentration and environmental factors.

3. RESULTS AND DISCUSSION

3.1 The surface dissolved CH_4 concentration and sea-to-air flux in different water masses in the “Haima” cold seep

The surface CH_4 concentrations and sea-to-air flux in the “Haima” cold seep were summarized in Table. 1. The surface CH_4 concentrations ranged from 0.50 to 53.20 nM, with a mean concentration of 12.18 nM. The saturation ranged from 26% to 2767%, with an average saturation of 634%. The sea-to-air flux ranged from 2.33 to 192.75 $\mu\text{mol}/\text{m}^2/\text{d}$, with a mean flux of 38.56 $\mu\text{mol}/\text{m}^2/\text{d}$.

Table. 1 Observed concentration of dissolved CH_4 and sea-to-air flux in “Haima” cold seep

Site	C_{obs} (nmol/L)	C_{eq} (ppm)	T (°C)	R (%)	F ($\mu\text{mol}/\text{m}^2/\text{d}$)
ROV1	0.50	1.89	29.67	26	-5.35
ROV2	2.20	1.89	29.58	114	1.02
ROV3	1.30	1.89	29.81	68	-2.33
ROV4	53.20	1.89	29.71	2767	192.75

ROV5	3.70	1.89	29.79	193	6.71
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It can be seen that the surface seawater dissolved CH_4 concentration of the five stations has a large spatial heterogeneity, with the minimum value appearing in ROV1 and the maximum value appearing in ROV4. However, according to the geographical environment of the five stations. It is speculated that ROV1, ROV2, and ROV3 are experiencing or have experienced CH_4 leakage, while ROV4 and ROV5 may be common seafloor. However, the survey results of dissolved CH_4 concentration in surface seawater were just the opposite, which may reflect that a strong CH_4 oxidation process occurred at the cold seep leakage site, resulting in less CH_4 escapes from the cold seep area. However, ROV4 and ROV5 are close to ROV1, under the effect of turbulence and other factors, CH_4 diffusion in the water column resulted in higher CH_4 concentration of ROV4 and ROV5. Simultaneously, TOC in the ROV4 water column was relatively higher, and its oxidative decomposition may produce more CH_4 , resulting in higher CH_4 concentrations than other stations. Moreover, the saturation of CH_4 in surface seawater of ROV1 and ROV3 was low and the sea-to-air CH_4 flux was negative. It is speculated that the dissolved CH_4 mainly comes from the atmosphere. According to the results of the voyage in July 2022 (unpublished data), the CH_4 concentration in the air of cold seep areas is higher than in other areas, which may confirm this assumption.

Before this research, scholars have made a lot of investigations on dissolved CH_4 concentration and sea-to-air flux in surface seawater such as estuaries and continental shelves. According to the study by Sun et al. [18], the surface dissolved CH_4 concentration in the East China Sea (ECS) was 4.9 ± 3.2 nM, the saturation was $203 \pm 126\%$, and the sea-to-air flux was 9.77 ± 16.0 $\mu\text{mol}/\text{m}^2/\text{d}$. While another study found that in the continental shelf of ECS, the surface dissolved CH_4 concentration was 12.5 ± 3.79 nM, the saturation was $675.86 \pm 204.37\%$, and the sea-to-air flux was 54.75 ± 19.38 $\mu\text{mol}/\text{m}^2/\text{d}$ [10]. In the South China Sea, the surface dissolved CH_4 concentration was 4.5 ± 3.6 nM, the saturation was $230 \pm 184\%$, and the sea-to-air flux was 8.6 ± 6.4 $\mu\text{mol}/\text{m}^2/\text{d}$ [19]. Zhou et al. discovered that the surface dissolved CH_4 concentration ranged from 2.4 to 5.9 nM, the saturation was from 134% to 297%, and the sea-to-air flux was 2.9 ± 24.8 $\mu\text{mol}/\text{m}^2/\text{d}$ in the Northern South China Sea [20]. However, in the western Pearl River Estuary, the surface dissolved CH_4 concentration ranged from 6.9 to 173.7 nM, the saturation was from 329% to 7896%, and the sea-to-air flux was 63.5 ± 32.2 $\mu\text{mol}/\text{m}^2/\text{d}$ [20]. Another study

investigated CH₄ emissions from the shelf and west slope of the back-arc Okinawa Trough (OT), East China Sea, the dissolved from the shelf and west slope of the OT, which ranged from 2.7 to 24.7 nM, with an average of 6.5 nM, and the sea-to-air flux ranged from 0.74 to 116 μmol/m²/d, with an average of 26.2 μmol μmol/m²/d [10]. It can be seen that the air-to-sea CH₄ flux in the “Haima” cold seep area is higher than that in the general sea surface but lower than that in the estuary area. This is mainly because the source of dissolved CH₄ in the estuaries is extensive. Moreover, when compared with the OT cold seep area in the ECS, the CH₄ flux is equivalent. This may show that the cold seep area may leak more CH₄ into the atmosphere. Therefore, in future research, we should pay more attention to the CH₄ emissions in the cold seep area, which is very important for controlling global warming.

3.2 Vertical distribution of dissolved CH₄ in the “Haima” cold seep

The vertical distribution of CH₄, salinity, temperature, and DO was shown in Fig. 2. It can be seen that with the increase in depth, the temperature decreased. DO and salinity showed a similar trend following different water depths. DO decreases with the increase of depth beyond the surface 100 m, after showing an increasing trend in the depth of 100–400 m, while decreasing again at 400–900 m, and slowly increasing at 900–1400 m; The salinity increased rapidly with the increase of depth at the surface layer of 150 m, while decreased at 150–400 m, and slowly increased again at the bottom layer of 150 m.

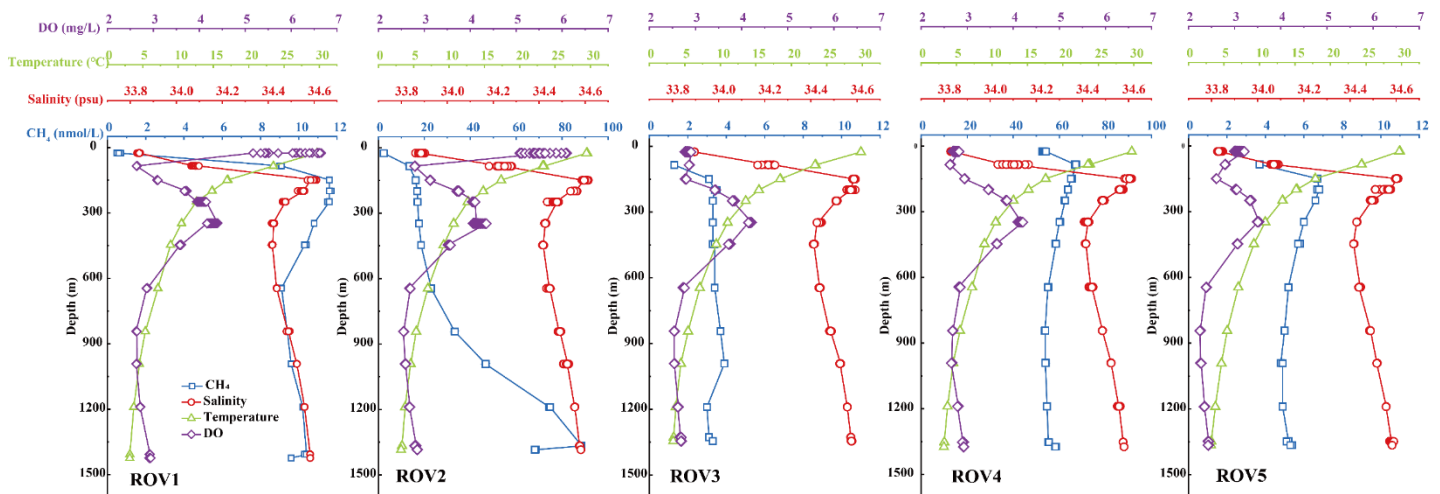


Fig. 2 Vertical distribution of CH₄ (blue), Salinity (red), temperature (green), and DO (purple).

The concentration of dissolved CH₄ in the five stations all showed that it was lower in the surface layer and higher in the bottom layer. Above the surface of 150 m, the concentration increased with the increase of depth and reached the maximum at about 150 m except for ROV2. Since methanogens are strictly anaerobic bacteria, the extent of CH₄ production in aerobic seawater remains to be discussed. One possible mechanism of biological production is that the anoxic microenvironment in particles (such as dead cells, fecal particles, and viscera of zooplankton) acts as the site of methane generation [20, 21]. In this study, the DO in this layer was just low, so it is speculated that methanogens may produce CH₄ by reducing carbon dioxide and a small amount of organic matter in the sinking particles and zooplankton fecal particles. However, with the continued increase of depth, the concentration of dissolved CH₄ shows different trends. ROV1 decreased initially and increased afterward, ROV2

continued to increase, ROV3 tended to be stable (the change is less than 1 nM), and ROV4 and ROV5 showed a similar change trend. The difference in bottom CH₄ concentration was affected by multiple factors, such as hydraulic conditions, hydrate leakage, sediment release, etc. In addition, due to the limitation of experimental conditions, the number of sampling stations in this study was limited, so the results still have some uncertainty. Therefore, in the following research, we can increase the sampling stations and use time series monitoring to improve the accuracy of monitoring results.

3.3 The drivers of dissolved CH₄ concentration in the seawater

The relationship between environmental factors and dissolved CH₄ concentration was analyzed by PCA. The Kaiser normalized orthogonal rotation method was used during the PCA analysis process, with Kaiser-Meyer-Olkin

(KMO) ($0.583 > 0.5$) and Bartlett spherical test ($0.000 < 0.05$). Three principal components whose eigenvalues were greater than 1 were obtained (Fig. 3, Table. 2). The variance contributions of these three principal components to each variable were 39.58%, 19.75%, and 12.73%, respectively. The results indicated that PCA leads to a reduction of the initial dimension of the dataset to three components which explains 72.05% of the data variation, which could explain most of the information about the effects of these 10 environmental factors on dissolved CH_4 concentration. The factor load was shown in Table. 2, the first principal component (PC1) was mainly composed of depth, salinity, NO_3^- , pH, DO, and temperature, which had a highly positive load on the first principal component, reaching -0.886, -0.752, -0.859, 0.947, 0.548, and 0.987, respectively. Therefore, PC1 can reflect the enrichment degree of these environmental factors. The second principal component (PC2) was mainly composed of CH_4 , SO_4^{2-} , TS and TOC, the factor load reached 0.499, 0.786, 0.766, and 0.658, respectively. The third principal component (PC3) was composed of CH_4 and TOC, and the factor load was 0.781 and 0.594.

Table.2 Loading of different environmental factors

Component	Component matrix		
	PC1	PC2	PC3
Depth	-0.886	-0.011	0.089
Salinity	-0.752	0.059	-0.017
NO_3^-	-0.859	0.165	-0.057
CH_4	-0.027	0.499	0.781
SO_4^{2-}	0.086	0.786	-0.381
TS	0.190	0.766	-0.493
TOC	0.137	0.658	0.594
pH	0.947	0.066	0.033
DO	0.548	-0.361	0.134
Temperature	0.987	-0.037	0.002
IC	-0.173	-0.344	0.135

It can be seen that the concentration of dissolved CH_4 in seawater was affected by factors such as SO_4^{2-} , TS, and TOC. As we all know, the anaerobic oxidation of methane requires the participation of sulfate, which further verifies that the AOM reaction plays a crucial role in regulating the release of CH_4 in the cold seep area. Moreover, microorganisms can also react with TOC to generate CH_4 , which indicates that in the future control of CH_4 , these two aspects can be started.

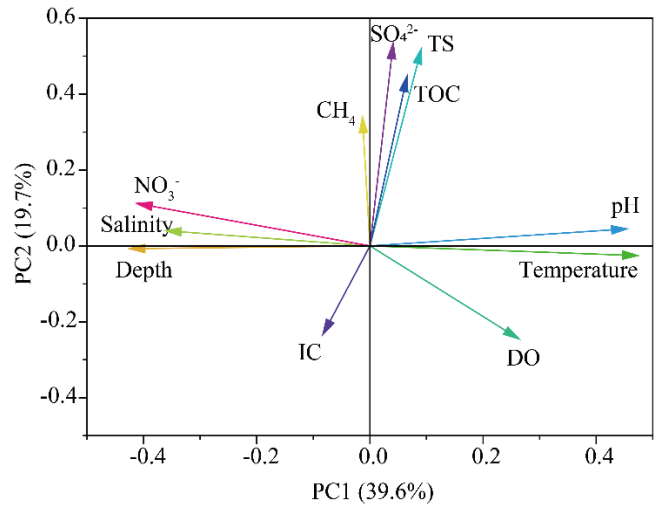


Fig. 3 Loading plots corresponding to the first two factors of the principal components

4. CONCLUSIONS

In order to better understand the CH_4 distribution of cold seep areas. This study investigated the distribution characteristics of dissolved CH_4 in the water column in the “Haima” cold seep area. Moreover, we calculated the sea-to-air flux and studied the relationships between environmental factors. The results showed that the surface dissolved CH_4 concentrations ranged from 0.50 to 53.20 nM, with a mean concentration of 12.18 nM, and the saturation ranged from 26% to 2767%, with an average saturation of 634%. The sea-to-air flux ranged from -2.33 to 192.75 $\mu\text{mol}/\text{m}^2/\text{d}$, with a mean flux of 38.56 $\mu\text{mol}/\text{m}^2/\text{d}$. Through comparison, It can be found that CH_4 concentration in the “Haima” cold seep area was higher than that in the general ocean surface but lower than that in the estuary area when compared with the previous studies. In addition, the vertical distribution results showed that the CH_4 concentration in the water column was lower in the surface layer while high in the bottom layer, and the maximum value appeared at about 150 m. By PCA analysis, it can be found that SO_4^{2-} and TOC were important factors affecting the dissolved CH_4 concentration. However, due to the limited sampling points, more sampling points need to be set in this area to better evaluate the CH_4 flux in this area.

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