

Supporting Information for

Significant methane undersaturation during austral summer in the Ross Sea (Southern Ocean)

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Introduction

This supplement includes an expanded explanation of CH₄ analysis, the correlations between water masses and CH₄ saturation, a conceptual diagram of dissolved CH₄ in the Ross Sea, the T-S definition of water mass classification, and information on the vertical distribution of main water masses.

Text S1. Description of CH₄ analysis

Water samples from the BOD bottles were dispensed into 20 ml glass vials (triplicate for each bottle) prior to analysis. CH₄ concentrations were determined by an Agilent 7890A gas chromatograph that was fitted with a flame ionization detector (FID) using a gas purge-and-trap method. Briefly, seawater was introduced into a stripping chamber and purged with ultrahigh-purity (UHP) helium (70 ml/min). During sparging, the gas stream passed through a Nafion tube to remove water vapor before flowing into a stainless-steel trap. The trap was filled with 5A molecular sieve and cooled in liquid nitrogen to concentrate CH₄. After extraction (5 min), the trap was attached to an electronic copper wire and heated to release gas into the gas chromatograph using high-purity nitrogen as the carrier gas (30 ml/min). Subsequently, CH₄ was separated on three stainless steel columns (3 m × 3 mm) packed with Hayesep-Q (80/100 mesh) and quantified with the FID at 250 °C. The peak areas for CH₄ quantification were calibrated by using known-volume injections of CH₄ standards (CH₄:N₂ mixtures of 1.0, 3.0, 5.2, 7.1, 12.0, and 29.9 ppm, National Institute of Metrology, China) (**Figure S1**). The 3.0 ppm standard was used to monitor the signal drifting every three hours because it is the best match concentration with that in seawater. All standards were introduced into the stripping chamber and analyzed following the same procedure as that for the water samples.

The blank refers to the pre-purged seawater that was without CH₄ but was analyzed following the same procedure. We used two standard deviations of 10 times blank of purge-trap concentrations (20 ml) as the definition of the limit of detection (**Table S4**), which yields 0.04 nmol/L. Our results are comparable to the similar method reported by Zhang et al. (2004), whose limit of detection was 0.06 nmol/L. We also used the control sample to test the reproducibility (**Table S5**). The control sample is the equilibrium seawater (sparging with air for 48 h) with the addition of saturated HgCl₂.

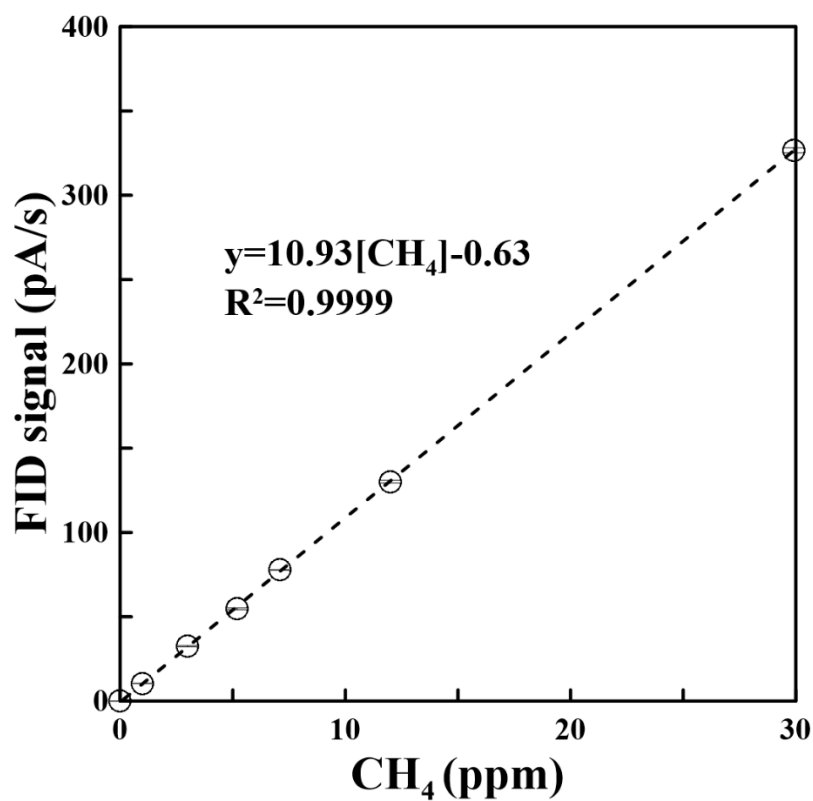


Figure S1. Correlations between FID signal and CH₄ standard. Error bars represent 1 standard deviation of triplicates. When error bars are not visible, they are within the area of the symbol.

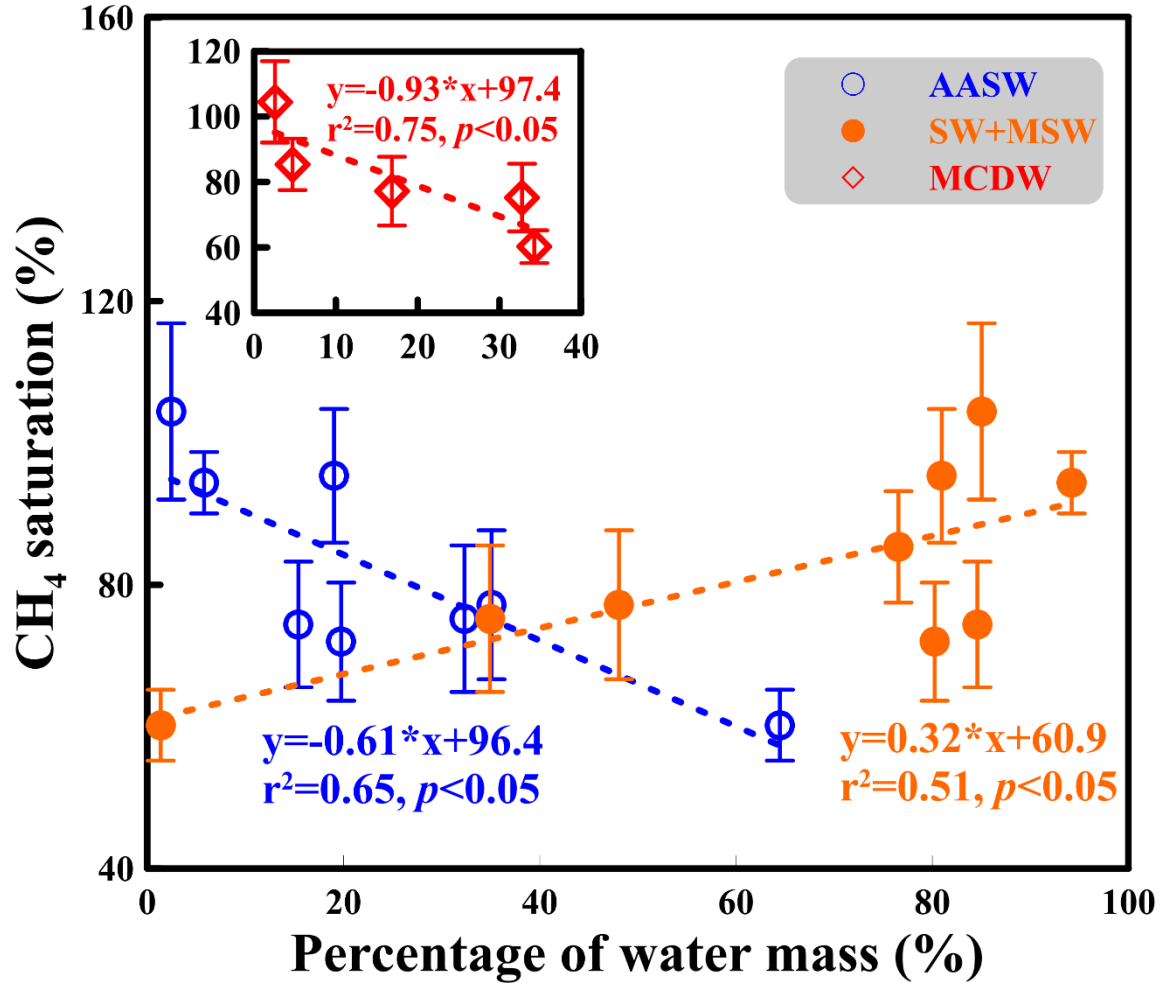


Figure S2. Correlations between water masses and CH₄ saturation (if available) at all stations (0–200 m) excluding the near-bottom samples at station R7 (see text). The SW and MSW were combined because the MSW was originated from the SW and they had close hydrographic features (Figure 2a) and similar CH₄ signals. The analytical errors are depicted by the error bars (only show the negative direction to reduce overlaying).

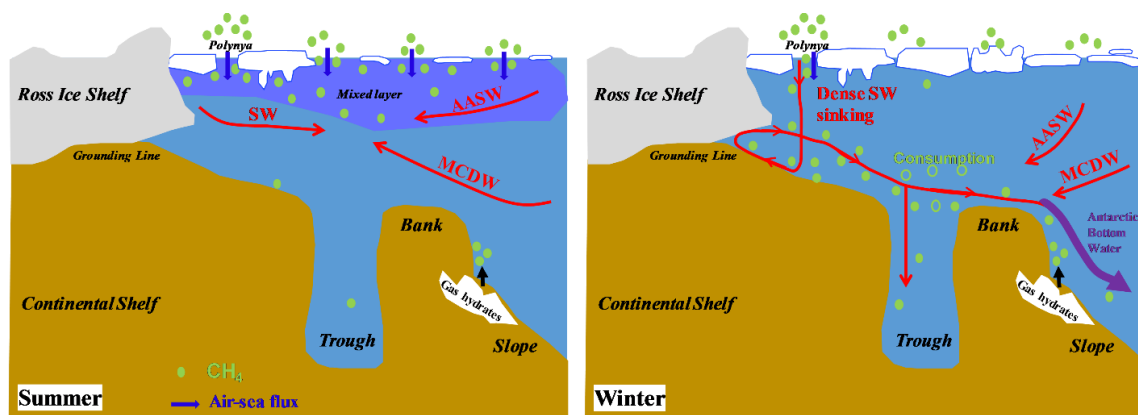


Figure S3. Conceptual diagram showing the water transport and air-sea exchange affecting CH_4 removal in the Ross Sea. Sea ice melting and CH_4 -poor AASW intrusion in summer increase CH_4 diffusion into the ocean surface; dense SW sinking (as a “water pump” for delivering CH_4) in winter transports mixed-layer CH_4 into the deep ocean; CH_4 that originated from the atmosphere is sealed in troughs, consumed in the water, and joins the circulation of Antarctic Bottom Water, making the Ross Sea a potential sink for atmospheric CH_4 .

Table S1. Water mass definitions and their characteristics (θ , salinity, and CH_4 saturation) calculated in this study.

Water mass*	Definition	Reference	θ (mean \pm SD)	Salinity (mean \pm SD)	Saturation (mean \pm SD)	Variability in CH_4 saturation [#]
AASW	$\theta > -1.8$, $S < 34.45$	Orsi and Wiederwohl (2009)	0.7 ± 0.8	34.23 ± 0.16	79 ± 18	5
SW	$-1.9 < \theta < -1.8$, $S > 34.50$, $\gamma^n > 28.27$	Williams et al. (2016)	-1.9 ± 0.0	34.74 ± 0.04	82 ± 16	9
MSW	$\theta > -1.8$, $S > 34.50$	Orsi and Wiederwohl (2009)	-1.6 ± 0.3	34.60 ± 0.07	85 ± 27	N.A
ISW	$\theta < -1.9$	Schodlok et al. (2016)	-2.0 ± 0.0	34.75 ± 0.01	90 ± 22	N.A
MCDW	$\theta > -1.8$, $28.00 < \gamma^n < 28.27$	Orsi and Wiederwohl (2009)	-1.0 ± 0.6	34.47 ± 0.02	91 ± 21	N.A

*AASW: Antarctic Surface Water, SW: Shelf Water, MSW: Modified Shelf Water (MSW), ISW: Ice Shelf Water, MCDW: Modified Circumpolar Deep Water;

[#]Standard deviation calculated from the station only dominated by a specific water mass (>60% contribution). N.A means no station was dominated by this water mass.

Table S2. Summary of vertical distribution of water masses at stations R1-R10 in the Ross Sea during sampling period.

Station	Bottom Depth (m)	Layers of which water mass occupied (m)*				
		AASW	SW	MSW	ISW	MCDW
R1	533	NaN	50–196; 294–511	25–50	196–294	0–25
R2	880	0-51	77-880	51–77	NaN	NaN
R3	1022	0-25	102–201; 303–1022	51–102	201–303	25-51
R4	373	0-71	148–373	71–148	NaN	NaN
R5	331	0-51	51–331	NaN	NaN	NaN
R6	501	0-99	299–501	99–299	NaN	NaN
R7	285	0-100	NaN	148–285	NaN	100–148
R8	393	0-100	NaN	200–393	NaN	100–200
R9	461	0-149	452–461	300–452	NaN	149–300
R10	470	0-303	469–470	464–469	NaN	303–464

*Calculated from temperature/salinity properties of each water mass (Table S1). NaN represents the absence of specific water at this station.

Table S3. Estimation in percentage of water mass at stations R1-R10 in the Ross Sea during sampling period.

Station	Percentage of water mass (%)				
	AASW	SW	MSW	ISW	MCDW
R1	0.0	71.9	4.7	18.8	4.7
R2	5.8	91.3	3.0	0.0	0.0
R3	2.4	80.0	5.0	10.0	2.5
R4	19.0	60.3	20.6	0.0	0.0
R5	15.4	84.6	0.0	0.0	0.0
R6	19.8	40.3	39.9	0.0	0.0
R7	35.1	0.0	48.1	0.0	16.8
R8	25.4	0.0	49.1	0.0	25.4
R9	32.3	2.0	33.0	0.0	32.8
R10	64.5	0.1	1.2	0.0	34.3

Table S4. Concentrations of blank in the purge-and-trap method.

No.	Concentration (nM)
1	0.49
2	0.44
3	0.44
4	0.49
5	0.51
6	0.46
7	0.46
8	0.47
9	0.46
10	0.47
Average	0.47
Standard deviation	0.02
Limit of detection	0.04

Table S5. Concentrations of control samples in the purge-and-trap method.

No.	Concentration (nM)
1	3.01
2	2.98
3	3.45
4	3.11
5	3.13
6	3.01
7	3.05
8	2.98
9	3.00
10	2.91
11	3.00
Standard deviation	0.14
Precision	5%
Average	3.06
Theory concentration*	2.71

*Calculated in the room temperature (21 °C) based on Henry's law (Wiesenburg and Guinasso, 1979).