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Simulating Methane in the Global Ocean

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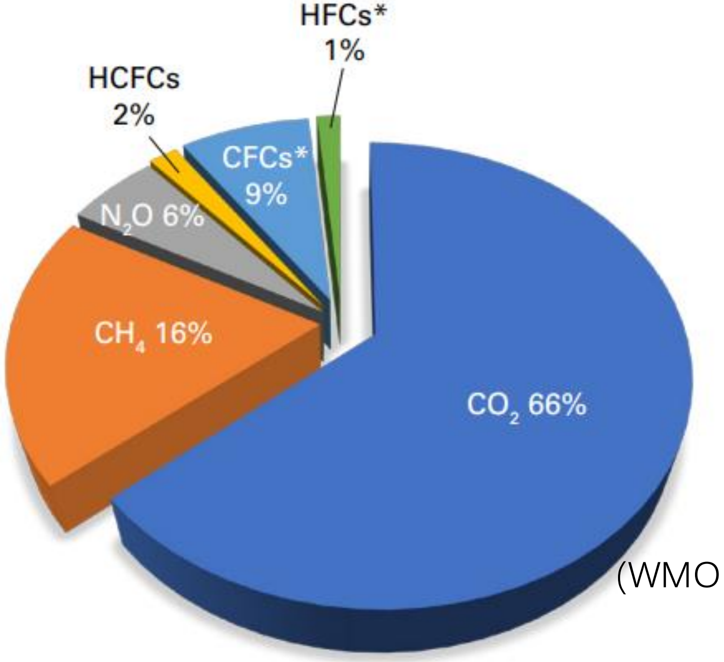
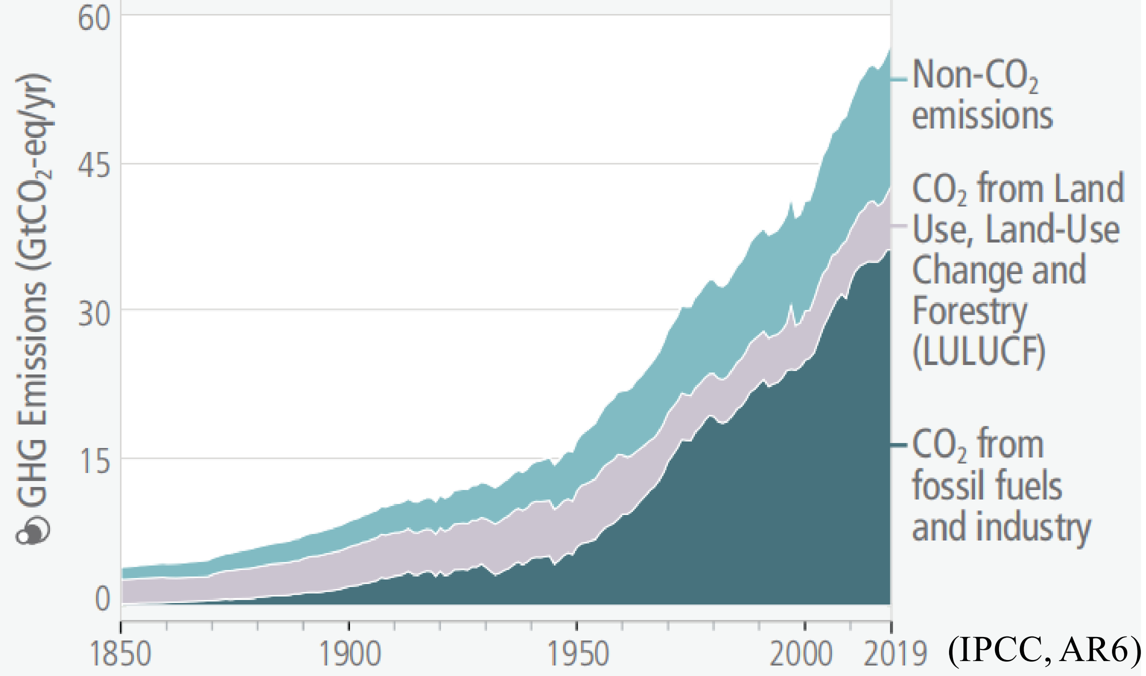
Background: Marine CH_4 & N_2O

Contribution of the most important GHG to the increase in global radiative forcing from pre-industrial era to 2024



(WMO, 2024)

Increased emissions of GHGs

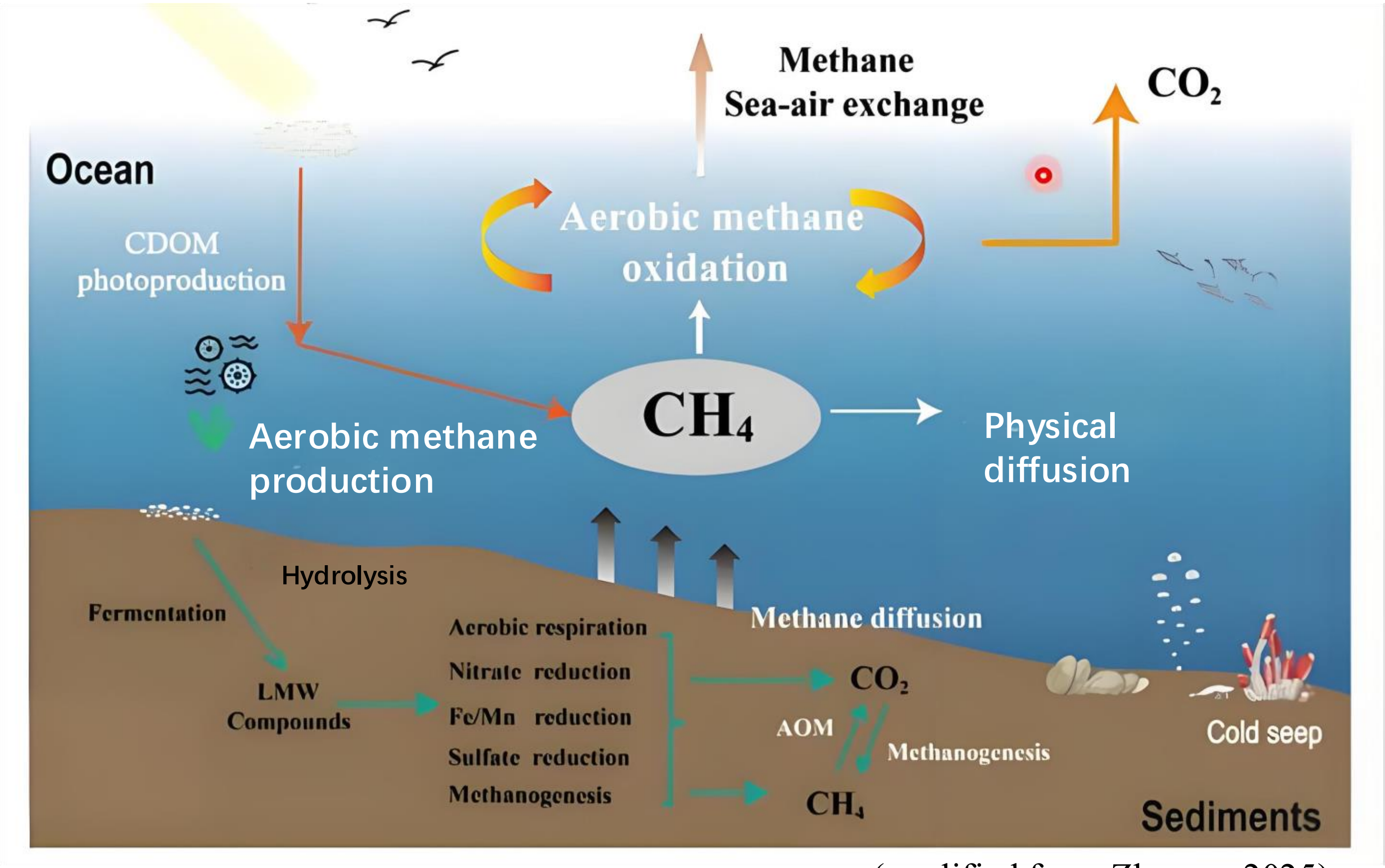


(IPCC, AR6)

- Methane (CH_4) is a powerful greenhouse gas (≈25× CO_2 over 100 years).
- Oceans act as a complex and spatially heterogeneous methane source, controlled by diverse biogeochemical processes.
- Over 100 countries committed to a 30% methane reduction by 2030, reflecting a strategic shift toward addressing non-CO_2 greenhouse gases.

Marine CH_4 Source & Sink

Major Sources and Sinks of Oceanic Methane



(modified from Zhuang, 2025)

Sources

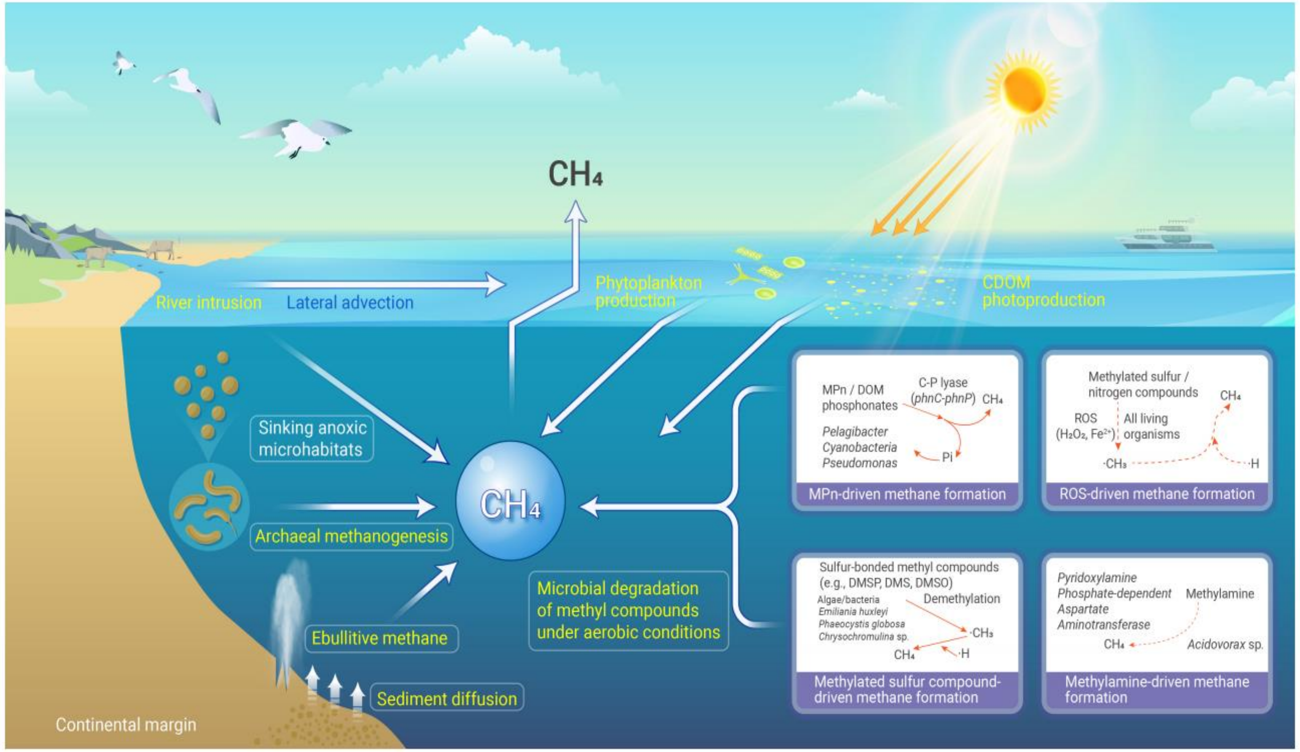
- Methanogenesis by methanogens in anoxic sediments
- Aerobic methane production
- Geological methane sources (methane hydrate destabilization and seepage)

Sinks

- Anaerobic oxidation of methane (in sediments)
- Aerobic oxidation of methane (water column)
- sea-air exchange

Aerobic methane production

- **The Methane Paradox**: Methane is produced by methanogenic archaea under strictly anaerobic conditions; however, in the oxygen and sulfate-rich upper layers of marine water bodies, methane concentrations are relatively supersaturated compared to the atmosphere.



Sources of methane and pathways for methane production in oxygenated seawater (Mao et al., 2024)

Several mechanisms have been proposed to explain methane production in oxygenated waters:

•**Micro-anaerobic CH_4 production**: sinking particles, zooplankton and fish guts *(Oremland, 1979; Karl & Tilbrook, 1994; Schmale et al., 2018)*

•**Aerobic CH_4 production by phytoplankton** *(Lenhart et al., 2016; Klintzsch et al., 2019)*

•**Photochemical CH_4 production:** Photodegradation of dissolved organic matter (DOM) *(Fichot & Miller, 2010)*

•**Microbial degradation of organic phosphorus compounds**: Aerobic CH_4 production from methylphosphonates and related compounds *(Karl et al., 2008; Repeta et al., 2016; von Arx et al., 2023)*

Simulating CH_4

- **Like all other biogeochemical tracers, the evolution of methane concentration is modeled as advection-diffusion, supplemented by local sources and sinks:**

$$\frac{\partial[\mathrm{CH_4}]}{\partial t} = \underbrace{P_{\mathrm{sed}} + P_{\mathrm{aer}} + P_{\mathrm{seep}}}_{\textbf{Sources}} - \underbrace{(O_{\mathrm{ana}} + O_{\mathrm{aer}} + F_{\mathrm{air-sea}})}_{\textbf{Sinks}}$$

Sources:

- Paer: Aerobic methane production (e.g., microbial/photochemical)
- Psed: Methanogenesis in anoxic sediments
- Pseep: bubble-driven (gas hydrates, geological sources)

Sinks:

- Oana: Anaerobic oxidation of methane (sediments)
- Oaer: Aerobic oxidation of methane (water column)
- Fair–sea: Sea–air methane exchange

Simulating CH_4: Aerobic production

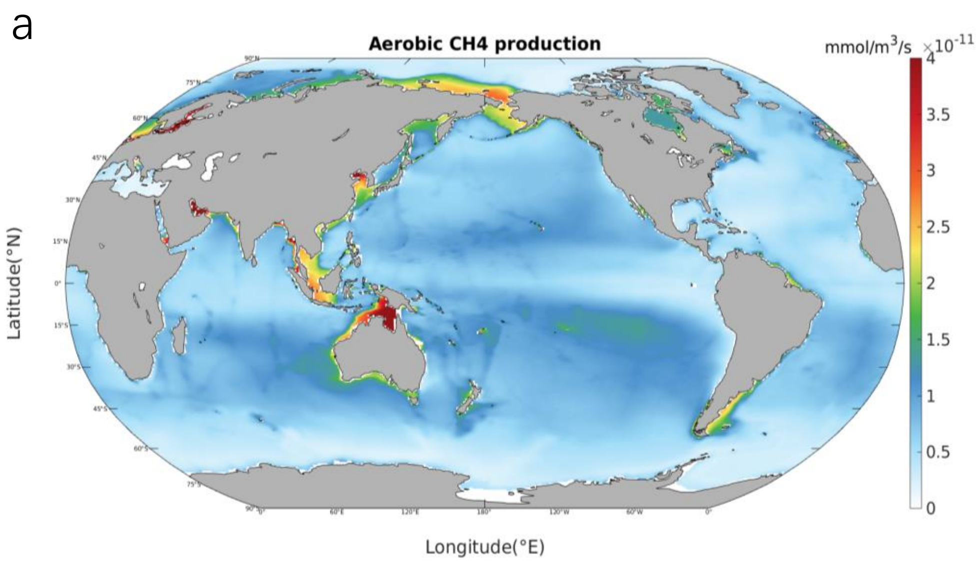
$$P_{aer} = (a \times b \times c \times DOP_{remin(k)}) \times R_{c2p}$$

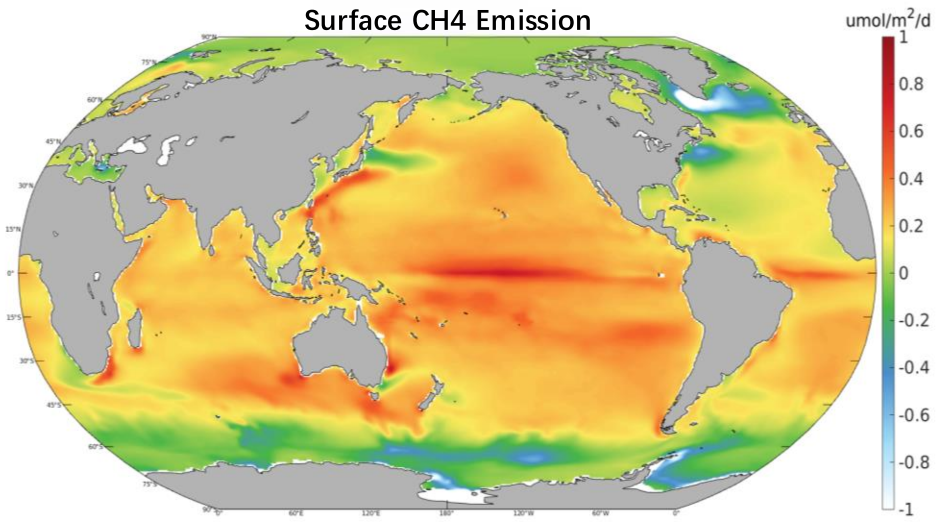
a: Fraction (approximately 1/4 - 1/3) of phosphonates in semi-labile DOP (Clark et al., 1999; Kolowith et al., 2001; Sannigrahi et al., 2006).

b: methylphosphonate (MPn) fraction in phosphonates： 1/(1+1.7+0.5)=31.25% (Repeta et al., 2016)

c: Fraction (0.2%-0.3%) of the MPn inventory is needed to circulate daily to support the entire atmospheric methane flux (Repeta et al., 2016).

R_{c2p}: C/P ratio in OP





Methane Weight Function

✓ Combined consideration of redox condition, POC flux and SMT depth

Diffusive fluxes of CH_4 and SO_4^{2-} to the sulfate–methane transition (SMT) depend on SMT depth

$$P_{sed} = f \times ch4\_sed\_scalef \times \text{other\_remin} \times 0.5$$

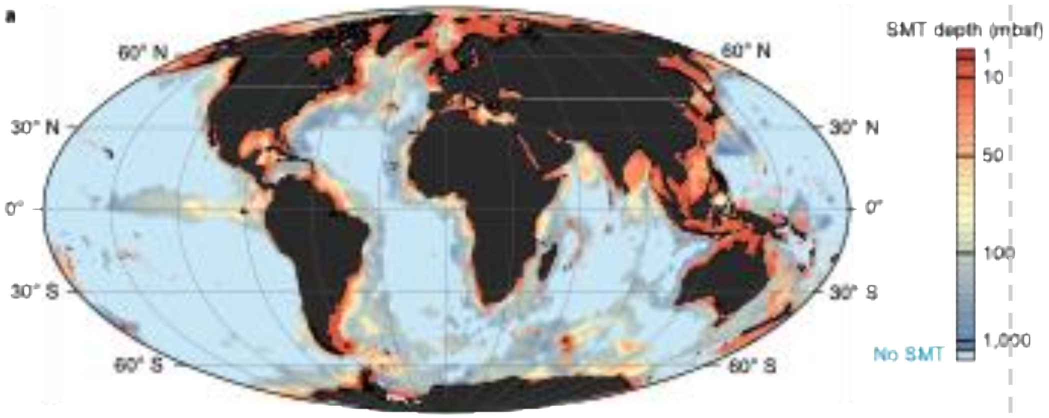
- f denotes the fraction of global subseafloor organic matter degradation via methanogenesis; the remaining degradation is mediated by aerobic respiration (6.9%) and sulfate reduction (64.5%) (Bradley et al., 2020).
- *ch4_sed_scalef* is a weighted factor that accounts for regional differences in diffusive methane fluxes to the SMT, calculated using model area, areas of different SMT depths, and estimated diffusive fluxes of CH_4.

Table 1 | Average SMT depth, as well as average diffusive fluxes of SO_4^{2-} and CH_4 to the SMT for different depth regions with corresponding standard deviations in parentheses

Region (water depth (m))	Seafloor area[b] (km²)	SMT depth (mbsf)	J_{SO4} (mmol m^{-2} d^{-1})	J_{CH4} (mmol m^{-2} d^{-1})
Inner shelf (0–10)	2.59×10^6	0.5 (±0.7)	2.17 (±2.00)	0.87 (±0.67)
Inner shelf (10–50)	9.18×10^6	2.0 (±2.0)	0.57 (±0.66)	0.27 (±0.26)
Outer shelf (50–200)	1.27×10^7	4.0 (±3.1)	0.23 (±0.27)	0.13 (±0.12)
Slope (200–2,000)	3.01×10^7	12.8 (±12.1)	0.078 (±0.096)	0.051 (±0.048)
Rise (2,000–3,500)	6.28×10^7	143.4 (±222.0)	0.0069 (±0.0069)	0.0066 (±0.0054)
Abyss (>3,500)[a]	2.38×10^8	168.9 (±144.5)	0.0045 (±0.0045)	0.0047 (±0.0037)

Data were calculated for every 0.1° by 0.1° grid of the world ocean (n=6,485,401). See Supplementary Table 4 for values estimated directly from correlations with sedimentation rates. [a]Approximately 66% of abyssal sediments in this study have no SMT. Thus, the value reported here corresponds to the average over 34% of the abyss, where an SMT is predicted to occur. [b]The total area covered in this study equals 3.54×10^8 km², corresponding to ~98% of the total ocean.

Marine SMT depth



(Egger et al., 2018, Nature Geosci)

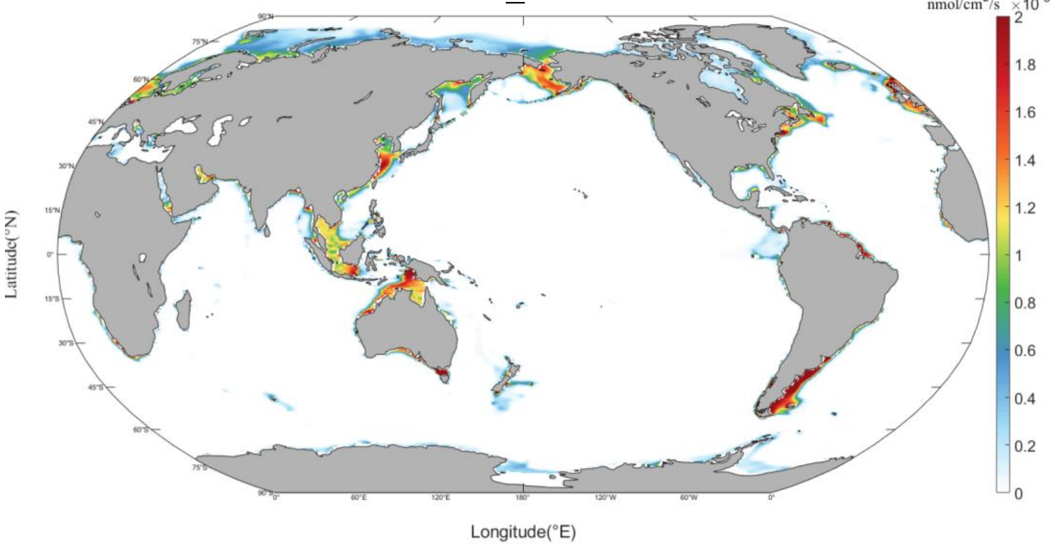
Methanogenesis in Sediments

✓ **Combined consideration of redox condition, POC flux and SMT depth**

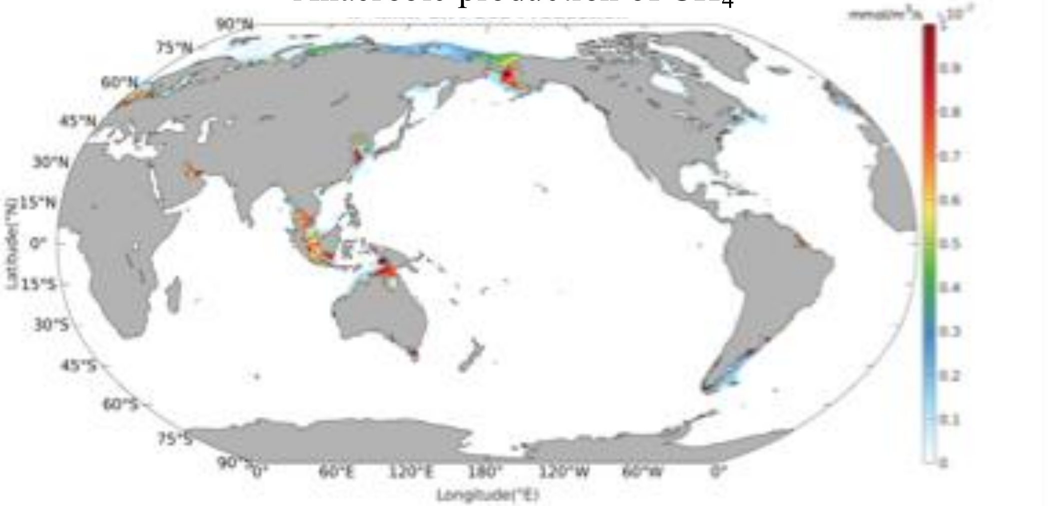
$$P_{sed} = f \times ch4\_sed\_scalef \times \text{other\_remin} \times 0.5$$

- ×0.5： In methanogenesis, half of the carbon degraded produces methane, and the other half produces CO_2 or carbonate (e.g. $CH_3COOH \rightarrow CH_4 + CO_2$)
- other_remin estimates organic matter remineralized in the sediments by the processes other than oxic remineralization and denitrification

Other_remin

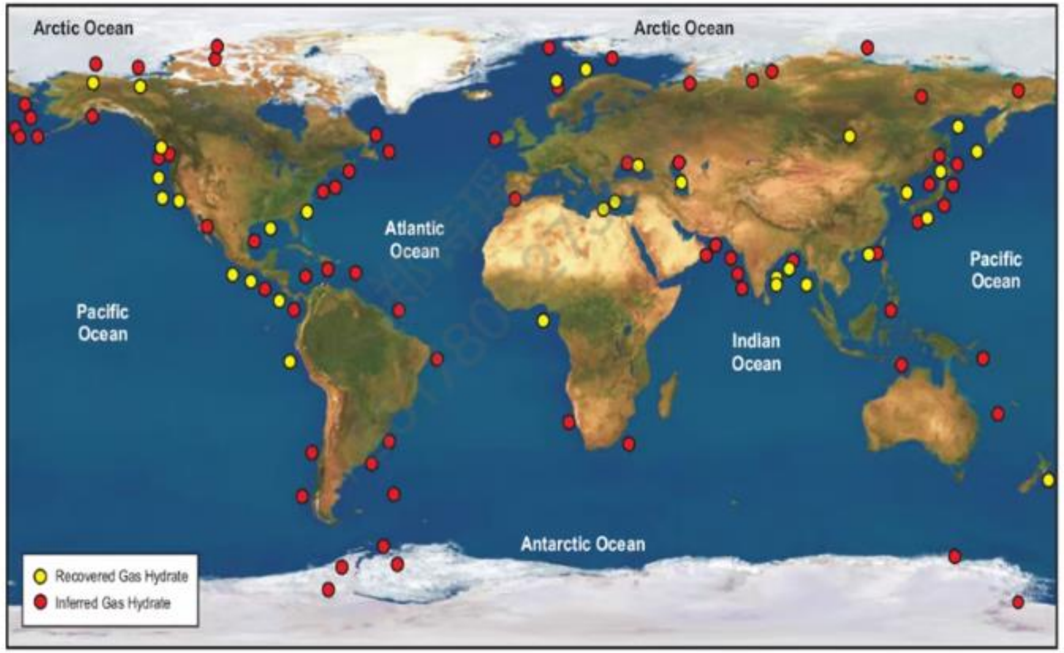


Anaerobic production of CH_4

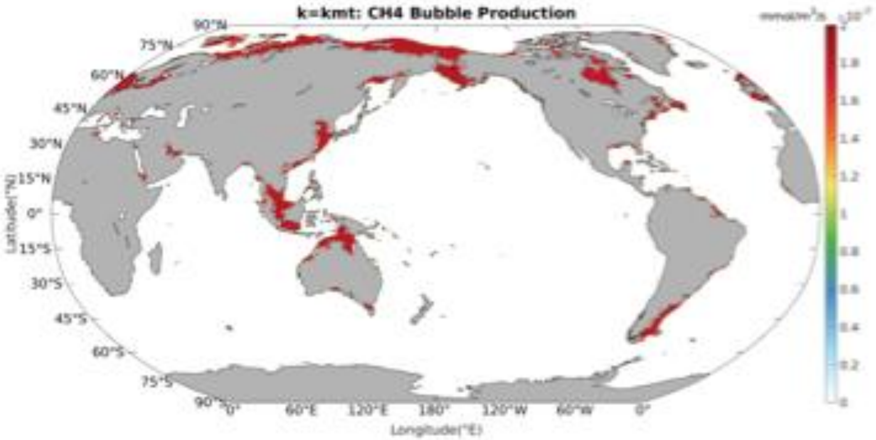


Ebullitive methane emissions (P_{seep})

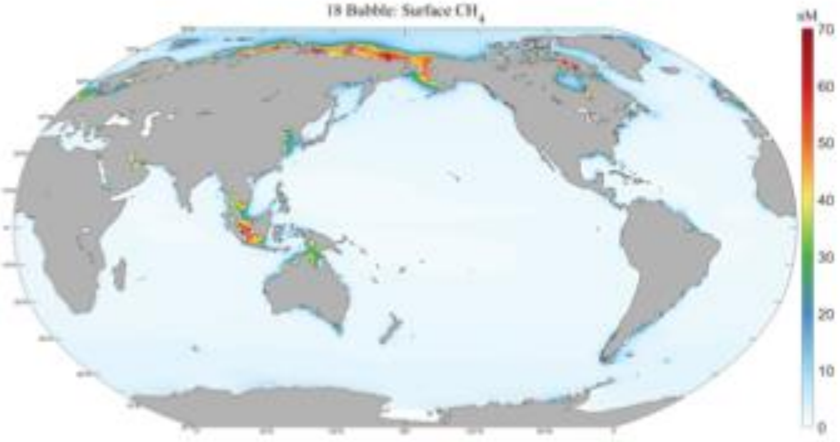
- Extrapolating rate measurements from active seafloor seeps across regions of probable seepage indicates that global CH_4 ebullition from continental shelf sediments (0–200 m) likely ranges from **18** to 48 Tg/yr (Hornafius et al., 1999).



Gas hydrates (500-10,000 gigatons)



CH_4 seepage (18Tg/yr)



Surface CH_4 with 18Tg/yr ebullition

Representing CH_4 Removal

- **Assuming 80% removal due to methane anaerobic oxidation in sediments** ($P_{sed} \times 0.2$: to account for anaerobic oxidation of methane in sediments.)

- **Removal in water column:**

Perform fitting with 8 classic equations based on measured CH_4 oxidation lifetime in the global ocean:

Linear: k = a·C + b

Michaelis-Menten: k = (Vmax·C)/(Km + C)

Logistic: k = Vmax/(1 + e^(-ks·(C-C0)))

Power-law: k = a·C^b

Hill Equation: k = (Vmax·C^n)/(Km^n + C^n)

Double Michaelis-Menten: k = (Vmax1·C)/(Km1+C) + (Vmax2·C)/(Km2+C)

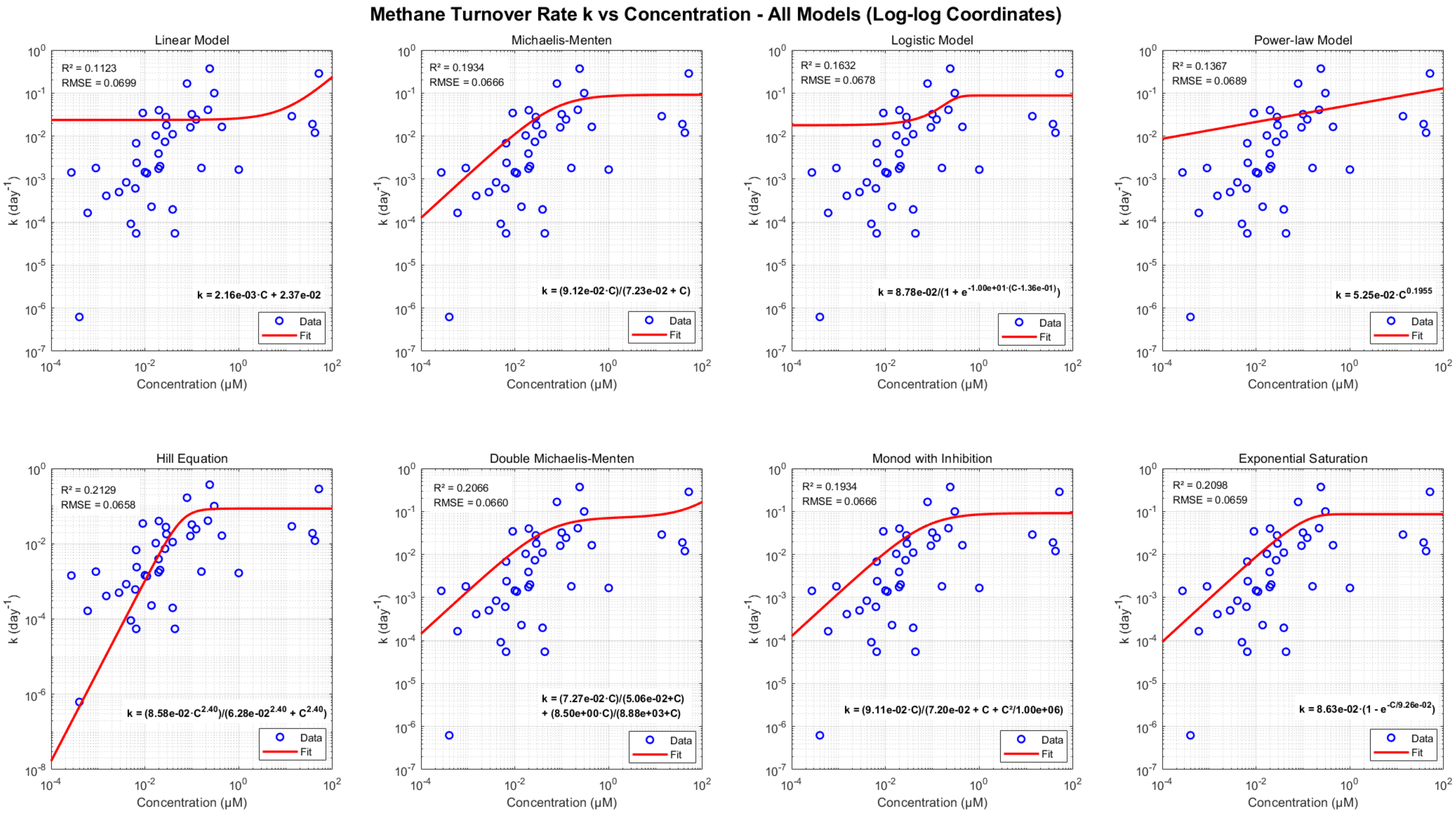
Monod with Inhibition: k = (Vmax·C)/(Km + C + C²/Ki)

Exponential Saturation: k = Vmax·(1 - e^(-C/K))

✓ === Summary of All Fitting Results (μM units) ===

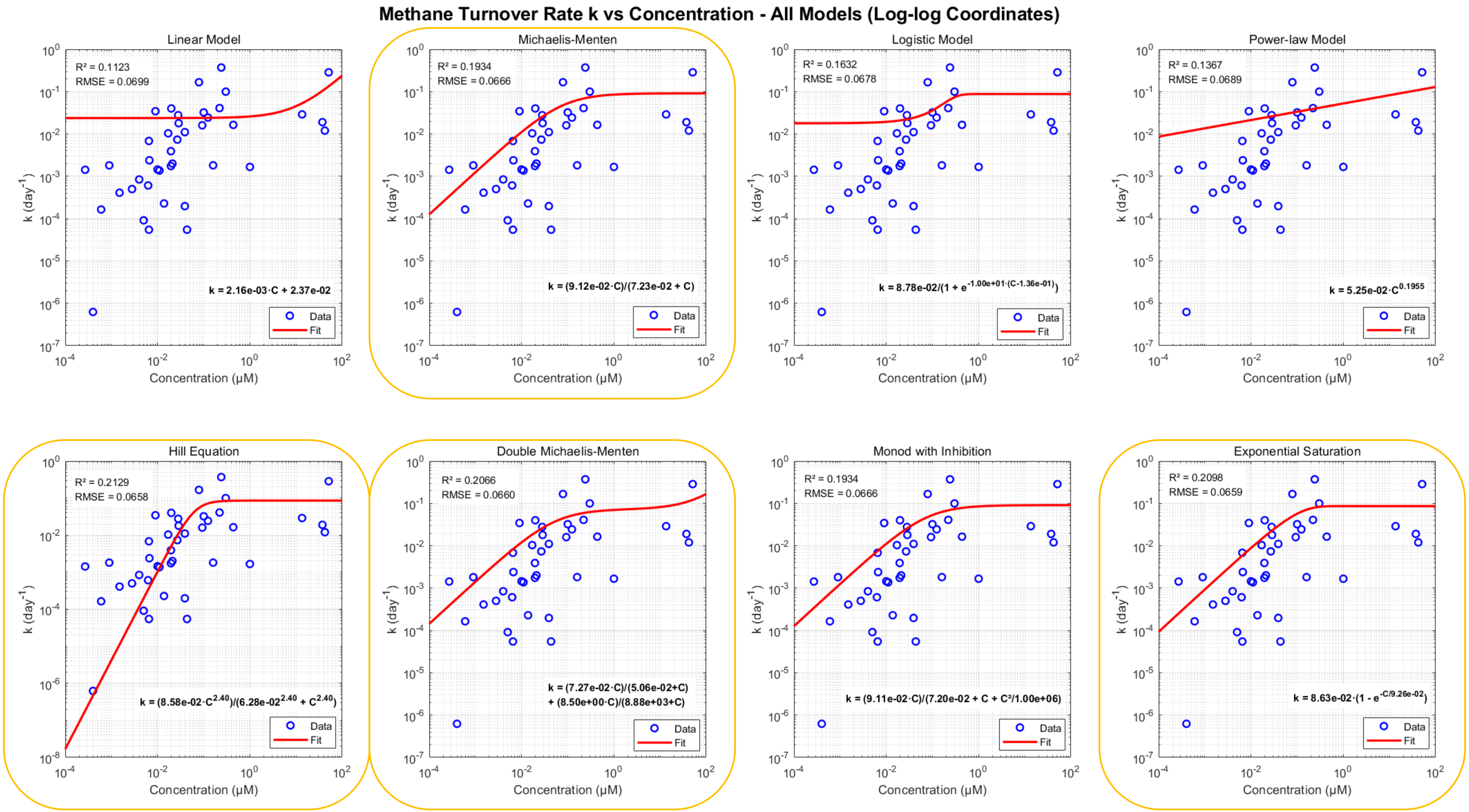
Model	R^2	RMSE
Linear Model:	0.1123	0.0699
Michaelis-Menten:	**0.1934**	**0.0666 (4.97)**
Logistic Model:	0.1632	0.0678
Power-law Model:	0.1367	0.0689
Hill Equation:	**0.2129**	**0.0658 (7.56)**
Double Michaelis-Menten:	**0.2066**	**0.0660 (3.34)**
Monod with Inhibition:	0.1934	0.0666
Exponential Saturation:	**0.2098**	**0.0659 (5.35)**

MOX fit



Methane Turnover Rate k vs Concentration - All Models (Log-log Coordinates)
Linear Model
R² = 0.1123
RMSE = 0.0699
k = 2.16e-03·C + 2.37e-02
Michaelis-Menten
R² = 0.1934
RMSE = 0.0666
k = (9.12e-02·C)/(7.23e-02 + C)
Logistic Model
R² = 0.1632
RMSE = 0.0678
k = 8.78e-02/(1 + e^-1.00e+01·(C-1.36e-01))
Power-law Model
R² = 0.1367
RMSE = 0.0689
k = 5.25e-02·C^0.1955
Hill Equation
R² = 0.2129
RMSE = 0.0658
k = (8.58e-02·C^2.40)/(6.28e-02^2.40 + C^2.40)
Double Michaelis-Menten
R² = 0.2066
RMSE = 0.0660
k = (7.27e-02·C)/(5.06e-02+C)
+ (8.50e+00·C)/(8.88e+03+C)
Monod with Inhibition
R² = 0.1934
RMSE = 0.0666
k = (9.11e-02·C)/(7.20e-02 + C + C²/1.00e+06)
Exponential Saturation
R² = 0.2098
RMSE = 0.0659
k = 8.63e-02·(1 - e^-C/9.26e-02)
Data
Fit
k (day^-1)
Concentration (μM)

MOX fit



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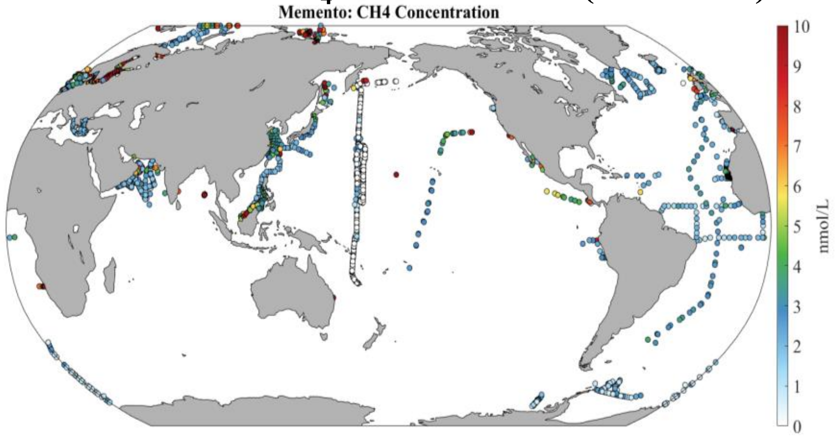
Data
Fit
k (day^-1)
Concentration (μM)

Determining Removal Equation

- Global diffusive CH_4 flux and ebullitive emissions are about **2–6** and **2–8** Tg/yr**,** respectively (Weber et al., 2018).
- The global open ocean CH_4 emission rate, estimated based on Pacific and Atlantic data is about 0.4 Tg C/yr (Bates et al., 1996; Rhee et al., 2009) .

Tested Equations ($Tg\ CH_4/yr$)	**Seepage Flux**	**Diffusive Flux**	**Water column prod**
Hill（18 Tg/yr ebullition)	**5.76**	**2.2**	**0.35**
Hill（48 Tg/yr ebullition)	**11.4**		
Exponential Saturation（18 Tg/yr ebullition)	3.73	0.67	-0.91
Exponential Saturation（48 Tg/yr ebullition)	9.4		
Michaelis-Menten（18 Tg/yr ebullition)	3.34	0.38	-1.78
Michaelis-Menten (48 Tg/yr ebullition)	9.17		
Double MM（18 Tg/yr ebullition)	3.25	0.26	-1.3
Double MM+48 Bubble（48 Tg/yr ebullition)	9.36		

MEMENTO CH_4 Concentration (1975-2014)



Study area	Measured Surface Cons. (nM)	Model Cons. (nM) 18	Model Cons. (nM) 48	Measured Flux (umol/m2/d)	Model Flux (umol/m²/d) 18	Model Flux (umol/m²/d) 48	Reference
Bohai Sea And Yellow Sea	2.9-33.75	16.37	24.66	0.02-89.14 (Mean: 10.63±12.32; 9.35± 10.98)	62.10	82.57	Zhang et al. (2023)
Caribbean Sea	/	/	/	0.014± 0.014 0.069± 0.070	0.032	0.041	Morell et al., 2001
The Ross sea	1.5-5.5	3.38	3.56	-0.44±0.34	-0.076	0.11	Ye et al., 2023;
the Arabian Sea	the southern part of the Arabian Sea : 1.79-5 northern region (latitude higher than 19°N: 6-8	3.06 12.28	3.86 19.81	0.17-0.36	0.89	1.13	Patra et al., 1998; Bange et al., 1998
the East China Sea	the coastal area: 9.1 ± 1.6 Open ocean: 4.3± 1.3	16.38 5.23	27.9 7.80	Open ocean: 6.5±7.4 Coastal areas: 11.5±11.9	14.50 27.32	15.66 30.27	Sun et al., 2018; Ye et al., 2016

CH_4 Sea-Air Flux

- **F**

$$F = k \times (CH_{4_s} - CH_{4_{sat}})$$

- **CH_4sat： Wiesenburg, D. A., and N. L. Guinasso Jr., Equilibrium solubilities of methane, carbon monoxide and hydrogen in water and seawater, J. Chem. Eng. Data, 24, 356-360, 1979.**

$$\ln CH_{4_{sat}} = (a\_0+ts(:)\times(a\_1+ts(:)\times(a\_2+ts(:)\times(a\_3)))+sss(:)\times(b\_0+ts(:)\times(b\_1+ts(:)\times(b\_2)))$$

$$ts(:) = \log(((T0\_Kelvin + 25.0) - sst(:)) / (T0\_Kelvin + sst(:)))$$

- **k (gas exchange rate)： Wanninkhof（1992）**

$$k_w(U, Sc) = 0.39U^2\left(\frac{Sc}{660}\right)^{-0.5}$$

- **Sc（Schmidt number）： Wanninkhof（2014）**

$$Sc = 1909.4-120.78t+4.1555t^2-0.080578t^3+0.00065777t^4$$

Sensitivity to parameter values

- Aerobic methane production $P_{aer} = \left(a \times b \times c \times DOP_{remin(k)}\right) \times R_{c2p}$

Fraction of phosphonates	0.25	0.29	0.33 (selected)
CH_4 Flux (Tg CH_4/yr)	7.72	7.78	7.83

Fraction of the MPn inventory	0.002	0.0025	0.003 (selected)
CH_4 Flux (Tg CH_4/yr)	7.68	7.76	7.83

- Anaerobic production of methane (in sediments)

Flux ratios between CH_4 and SO_4^{2-}	1:1	1.4:1 (selected)
CH_4 Flux (Tg CH_4/yr)	7.75	7.83

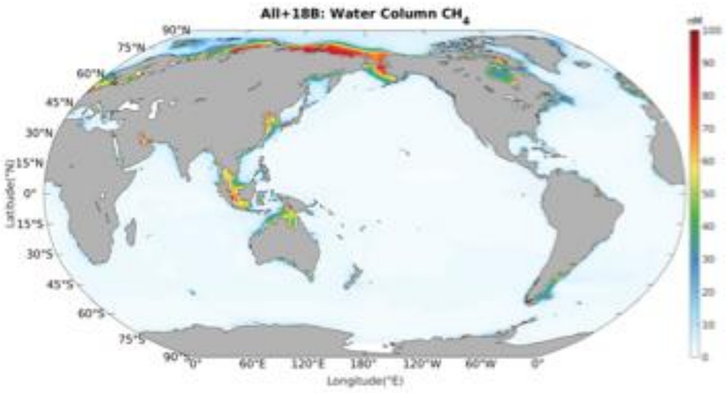
- Anaerobic oxidation of methane (in sediments)

AOM ratio (%)	70%	80% (selected)	90%
CH_4 Flux (Tg CH_4/yr)	8.42	7.83	7.21

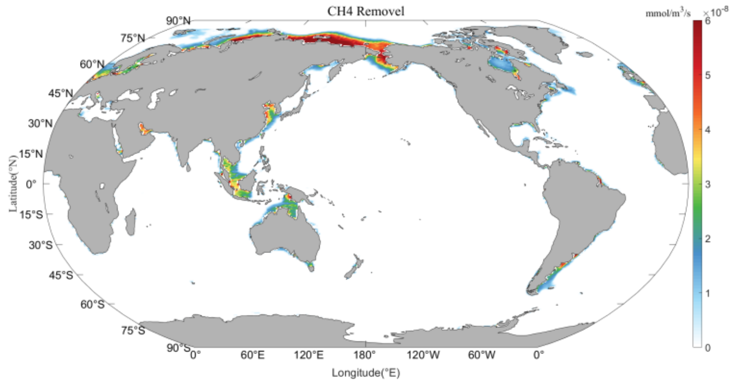
Simulated CH_4 distribution

Assuming 18Tg/yr from ebullitive CH_4 emissions

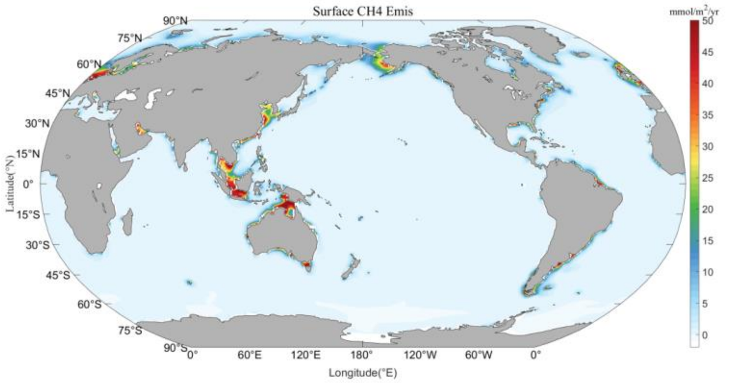
Average CH_4 concentration



Average CH_4 removal rates

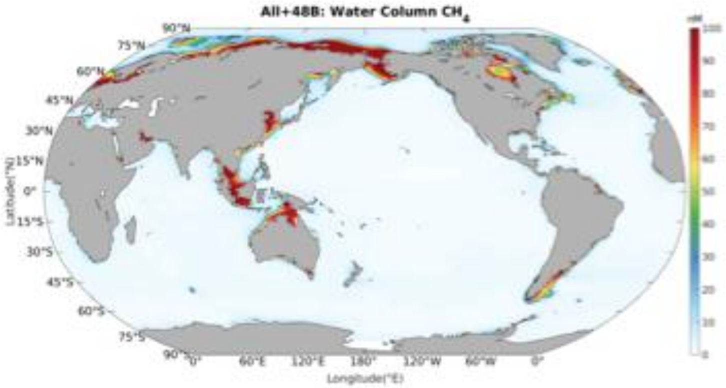


Air-Sea CH_4 Flux (7.9 Tg/yr total)

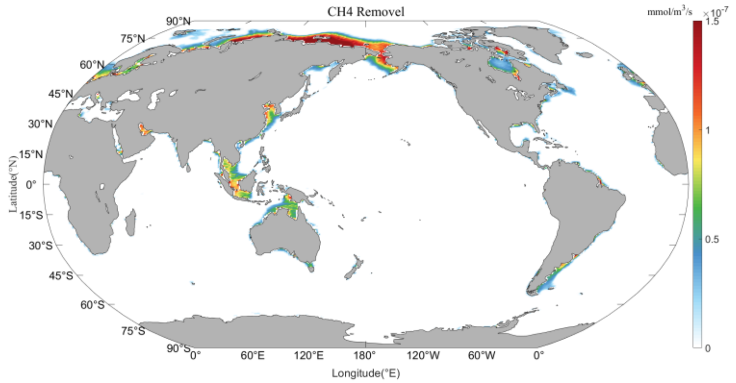


Assuming 48Tg/yr from ebullitive CH_4 emissions

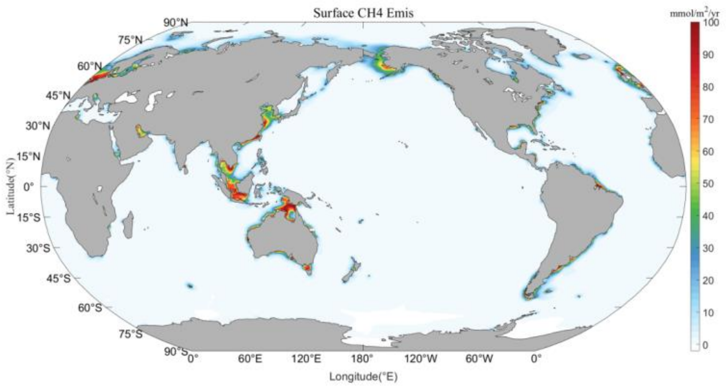
Average CH_4 concentration



Average CH_4 removal rates

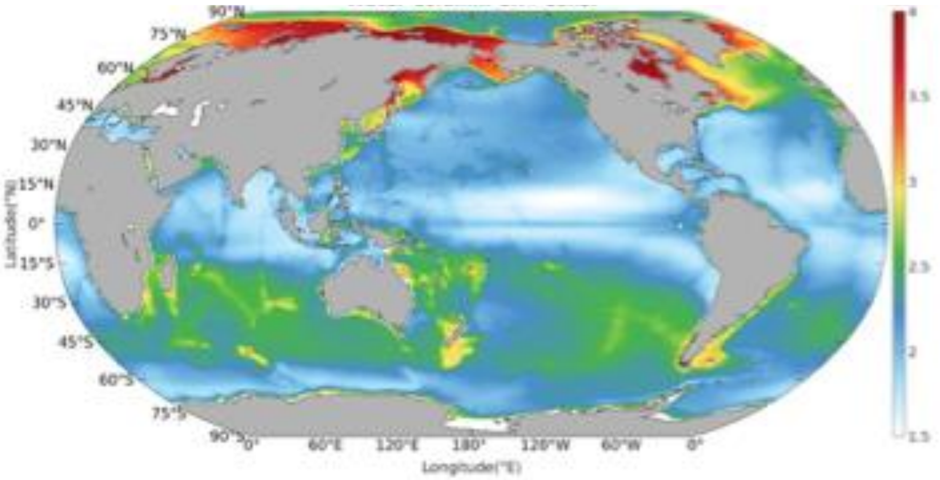


Air-Sea CH_4 Flux (13.4 Tg/yr total)

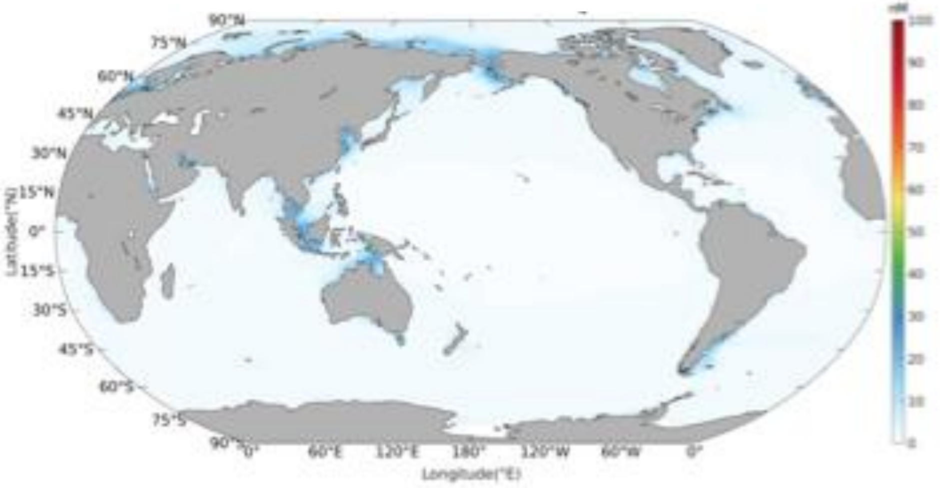


Contribution of various sources

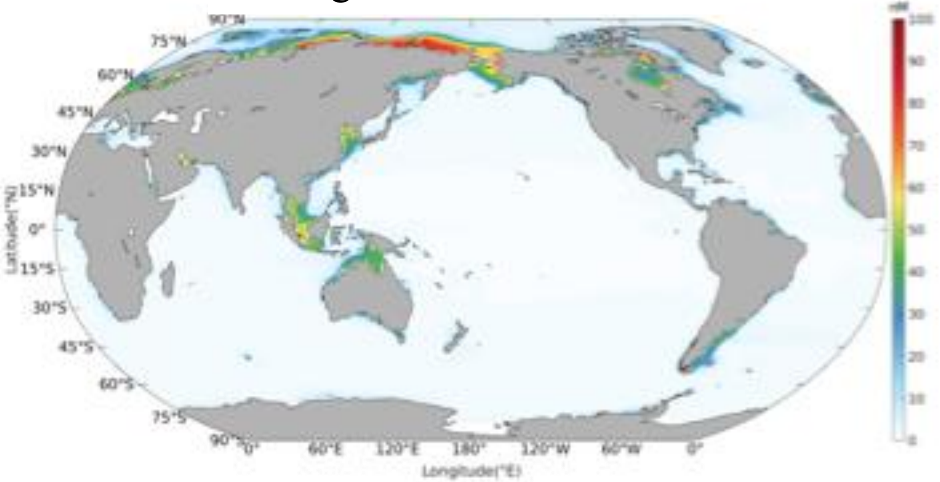
CH_4 concentrations with aerobic production alone



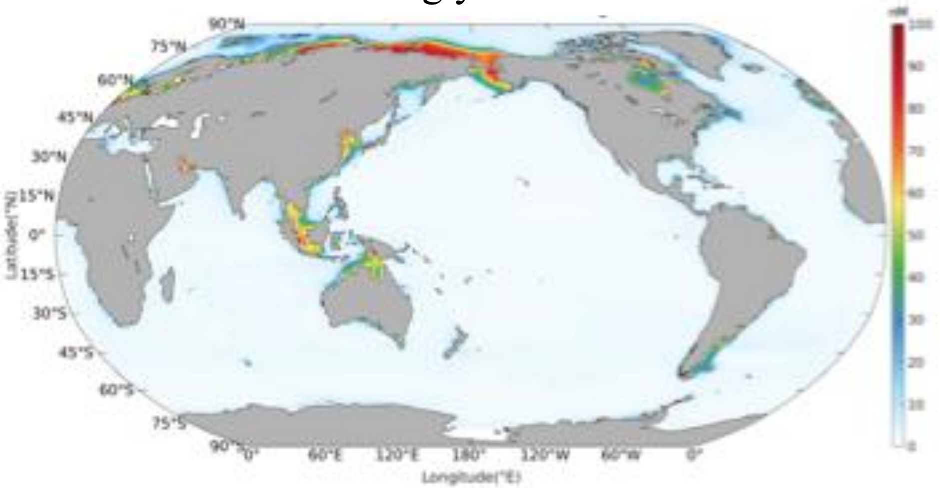
Anaerobic methane production



Geological methane sources



All with 18Tg/yr ebullitive release



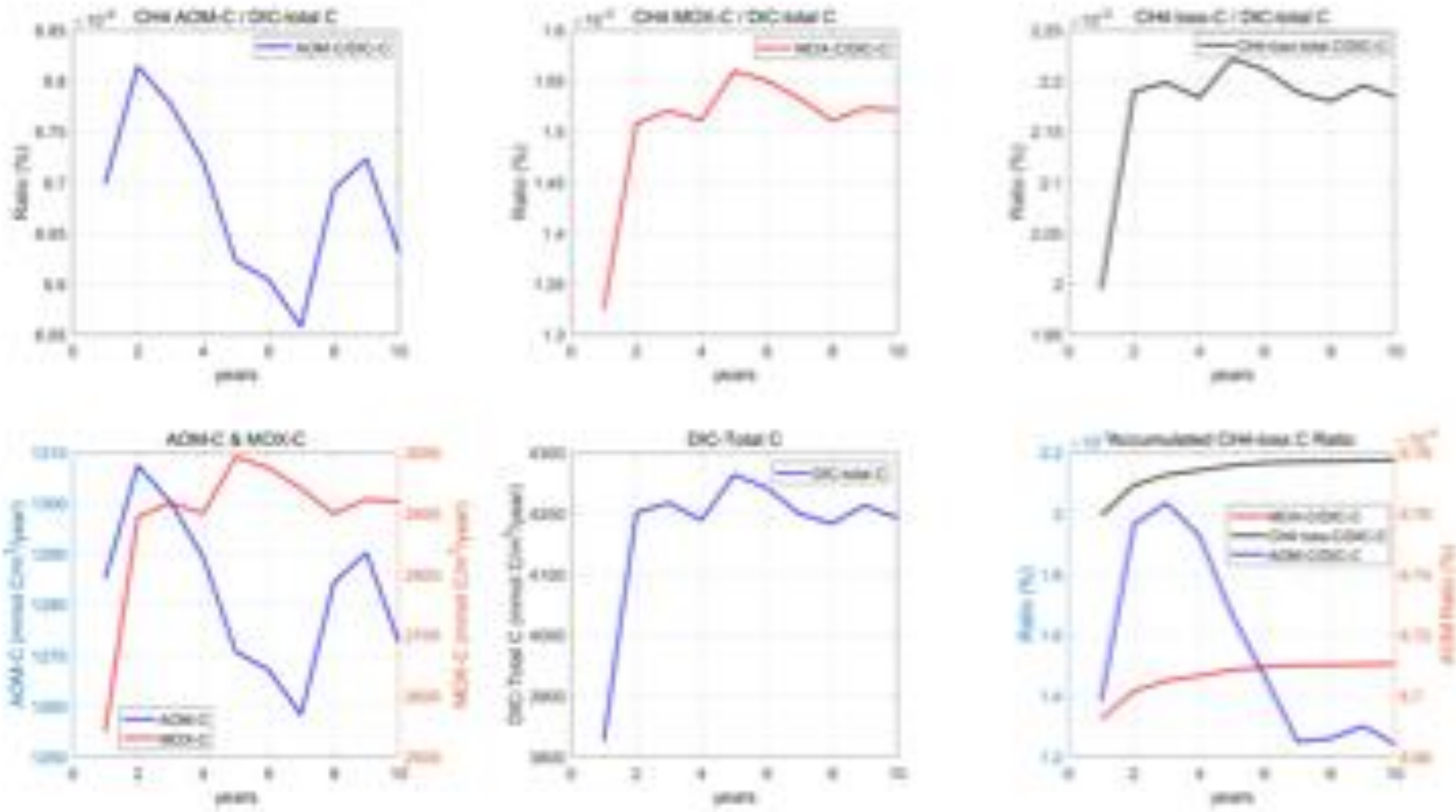
Geological sources constitute the dominant contribution to oceanic methane, occurring predominantly in coastal and shelf regions.

Conclusion

- Simulated large-scale distribution patterns of CH_4 match MEMENTO observations.
  - High CH_4 emission at coastal regions
- Simulated oceanic methane emissions range from 7.2 Tg/yr to 13.4 Tg/yr (previous estimates: 5~25Tg/yr by Saunois et al., 2016; 6–12 Tg/yr by Weber et al., 2019).
- Though sedimentary methanogenesis represents an important methane source, AOM limits methane escaping from sediments.
- Geological sources contribute localized, high-intensity methane fluxes. Variability in CH_4 ebullition drives uncertainty in oceanic methane emission.

Thanks!

Questions or Comments?



- Acetate cleavage (methanogenesis)：

$CH3COOH \rightarrow CH4+CO2$

- Anaerobic oxidation of methane (AOM):

$CH_4 + SO_4^{2-} \rightarrow CO_2 + HS^- + OH^- + H_2O$

- Aerobic oxidation of methane (MOX):

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

- Methane oxidation contributes a very small but measurable fraction of total DIC
- Cumulative trends and orders of magnitude are consistent, indicating stable methane-derived carbon inputs to the DIC pool

Methane Weight Function

- ✓ To ensure that the sum of global methane production accounts for 28.6% of other_remin, normalization of weights is required. The specific steps are as follows:

1. First, calculate the weight $\omega'(D)$ for each grid point in the global ocean based on the weight function mentioned above.
2. Then compute the global weighted integral, where other_remin is the 20-year mean value output by the model:

$$\text{sum\_w}=\sum_{ocean\ cell} \omega'(D) \times other\_remin \times tarea$$

$$\text{sum\_other}=\sum_{ocean\ cell} other\_remin \times tarea$$

3. Calculate the global average weight： w_avg=sum_w/sum_other
4. Set a spatially varying scaling factor R for each seabed grid point. The core function of R is to achieve spatial reallocation of methane production while keeping the global total unchanged. The calculation equation is:

$$R = 0.286 \times \frac{\omega'(D)}{\omega\_avg}$$

5. Finally, create a forcing field file for this proportion change factor R, replace 0.286 with it in the real-time P_{sed} calculation of the model, and define it as ch4_sed_scalef in the model.

Methanogenesis in Sediments

Initial test: Parameterization based on POC flux to sea floor

- ~3–4% of the organic carbon flux to the seafloor is converted to methane (Egger et al., 2018, Nature Geosci) .

$$P_{sed} = (0.03\text{-}0.04\_r8) * POC\%to\_floor * 0.5\_r8$$