厦門大學
XIAMEN UNIVERSITY

MEL
State Key Laboratory of Marine Environmental Science

近海海洋环境科学国家重点实验室（厦门大学）
State Key Laboratory of Marine Environmental Science (Xiamen University)

Simulating Marine Nitrous Oxide (N_2O) and Its Offset Effect during Iron Fertilization

Shanlin Wang, Shiyao Zheng, Liyang Zhan

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outline

01 Background

02 Methods

03 Model Validation

04 Ocean Iron Fertilization (OIF) Test & Results

N2O - Greenhouse Gas

Table 1. Global annual surface mean abundances (2023) and trends of key greenhouse gases from the GAW in situ observational network for GHG (WMO, 2024).

	CO_2	CH_4	N_2O
2023 global mean abundance	420.0±0.1 ppm	1934±2 ppb	336.9±0.1 ppb
2023 abundance relative to 1750[a]	151%	265%	125%
2022–2023 absolute increase	2.3 ppm	11 ppb	1.1 ppb
2022–2023 relative increase	0.55%	0.57%	0.33%
Mean annual absolute increase over the past 10 years	2.4 ppm yr^{-1}	10.7 ppb yr^{-1}	1.07 ppb yr^{-1}

[a] Assuming a pre-industrial concentration of 278.3 ppm for CO_2, 729.2 ppb for CH_4 and 270.1 ppb for N_2O. The number of stations used for the analyses was 146 for CO_2, 153 for CH_4 and 112 for N_2O.

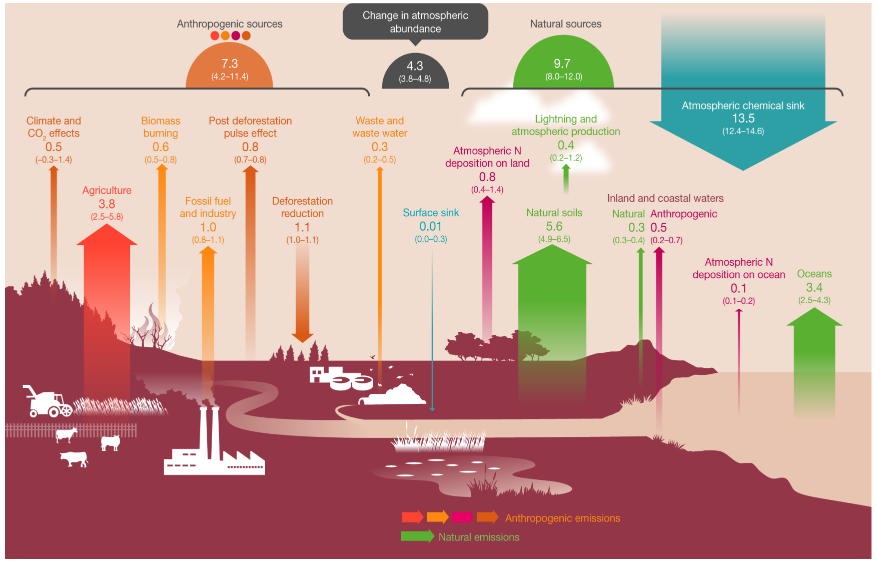


Fig 1. Global N_2O budget for 2007-2016: TgN/yr (Tian et al., 2020).

✓ **The ocean releases about 20% of nitrous oxide (N_2O) into the atmosphere, playing a crucial role in the global climate system.**

Marine N_2O Sources & Sinks

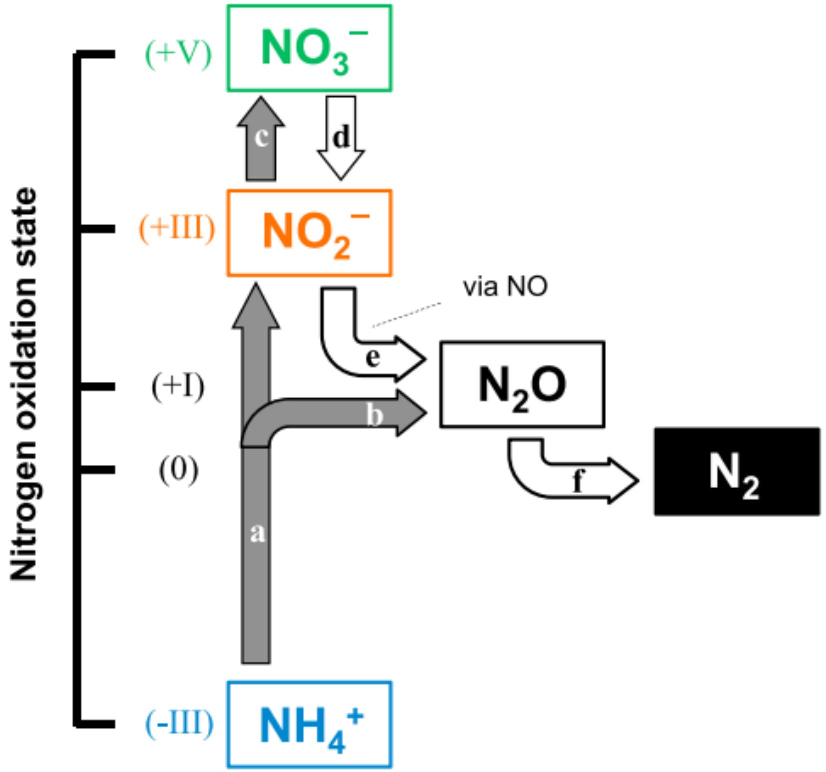


Fig 2. The nitrogen cycle processes relate to N_2O production and consumption in the ocean (Ji et al., 2018).

◆ **Main features**: nitrogen cycle, oxygen, microorganisms;

✓ **Sources**: Nitrification (main), Denitrification

- **Under aerobic conditions**:

  a → c

- **Under hypoxic conditions**:

  d → e

✓ **Other Sources**: Denitrification by Nitrifying Bacteria; Dissimilatory Nitrate Reduction to Ammonium, DNRA……

✓ **Sinks**: Denitrification (OMZs) → **f**

N_2O Distribution & Influencing Factors

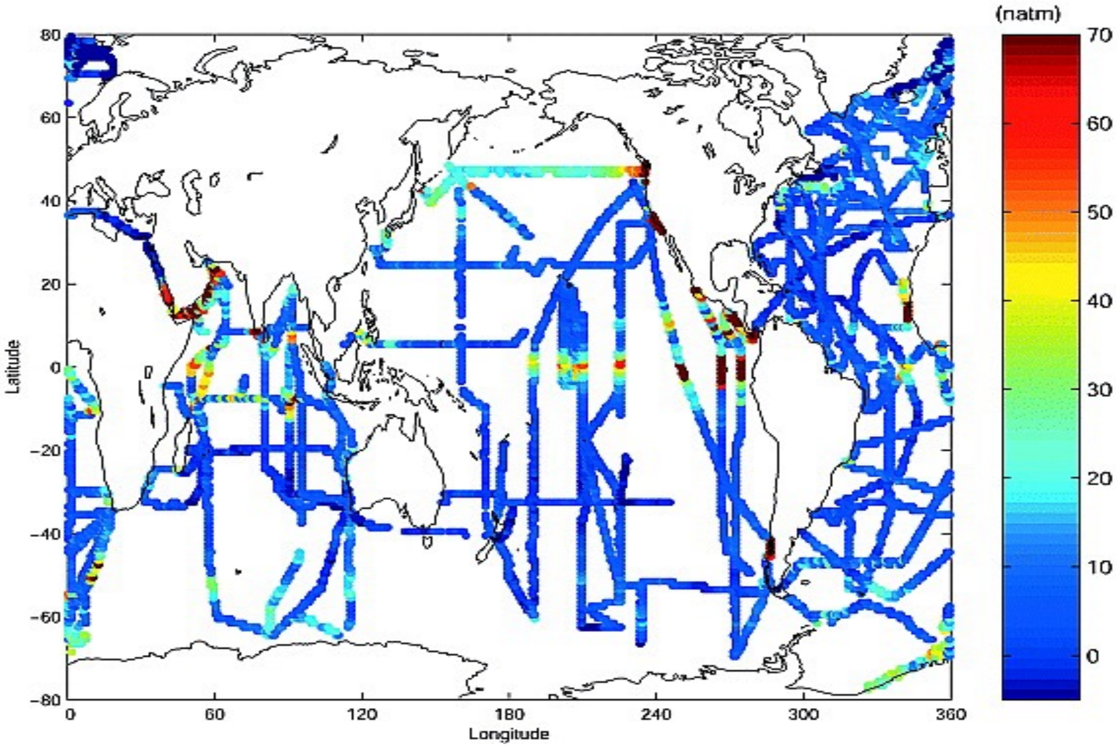
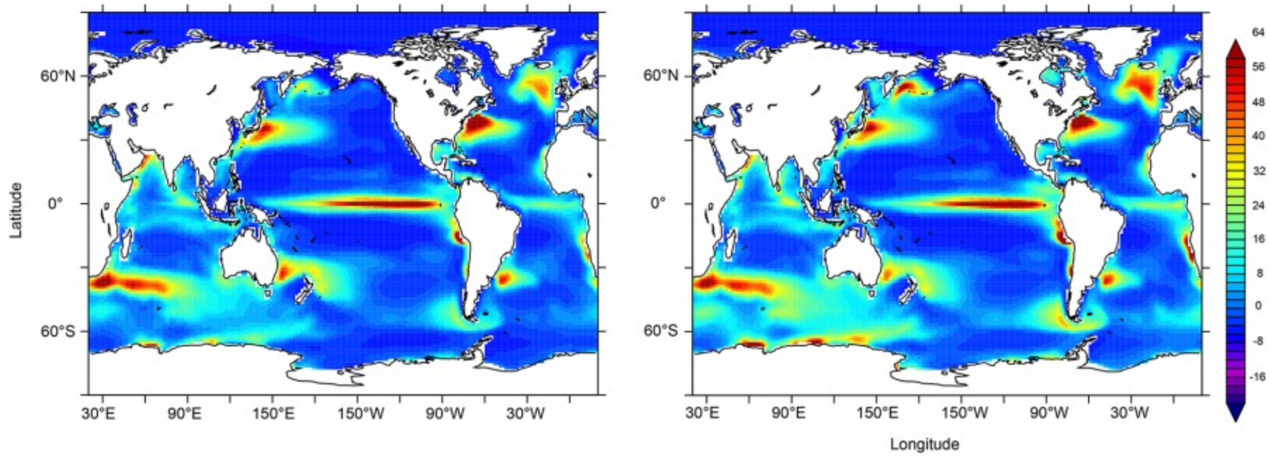


Fig 3. Global Ocean Surface Water **N_2O** Saturation (ΔpN_2O) (Weiss et al., 1992; Butler et al., 1988、1989；Lobert et al., 1996).

- ΔN_2O-Apparent oxygen utilization rate (AOU): Linear correlation
- Temperature
- Salinity
- Atmospheric pressure
- Wind Speed……
- NH_4^+
- NO_3^-
- NO_2^-
- Surface primary productivity and organic matter transport

N_2O Flux—Previous Model Results



IPSL
(Martinez-Rey et al., 2015)

NEMO
Buitenhuis et al., 2018

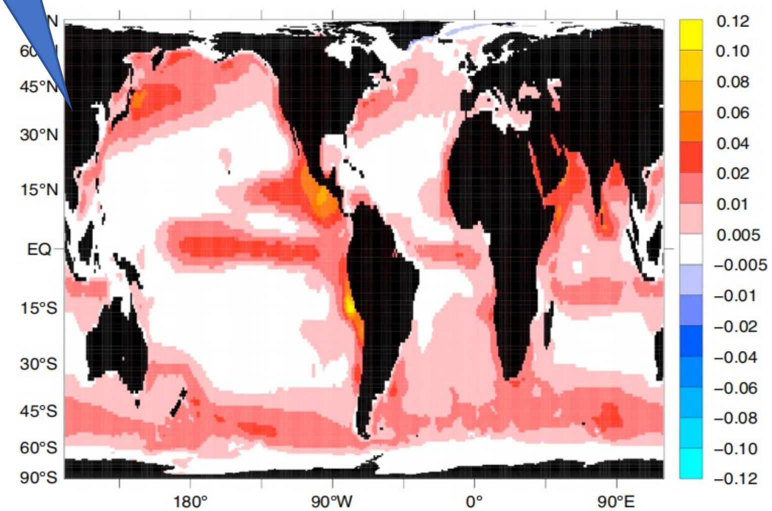
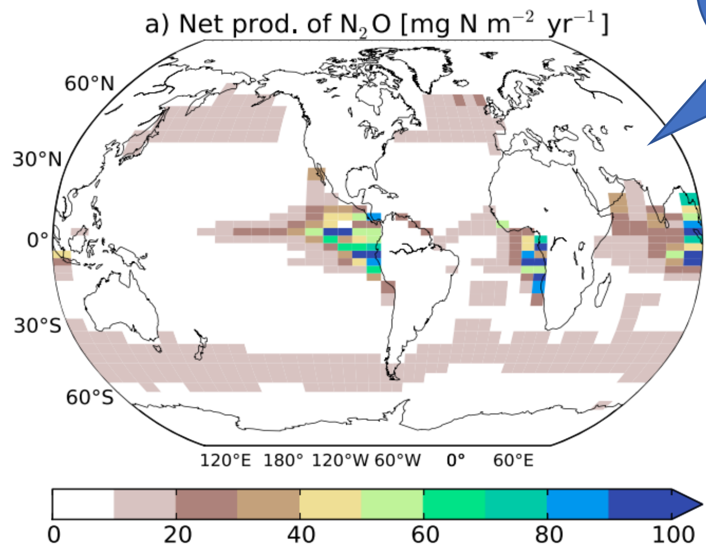


Figure 7. Global ocean N_2O flux (g N·m^{-2}·year^{-1}, color bar on the right) determined by a model simulation. Positive values indicate net flux from the ocean to the atmosphere. Simulations were performed with nitrification parameterization from this study (N_2O yield (%) = 0.2/[O_2] + 0.08), and denitrification parameterization of *e*-folding [O_2] = 10 μM. The result of global oceanic net N_2O production is 2.8×10^{12} g N/year.

The Bern3D Model
(Battaglia & Joos, 2018)



N_2O Production Parameterization in CESM2

1、P.TEMP

- **The first method is adapted from Butler et al. (1989), which uses oxygen consumption method and temperature dependent correction for N_2O yield;**
- **P. TEMP parameterization assumes that the generation of N_2O is only related to nitrification;**
- **N_2O Source** $(J^{P.TEMP}(N_2O))$, is then mathematically formulated as:

$$J^{P.TEMP}(N_2O) = (\gamma + \theta T)J(O_2)_{consumption}$$

- γ is a background yield ($\mathbf{2.0 \times 10^{-5}}$ mol **N_2O** (mol **O_2**)$^{-1}$consumed), θ is the temperature dependency of γ ($\mathbf{4.6 \times 10^{-8}}$ mol **N_2O** (mol **O_2**)$^{-1}$ K^{-1}), T is temperature (K) , $J(O_2)_{consumption}$is the sum of all biological O_2 consumption terms within the model;
- γ from Buitenhuis et al. (2018). While the ratio of θ is two orders of magnitude lower than the ratio used in Butler et al.'s (1989) original simulation. The use of original value will result in a significant increase in nitrous oxide production associated with OMZs in MARBL, deviating from the assumption of nitrification dominance.

N_2O Production Parameterization in CESM2

2、P.O_2Consumption

✓ The P.OMZ parameterization, formulated after： Suntharalingam et al. (2000, 2012)， assumes that the overall yield consists of a constant background yield and an oxygen-dependent yield. This gives:

$$N_2\text{Osource} = \alpha \cdot [Oxygen\ consumption\ rate] +$$

$$\beta \cdot f(O_2) \cdot [Oxygen\ consumption\ rate]\ \ z \le \boldsymbol{z_e} \quad \text{(euphotic depth)}$$

- MARBL does not have a clear setting for $\boldsymbol{z_e}$. The nitrification is light-inhibited and only occurswhere PAR is below 1 W/m^2. Therefore, only calculate the $N_2\text{O}$ production in grids with PAR ≤ 1 W/m^2;
- α is a background yield， (mol $N_2\text{O}$ (mol O_2)$^{-1}$ consumed); β is a yield parameter that scales the oxygen-dependent function; $\text{f}\,(O_2)$ is a unitless oxygen-dependent step-like modulating function, as suggested by laboratory experiments (Goreau et al., 1980):

$$\text{f}\,(O_2) = [O_2]\ /\ O_{max}\quad [O_2] < O_{max}$$

$$\text{f}\,(O_2) = e^{-k([O_2] - Omax)/Omax}\quad [O_2] > O_{max}$$

N_2O Production Parameterization

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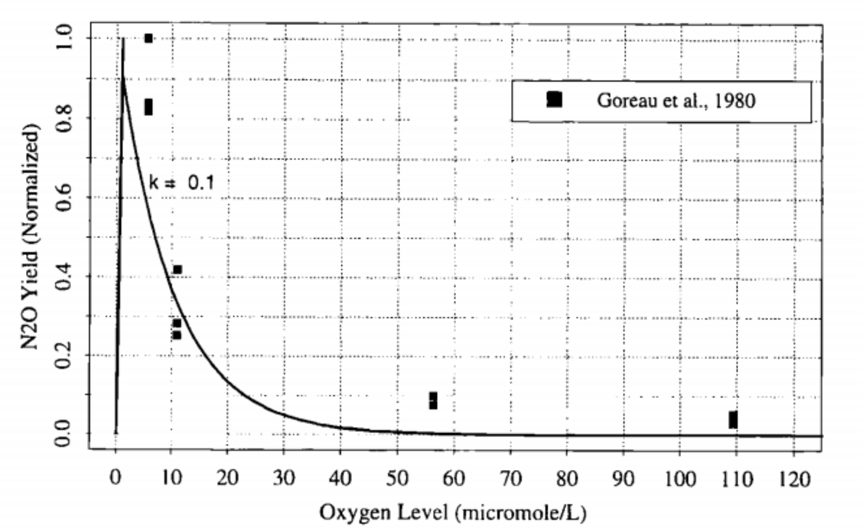


- MARBL does not have a clear setting for $\boldsymbol{z_e}$. The nitrification is below 1 W/m[2]. Therefore, only calculate the N_2O production ir
- α is a background yield, (mol N_2O (mol O_2)$^{-1}$ consumed); β is dependent function; $f\,(O_2)$ is a unitless oxygen-dependent ste laboratory experiments (Goreau et al., 1980):

$$f\,(O_2) = [O_2] \ / \ O_{max} \ \ [O_2] \ < \ O_{max}$$

$$f\,(O_2) = e^{-k(\,[O_2] - Omax\,)\,/Omax} \quad [O_2] \ > \ O_{max}$$

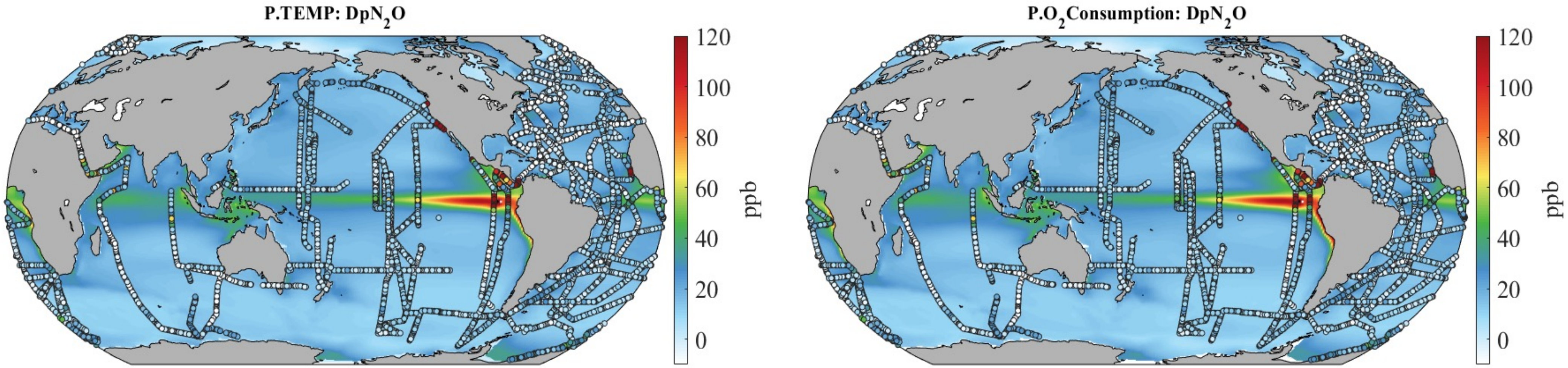
N_2O Production Parameterization

Table 2. $P.O_2$consumption parameters set

Parameter	Units	$P.O_2$consumption
$[O_2]$	$mmol/m^3$	Model
Omax	$mmol/m^3$	1.0 (Goreau et al., 1980)
k	/	0.1 (Goreau et al., 1980)
α	mol N/mol O_2	0.75e-4(Suntharalingam et al., 2012) 0.33e-5-2.26e-5 (Buitenhuis et al., 2018) 0-7e−5 (Battaglia & Joos, 2018)
β	mol N/mol O_2	0.1e-3(Suntharalingam et al., 2012) 1.7e-3-10.18e-3(Buitenhuis et al., 2018) 5e−5-2e−3 (Battaglia & Joos, 2018)

✓ **Chosen parameter set:** α = 3.3e-5, β = 9.1e-4

N_2O Sea-Air Pressure Difference



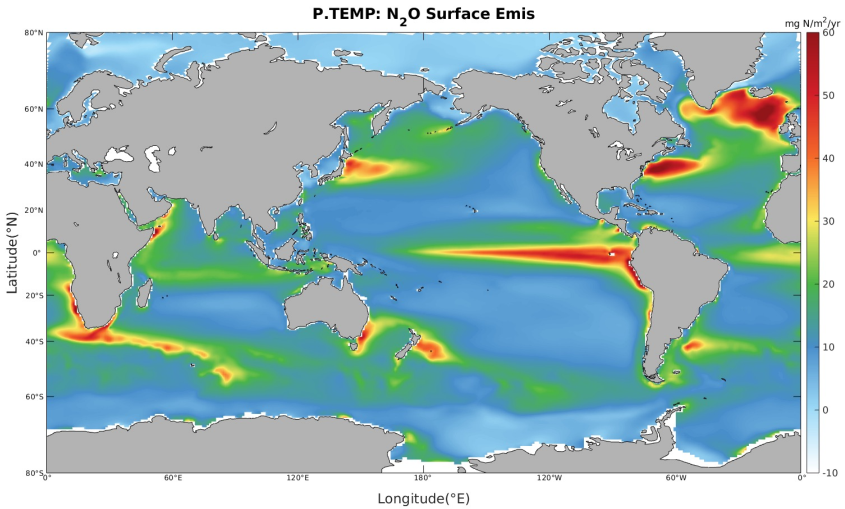
- **Figure 4**. Comparison of dpN_2O and MEMENTO measured data results from parameterized outputs of P. TEMP and P.O_2consumption;
- **High positive *dp*$\boldsymbol{N_2O}$** is observed in the equatorial and eastern tropical Pacific, northern Indian Ocean, and Agulhas Current vicinity; **Negative *dp*$\boldsymbol{N_2O}$** is observed in some high latitude regions of the Southern Ocean and Arctic Ocean.

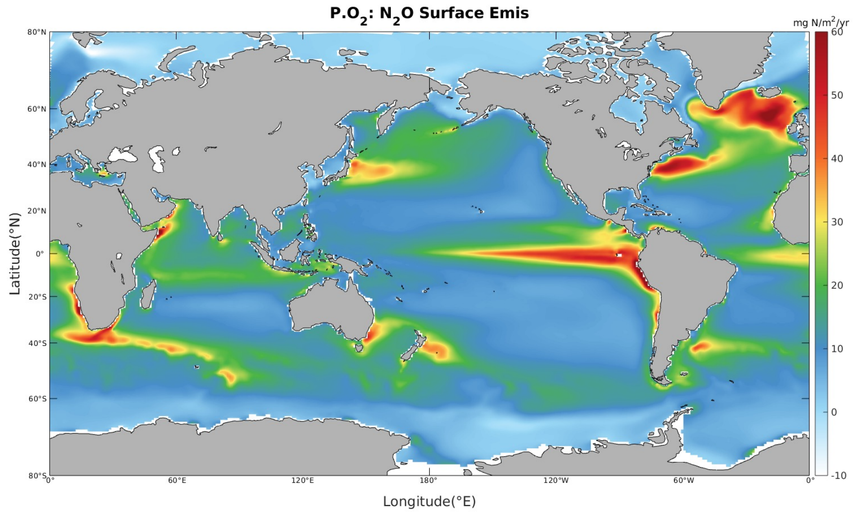
N_2O Sea-Air Pressure Difference

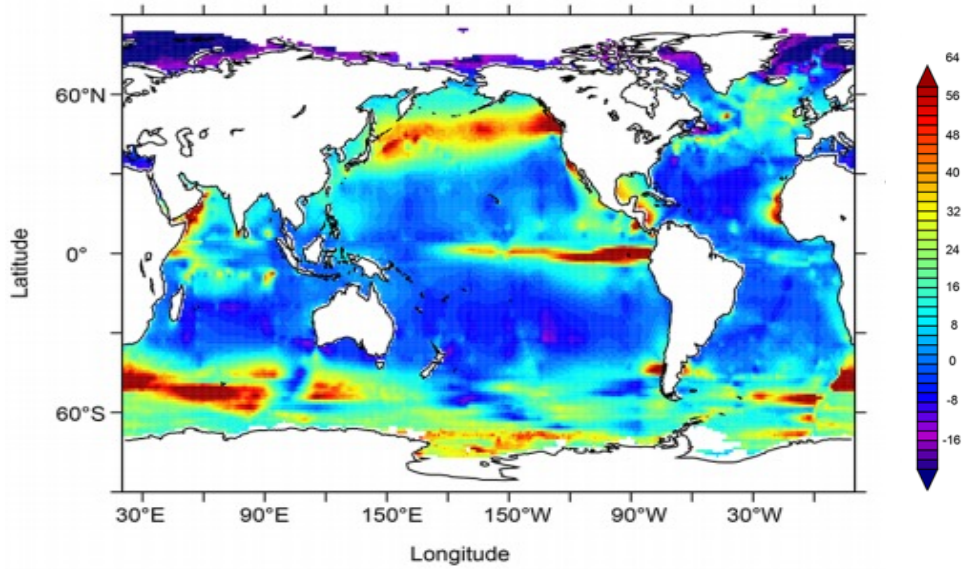
Table 3. Standard deviation and correlation coefficient between P.TEMP/P.O_2consumption and MEMENTO data.

	P.TEMP	P.O_2Consumtion	MEMENTO obs.
Standard deviation (in ppb dpN_2O)	5.2913	5.5664	5.4406
Correlation coefficient with obs.	0.4525	0.4590	/

N_2O Flux







- **Figure 10**. Comparison of simulated results of P.TEMP and $P.O_2$-consumption with Nevison et al. (2004);
- N_2O flux is relatively high in the equatorial and eastern tropical Pacific, northern Indian Ocean, northwestern Pacific, northern Atlantic, and Agulhas Current (**>50 mgN m²/yr); ** Low N_2O flux in the subtropical circulation of the Southern Ocean, Atlantic Ocean, and Pacific Ocean, as well as in the Southern Indian Ocean (**<10 mgN m²/yr).**
- The hotspots of N_2O emissions are consistent with the areas with higher POC flux (100m) output in the model.

Iron Hypothesis

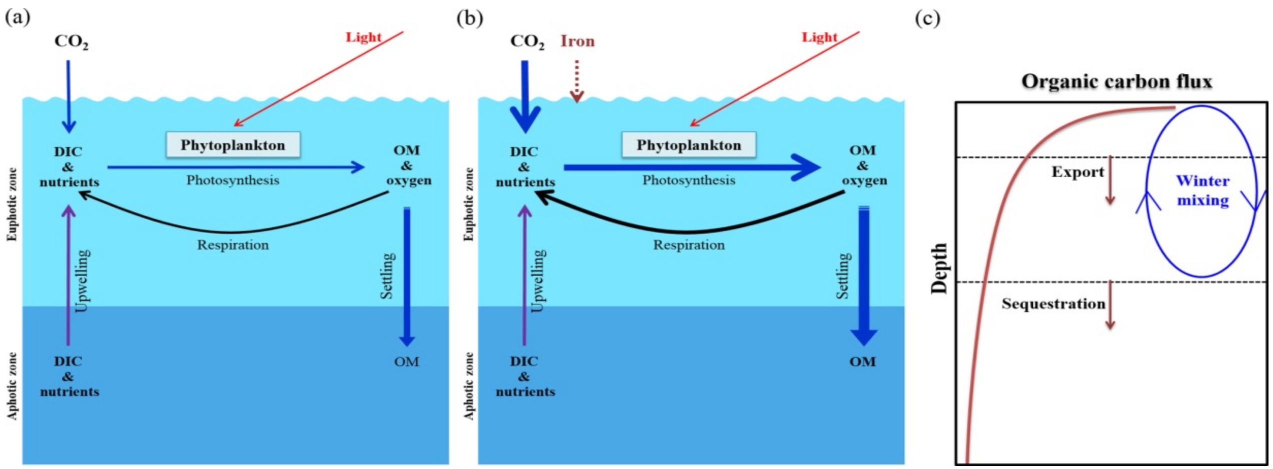


Figure 6. Martin's (1990) iron hypothesis (a) the effectiveness of biological pumps under normal conditions; (b) The effectiveness of biological pumps after iron enrichment; (c) Schematic diagram of the downward flux of organic carbon decreasing with water depth (Yoon et al., 2018).

- ✓ **Ocean "Iron Fertilization", especially in High Nutrient Low Chlorophyll (HNLC) sea areas, is considered a simple and efficient strategy to promote BCP and reduce atmospheric CO_2 concentration.**
- ✓ **However, Iron fertilization not only enhances ocean carbon sequestration, but also increases remineralization within the ocean, leading to an increase in N_2O production, which may weaken the effectiveness of CO_2 sinks (Jin & Gruber, 2003).**

OIF Test Areas

- **OIF areas: The Southern Ocean (significant oceanic carbon sink and the largest HNLC region)**;
- Different frontal zones in the Southern Ocean (SO) usually have significant differences in carbon sinks, nutrient limitations, water characteristics, etc. However, **the differential response of N_2O feedback to OIF in the latitudinal region where the fronts lie seems to be ignored**. This will be an important basis for determining the optimal fertilization location in the SO.

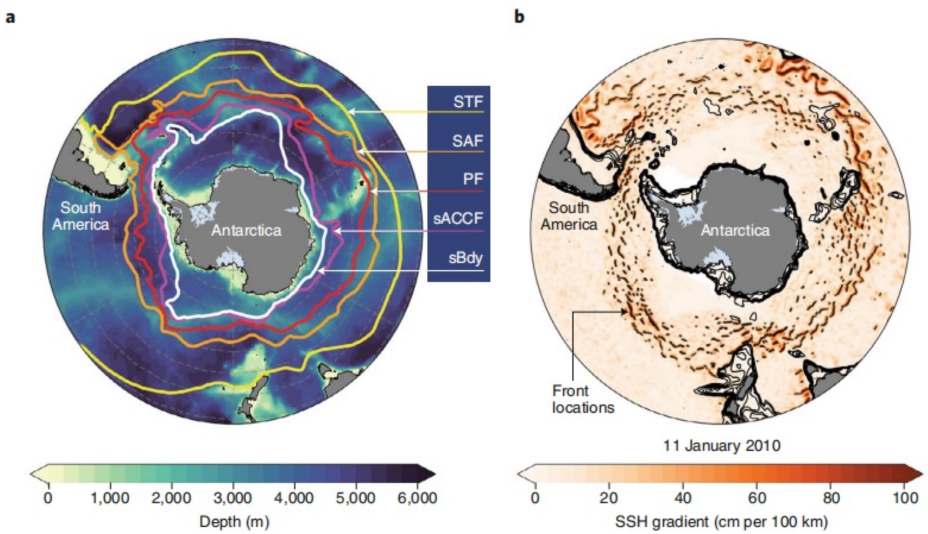


Figure 7. a. Fronts determined by Orsi et al. (1995), who used water quality standards. b: Daily snapshot of SSH gradients obtained from AVISO satellite altimetry products (color) on the grid (January 11, 2010). The dashed black line represents the position of the front or jets determined by the SSH gradient threshold.

Model Setup and Experimental Design

Table 4. CESM-N_2O model iron fertilization test setup.

Experiments	Sub-Antarctic Zone (SAZ)	Polar Frontal Zone (PFZ)	Antarctic-Southern Zone (ASZ)	SOFeX-S ($kg/m^2/s$)
Control	×	×	×	0
Test 1	√	√	√	1.62037×10^{-11}
Test 2	√	√	√	1.62037×10^{-11}
Test 3	40° S-45° S 140° W-145° W	50° S-55° S 140° W-145° W	60° S-65° S 140° W-145° W	1.62037×10^{-11}

- In the the fifth spin-up (model year 245), we introduce the parameterization for N_2O production and iron is added to the Southern Ocean in the 281st year of the simulation.
- **The SO is divided into three distinct zones: the Subantarctic Zone (SAZ), the Polar Frontal Zone (PFZ), and the Antarctic-Southern Zone (ASZ).** The boundaries of these regions are defined based on the frontal positions identified by Wainer & Gent (2019) using strong sea surface height (SSH) gradients from CESM-LME data.
- **Test 1**: which simulated large-scale, long-term OIF, continues for 25 years. **Test 2**: a short-term iron fertilization experiment for one month and one year. **Test 3**: the influence of the area scales of OIF on the feedback effect of N_2O is also tested.

Test 1: long-term, large-scale fertilization experiments

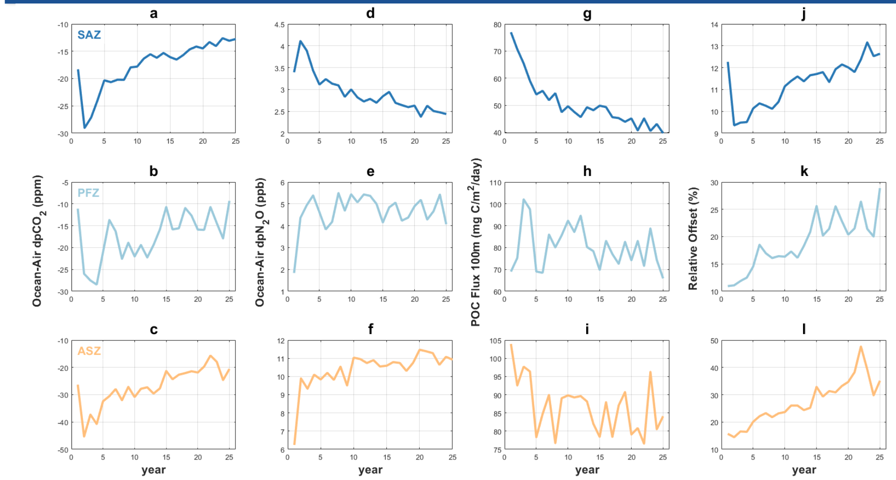


Fig 14. Changes in $dpCO_2$, dpN_2O, POC export (100m) and offset effect.

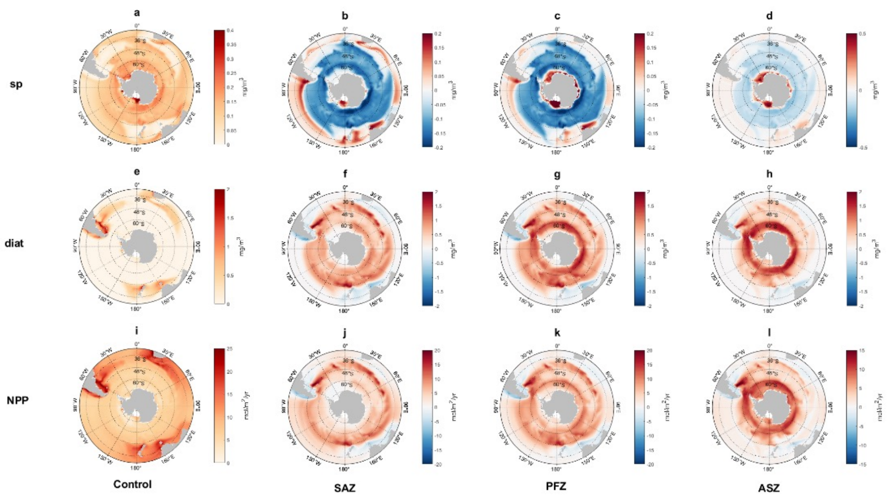


Fig 15. Changes in phytoplankton biomass and NPP.

Iron↑ NPP↑ pCO_2↓ POC_flux_100m↑ pN_2O↑ Offset Effect

Table 5. Mean annual change of the key biogeochemical variables in Test 1.

	ΔS_N_2O (Tg N/yr)	ΔpN_2O (ppb)	ΔpCO_2 (ppm)	ΔPOC_FLUX_100m (mg C /m^2/day)	ΔDIC (μmol/L)	ΔChla_tot (mg/m^3)	ΔPP (mgC /m^2/day)
SAZ	0.2010	2.9	-17.8816	48.5363	-4.5691	0.3841	165.9121
PFZ	0.2081	5.1	-20.4576	88.9511	-2.53	0.8623	272.0656
ASZ	0.1365	10.3	-29.0020	89.4247	-18.4588	1.1167	273.5460

Note. Positive values indicate increase relative to control group and negative values indicate decrease relative to control group.

N_2O Offsetting Effects

Table 6. Magnitude of N_2O Offsetting Effect (%).

	Test 1	Test 2	Test 3
	offset effect (%)	**offset effect (%)**	**offset effect (%)**
SAZ	11.07%	12.13% 12.27%	12.46% 8.65%
PFZ	17.78%	9.56% 10.94%	11.31% 13.66%
ASZ	25.43%	5.40% 15.69%	6.57% 10.05%

Note. Test 1/2/3 calculates the cumulative temporal integral of the fertilization-induced change of radiation feedback offset .

- ✓ **Offset Effect:** Convert the absorption of CO_2 and the emission of N_2O into CO_2 (units: t) equivalents (ΔCO_2-eq), and calculate the net radiation benefit through the GWP100 (Global Warming Potential over 100 years) ratio (N_2O being 265:1, IPCC, AR6):
- Net climate benefits (CO_2-eq) = $\Delta C\_CO_2 - (\Delta N\_N_2O \times GWP100\_N_2O)$
- $\% = [(\Delta N\_N_2O \times GWP\_N_2O) / \Delta C\_CO_2] \times 100\%$

- ✓ **Table 6.** Model simulations indicate that regional OIF experiments in the SO enhance the production of the greenhouse gas N_2O, thereby partially offsetting the carbon sequestration benefits of iron fertilization.
- ✓ The estimated range of the offset effect varies from **5.4% to 25.43%**, primarily depending on the **fertilization location, timing, and spatial extent.**

Conclusion

1、The negative feedback of Nitrous Oxide (N_2O) should be taken into account when considering the efficiency of iron fertilization (OIF)

2、The Polar Front Zone (PFZ) may be a compromise choice under the balance of fertilization efficiency and N_2O negative feedback

3、Medium scale area fertilization proves optimal as it can balance small-scale high-cost efficiency with the strong N_2O feedback from large-scale strategy


Thank you!
Comments and Questions?
TAN KAH KEE