


The ocean as a source of N_2O and CH_4

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Why are we interested in oceanic nitrous oxide (N₂O) and methane (CH₄)?

	Greenhouse gas	Stratos. O ₃ depletion	Tropos. chemistry	% contribution of oceanic areas to global emissions	Atm. mixing ratios
 N ₂ O	+	+		21 / 35 *	increasing
CH ₄	+	+	+	7 **	increasing

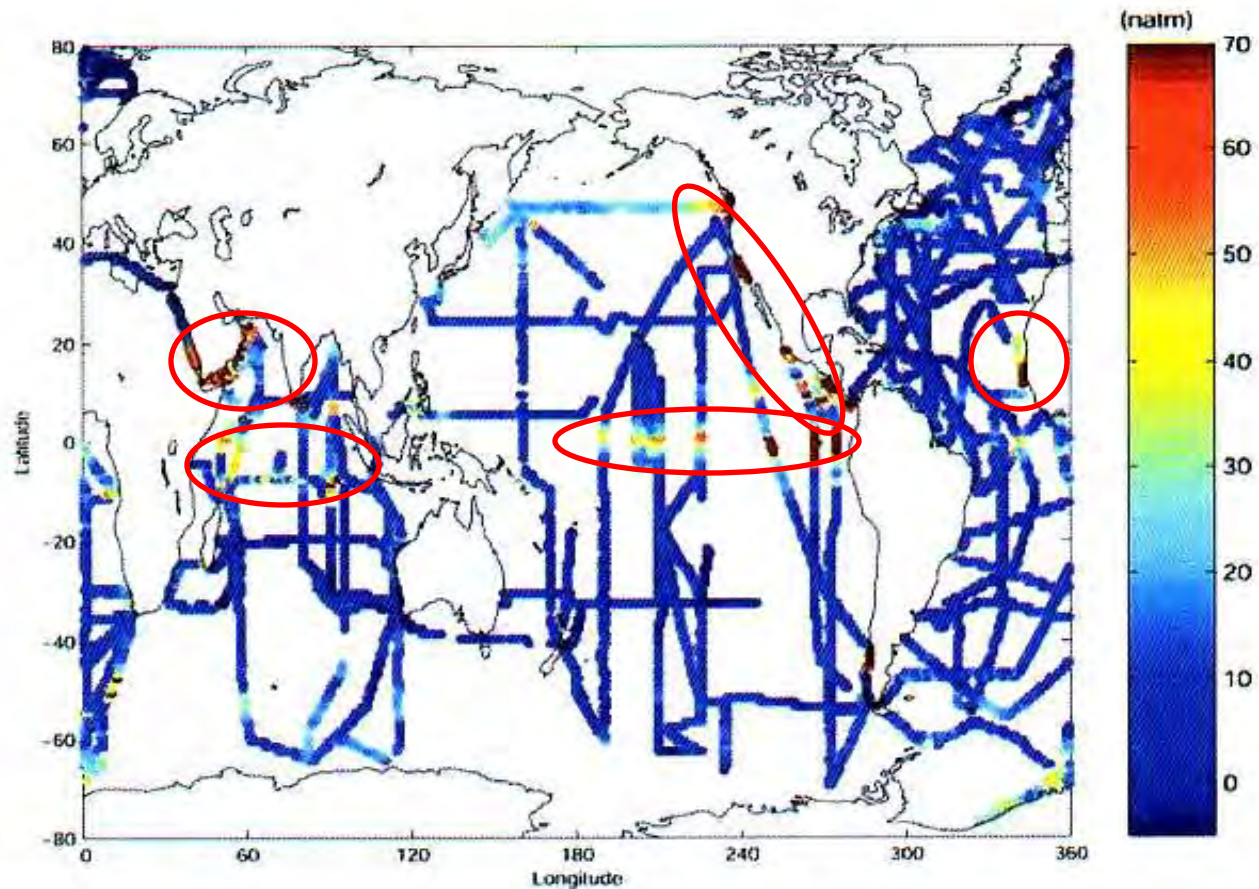
* total sources / natural sources (IPCC, 2013).

** = $100 \times 39 / 556$ (Bakker et al., 2014/IPCC, 2013).

Global distribution of surface ΔN_2O (in natm)

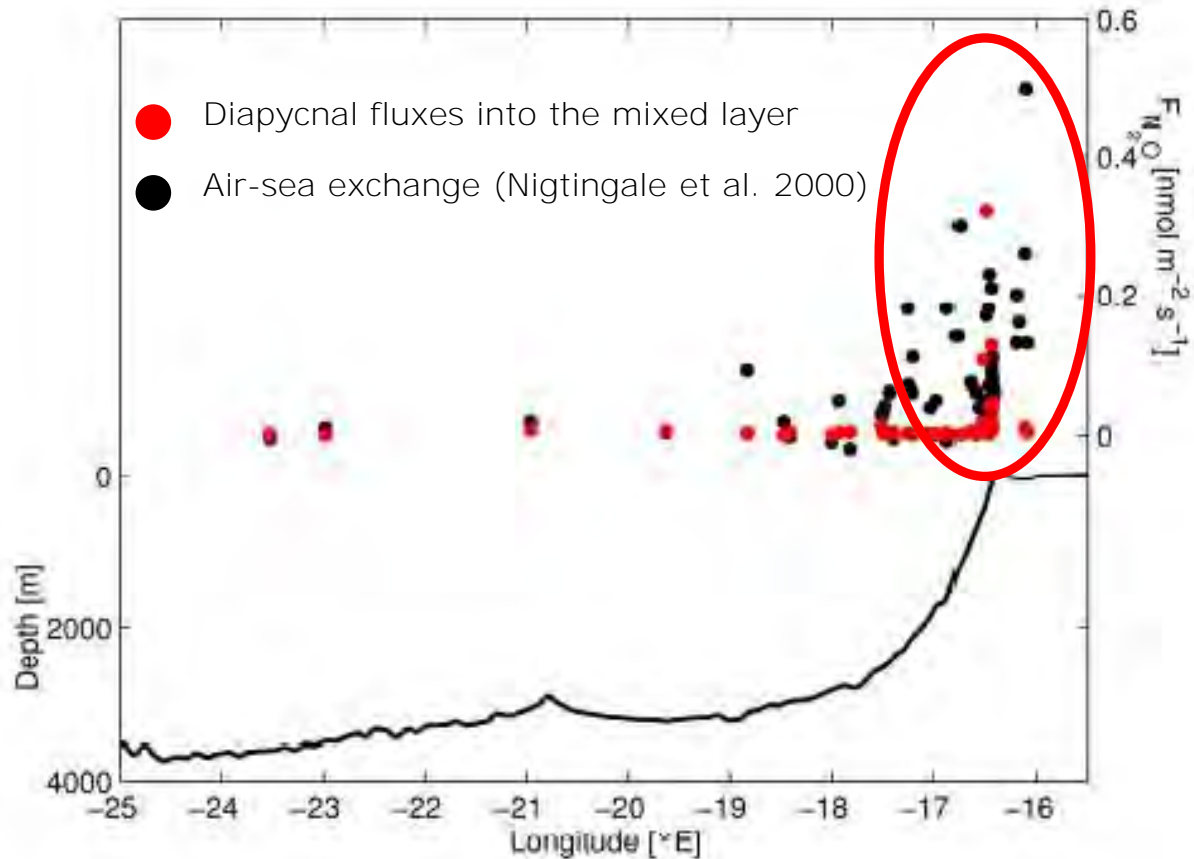
(Scripps & NOAA expeditions 1977-1996; Nevison et al., 2004)

$$\Delta pN_2O = pN_2O(\text{observed}) - pN_2O(\text{eq})$$



N₂O mixed layer fluxes in off Mauritania: diapycnal fluxes < air-sea exchange

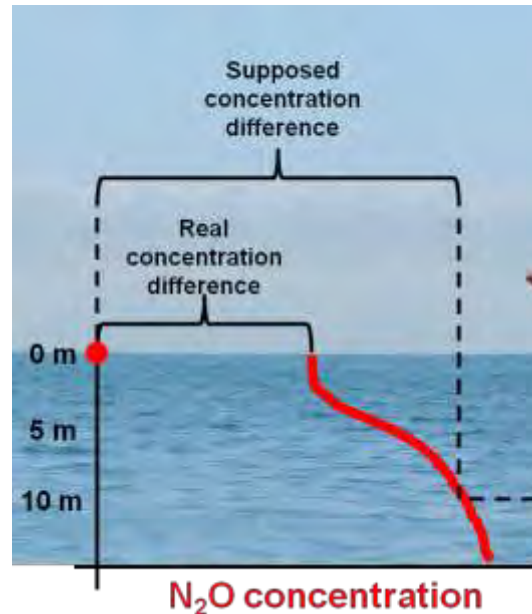
(Kock et al., 2012)



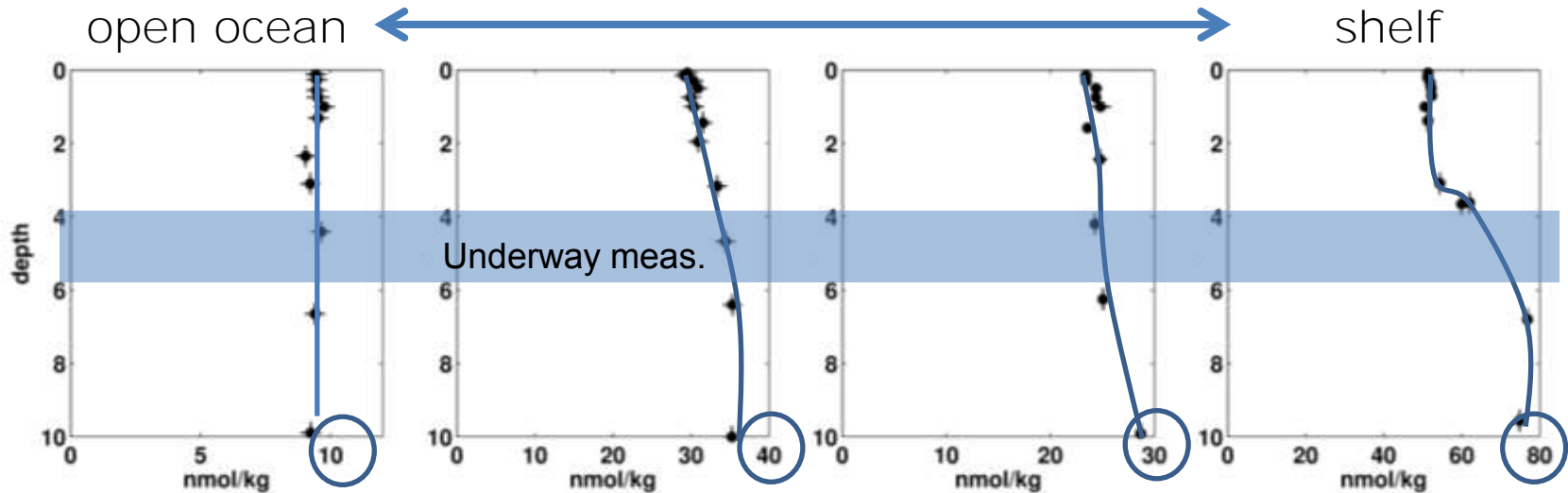
Inherent uncertainties of the N_2O air-sea flux density

$$F = k_w ([\text{N}_2\text{O}]_w - [\text{N}_2\text{O}]_{\text{eq}})$$

May be too high because of $[\text{N}_2\text{O}]$
gradients in the upper water column



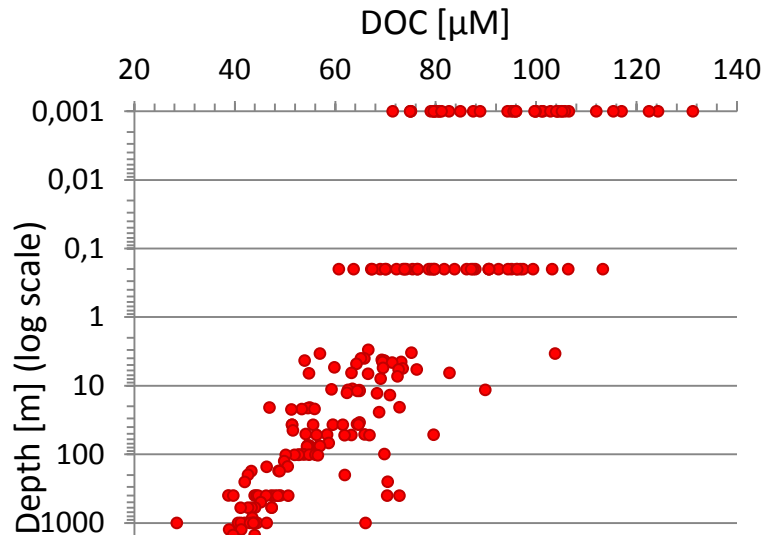
M91 (Peru upwelling): N₂O in upper 10m (Fischer et al., unpublished)



Inherent uncertainties of the N_2O air-sea flux density

$$F = k_w ([N_2O]_w - [N_2O]_{eq})$$

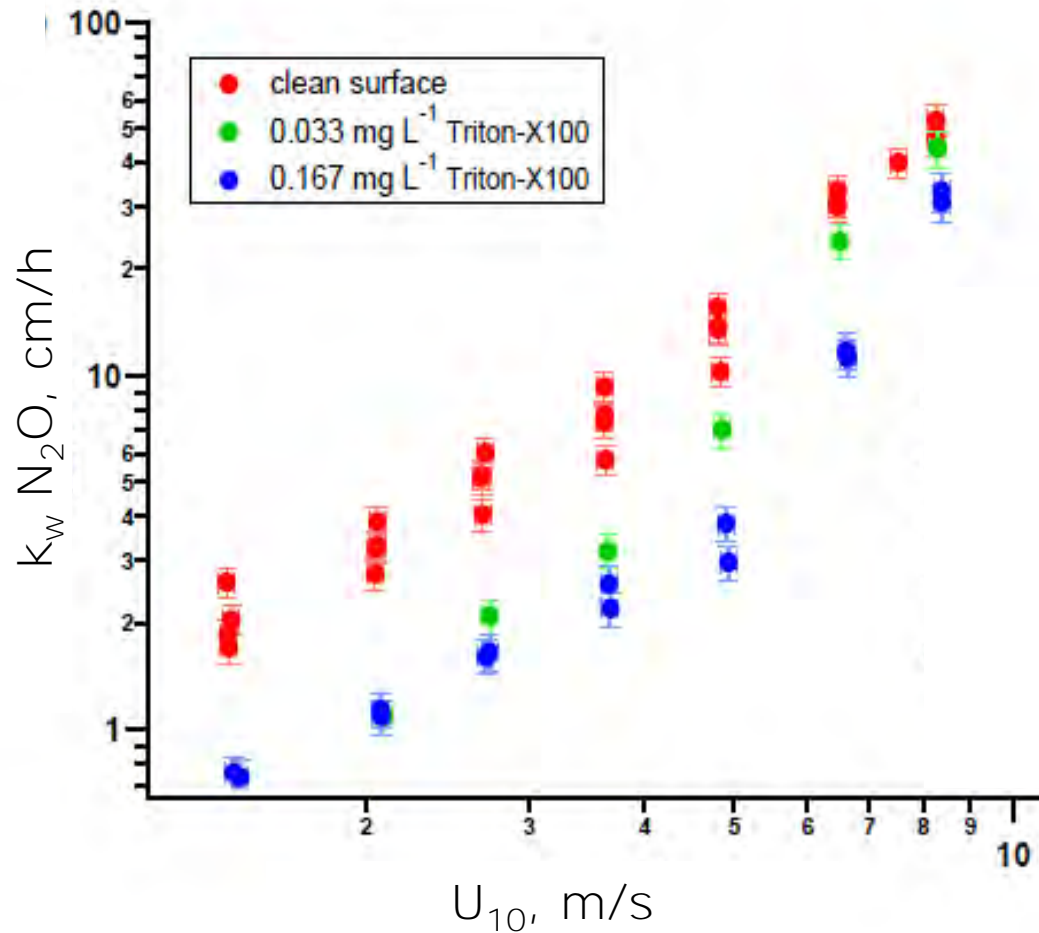
May be reduced by enrichment of
surfactants in sea surface micro layer



DOC data from M91, Galgani et al.

N₂O air-sea exchange is suppressed by surfactants

Results from a study in wind/wave tank (Aeolotron, U Heidelberg)
(Mesarchaki et al, 2015)



Short summary: N₂O

- The oceans are a major source of atm. N₂O
- Flux and emission estimates are still associated with a high degree of uncertainty
 - surfactants
 - conc. gradients towards air/sea interface
 - seasonal and interannual variabilities
 - ...

Why are we interested in oceanic nitrous oxide (N₂O) and methane (CH₄)?

	Greenhouse gas	Stratos. O ₃ depletion	Tropos. chemistry	% contribution of oceanic areas to global emissions	Atm. mixing ratios
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Why is the open ocean a CH₄ source at all?
 -> methanogenesis is strictly anaerobic!

N ₂ O	+	+	+	21 / 35 *	increasing
CH ₄	+	+	+	7 **	increasing

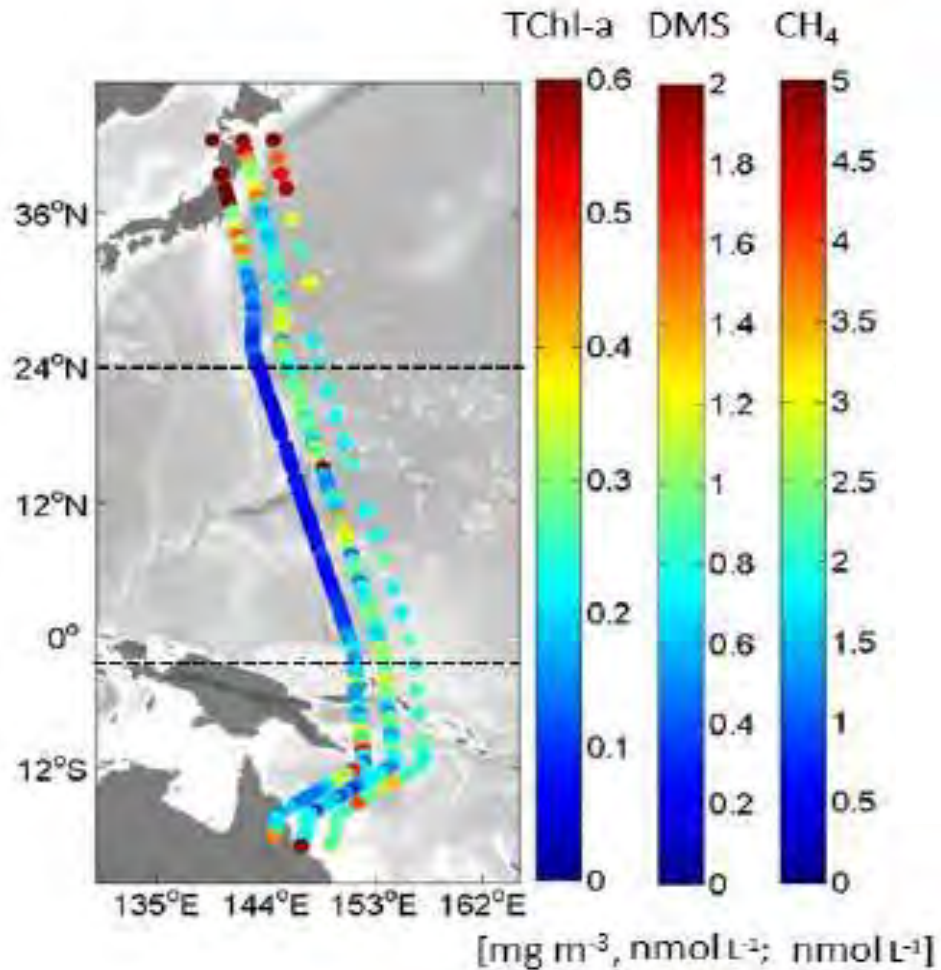
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CH₄ in the West Pacific Ocean

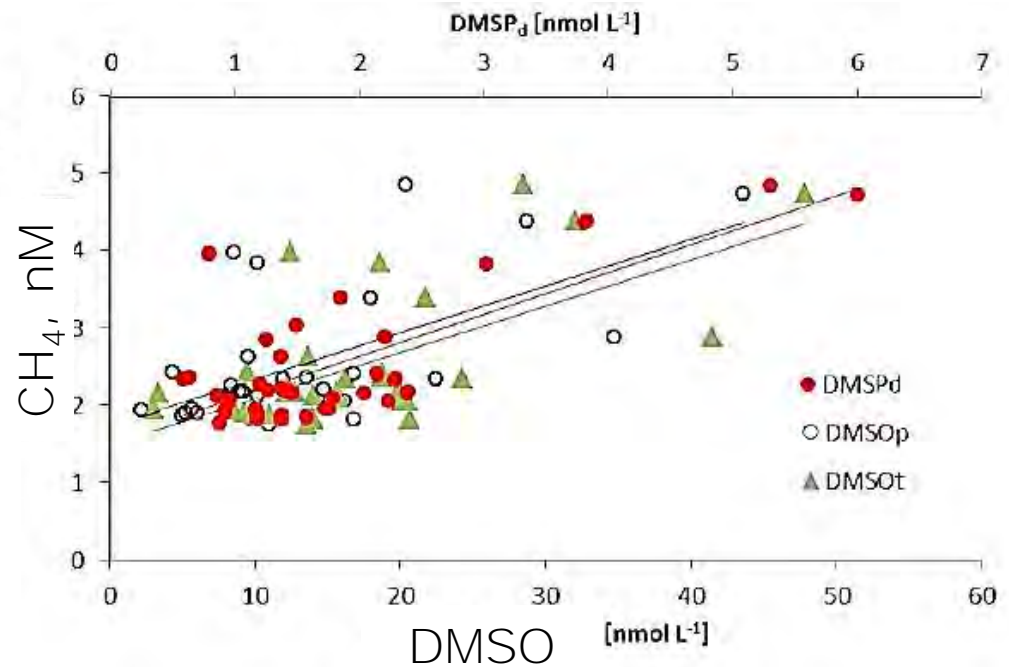
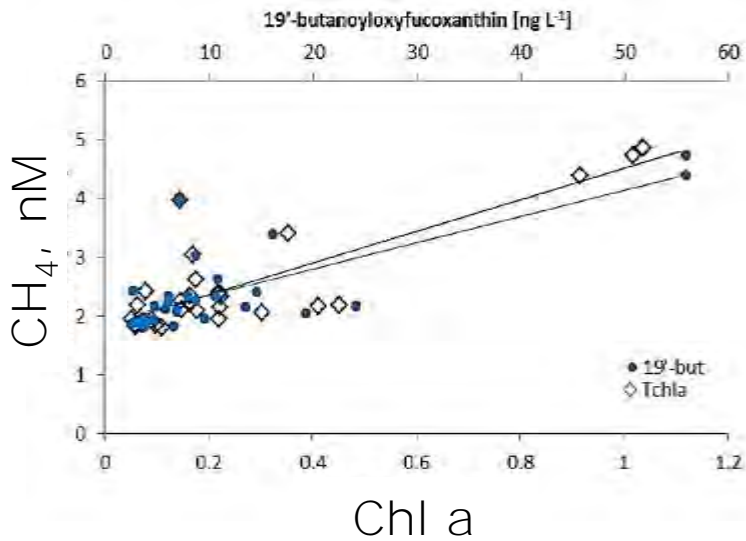
(TransBrom cruise, Oct. 2009)

(Zindler et al., 2013)



CH₄ in the West Pacific Ocean: Aerobic production in the surface layer?

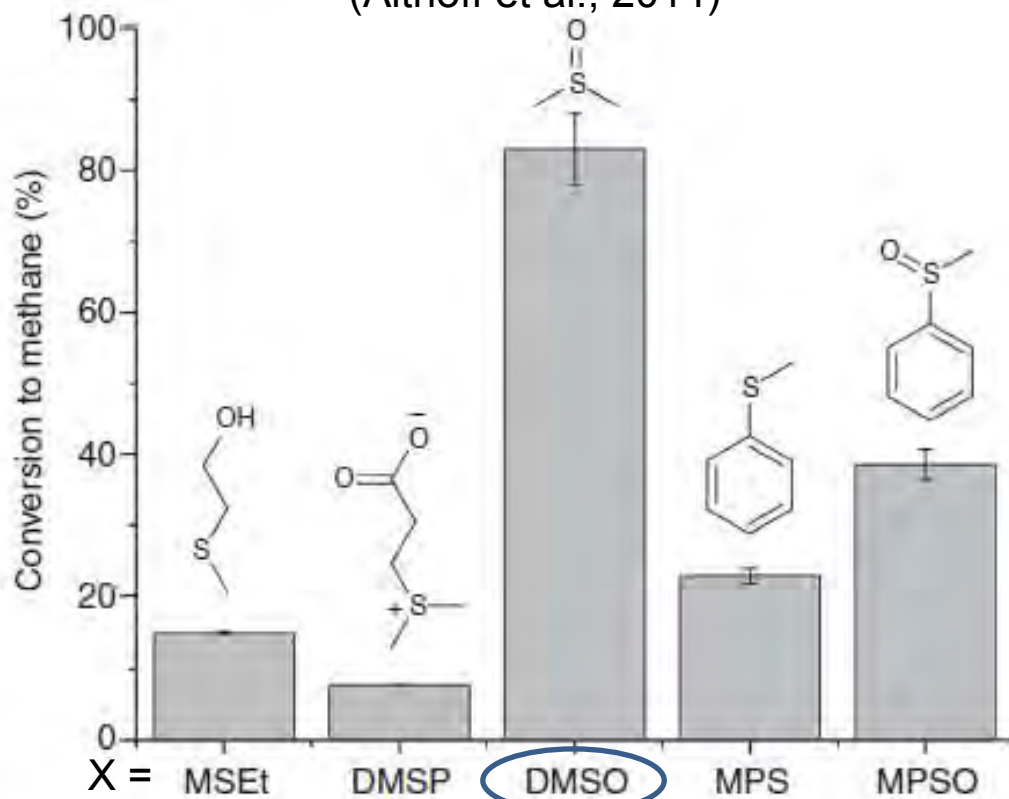
(Zindler et al., 2013)



DMSO =
dimethyl sulphoxide, (CH₃)₂SO

Abiotic methanogenesis from organosulphur compounds under ambient conditions

(Althoff et al., 2014)



In aqueous solution: $X + ASC + H_2O_2 + FH \rightarrow CH_4$

(ASC = ascorbic acid, FH = ferrihydrite, $5Fe_2O_3 \cdot 9H_2O$)

Short summary: CH₄

- The open ocean is a (minor) source of atm. CH₄
- There might be alternative CH₄ production pathways in the (oxic) upper ocean

Concluding remarks

- *There is a need to improve the estimates of oceanic emissions (= reduce the uncertainties: more data, better & comparable measurements)*
- *N₂O has been nominated one of only nine selected biogeochemical Essential Ocean Variables (EOV) by the International Ocean Carbon Coordination Project (IOCCP)*

What comes next?

- Establish a common measurement protocol for diss. concentrations
- Establish a global network of N₂O and CH₄ conc./flux measurements:
 - Time-series sites
 - Voluntary Observing Ship (VOS) lines
 - **(Sensors on floats, gliders, ...)**
 - Eddy covariance measurements: at coastal stations / on ships ?
 - ...