Diel and seasonal methane dynamics in the shallow and turbulent Wadden Sea

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Supplementary materials and methods

Endmember mixing modelling – Linear mixing of surface waters equilibrated with atmospheric CH_4 and bottom waters with maximum methane concentrations was modelled based on an endmember approach. Equilibrium with atmospheric methane was assumed for surface waters translating to CH_4 concentrations of ~ 3 nM (Wiesenberg and Guinasso, 1979) with a δD-value of ~ -85 ‰ (Whiticar, 1999). The second endmember was water with maximum CH_4 concentration in autumn at 3 m water depth at 0 h (i.e., 35.5 nM, δD-CH_4 = -254 ‰) and in summer at 3 m water depth at 36 h (i.e., 154.9 nM, δD-CH_4 = -250 ‰).

Rayleigh fractionation modelling - A Rayleigh fractionation model was constructed for hydrogen stable isotope compositions to test whether the enrichment in heavy isotopes (D) at low CH_4 concentrations was related to methane oxidation by methanotrophs (Whiticar, 1999). For this, samples with methane concentrations < 21 nM (δD-CH_4 = ~ -217 ‰) in autumn and < 61 nM (δD-CH_4 = ~ -244 ‰) in summer were defined as the methane source signal and thus the starting point of the Rayleigh fractionation model. These values were chosen because above these concentrations, the isotope effect imposed by MOx is masked by the high background CH_4 and/or is overprinted by methane entering the water column from sediments. The apparent isotope enrichment ε is then calculated according to an open system approach (Mariotti et al., 1981; Jacques et al., 2021):

$$\delta_s = \delta_{s,0} + \varepsilon_{open} \ln f \qquad (6)$$

Where δ_s and $\delta_{s,0}$ are the δD values of methane at a given concentration and of the source signal, respectively. f denotes the fraction of the remaining methane. Apparent ε-values for δD-CH_4 were -97.26 ‰ in autumn (Fig. S2) and comparable to previous reported fractionation factor (Jacques et al., 2021). Note that for δD-CH_4 in summer, there was no heavy isotope enrichment, precluding to calculate Rayleigh distillation for H/D in a well constrained manner.

Supplementary figures and tables

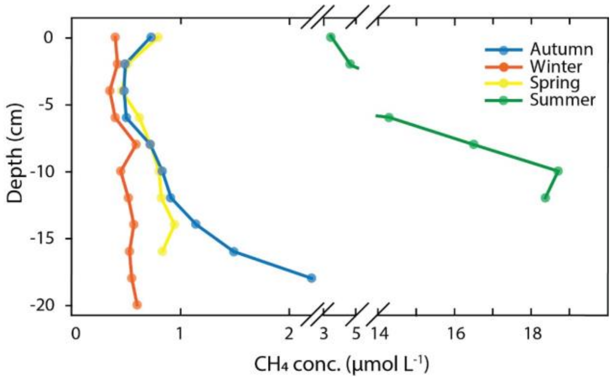

Figure S1. Concentrations of methane in sediments at the time-series station.

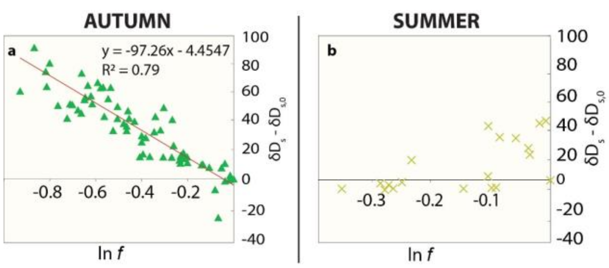

Figure S2. Rayleigh fractionation of stable hydrogen isotopes in (A) autumn and (B) summer. Samples with methane concentrations < 21 nM (δD-CH_4 = ~ -217‰) in autumn and < 61 nM (δD-CH_4 = ~ -244‰) in summer were defined as the methane source signal ($CH_{4(0)}$, δ_0). The apparent isotope enrichment ε was then calculated according to an open system approach. Note that δD-CH_4 values did not deviate consistently with methane concentrations <61 nM, precluding to calculate Rayleigh distillation for H/D in a well constrained manner.

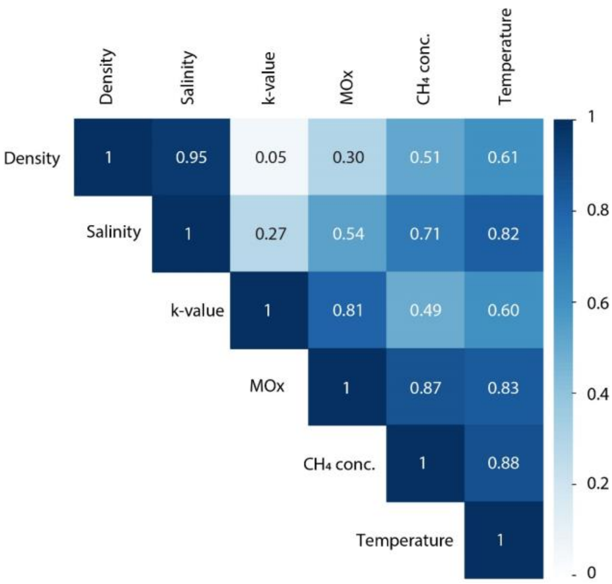

Figure S3. Pearson correlation matrix depicting the correlations between variables used in a principal component analysis.

Table S1. Differences in methane concentration, k, and MOx between tidal phases. Welch's t-test was applied to methane concentrations, first order rate constants and MOx at low tide and high tide. p-values marked in grey indicate non-significant differences ($p > 0.05$).

Season	Variable	LT (n)	HT (n)	Increase at LT vs. HT	Welch's t-test P(T<=t) two-tail
Autumn	CH_4 conc.	10	8	21%	0.34
Winter	CH_4 conc.	8	5	3%	0.47
Spring	CH_4 conc.	8	6	25%	0.13
Summer	CH_4 conc.	8	8	2%	0.94
Autumn	*k*	10	8	76%	0.003
Winter	*k*	8	5	8%	0.83
Spring	*k*	8	6	259%	5.5×10^{-5}
Summer	*k*	8	8	30%	0.07
Autumn	MOx	10	8	208%	0.03
Winter	MOx	8	5	9%	0.82
Spring	MOx	8	6	345%	6.4×10^{-6}
Summer	MOx	8	8	24%	0.38

Table S2. Contribution of individual variables to the principal components. Variables are centred and scaled before running PCA.

	PC 1	PC 2	PC 3	PC 4	PC 5
CH_4 conc.	20.1	0.49	40.34	6.57	32.49
k	9.72	32.51	42.77	0.55	14.43
MOx	18.5	14.13	2.41	13.09	15.79
Density	11.38	35.27	10.17	11.82	0.03
Temperature	22.31	0.02	0.72	67.72	0.87
Salinity	17.99	17.57	3.58	0.24	0.39

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