

## *Supplementary Datasheet S1*

# **Inter-Comparison of the Spatial Distribution of Methane in the Water Column from Seafloor Emissions at two Sites in the Western Black Sea Using a Multi-Technique Approach**

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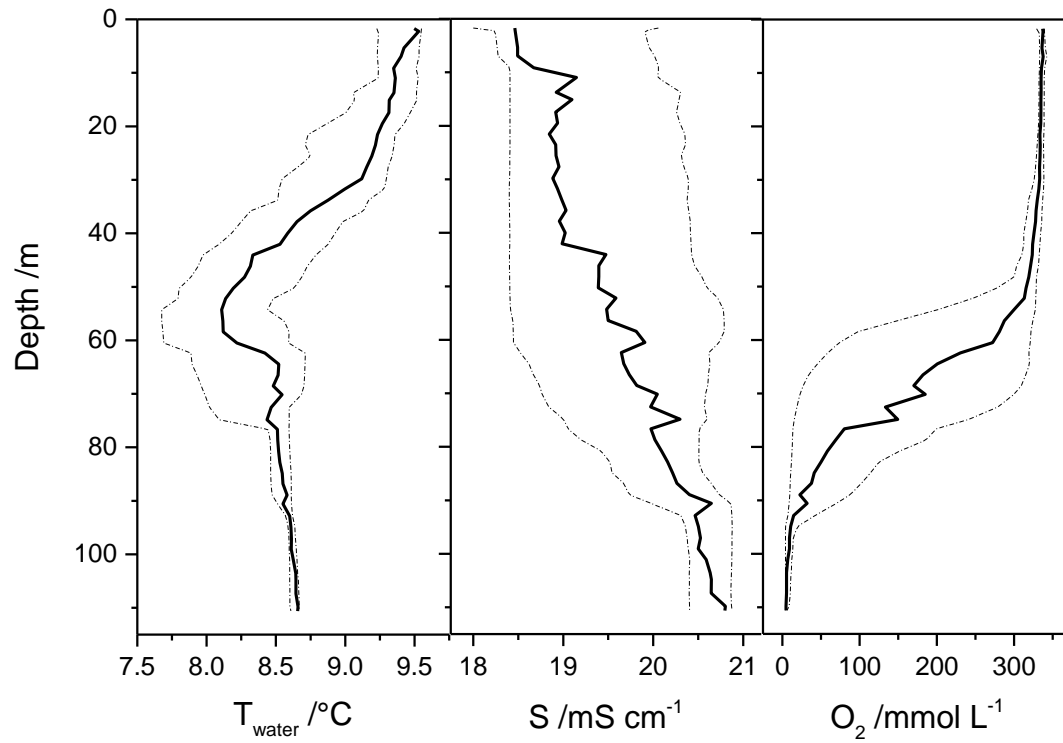
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Roberto Grilli

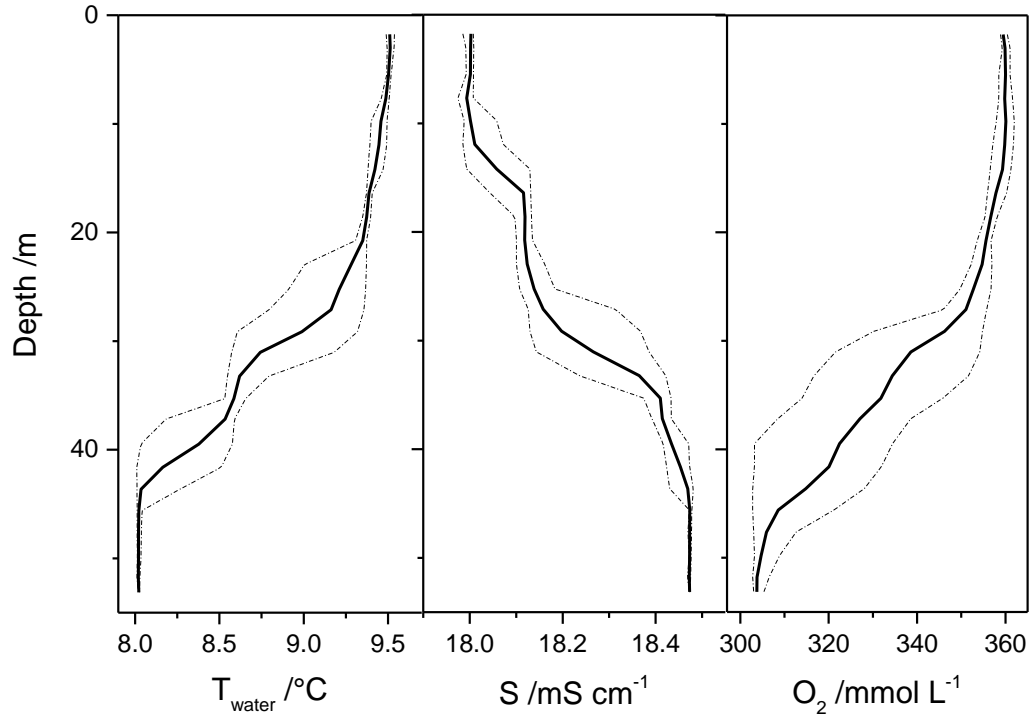
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## 1 Materials and methods

### 1.1 The study area



**Figure S1-1.** Temperature, electrical conductivity and dissolved oxygen data for the deeper site. In solid dark at 2-m average from the HY-01, -02 and -03 downward and upward profiles, and in dashed lines the minimum and maximum observed values.



**Figure S1-2.** Temperature, electrical conductivity and dissolved oxygen data for the shallower site. In solid dark at 2-m average from the HY-04 and -05 downward and upward profiles, and in dashed lines the minimum and maximum observed values. A problem in the water temperature measurement of the HY-04 upper-cast was found and this profile was therefore discharged.

## 1.2 The commercial sensor Franatech

The sensor provides a voltage for the methane sensitive element and a voltage for the temperature sensitive element. The models defined by the manufacturer are given by equations 1 and 2 below. The coefficients of the models were determined by the manufacturer following a calibration in February 2019.

$$c = e^{1,585 \cdot \ln \left\{ \left( 0,583 + 9,403 \cdot e^{-\frac{Vt}{0,450}} \right) \cdot \left( \frac{1}{VCH4} - \frac{1}{1,784 + 5,242 \cdot e^{\frac{-Vt}{1,104}}} \right) \right\}} \quad (1)$$

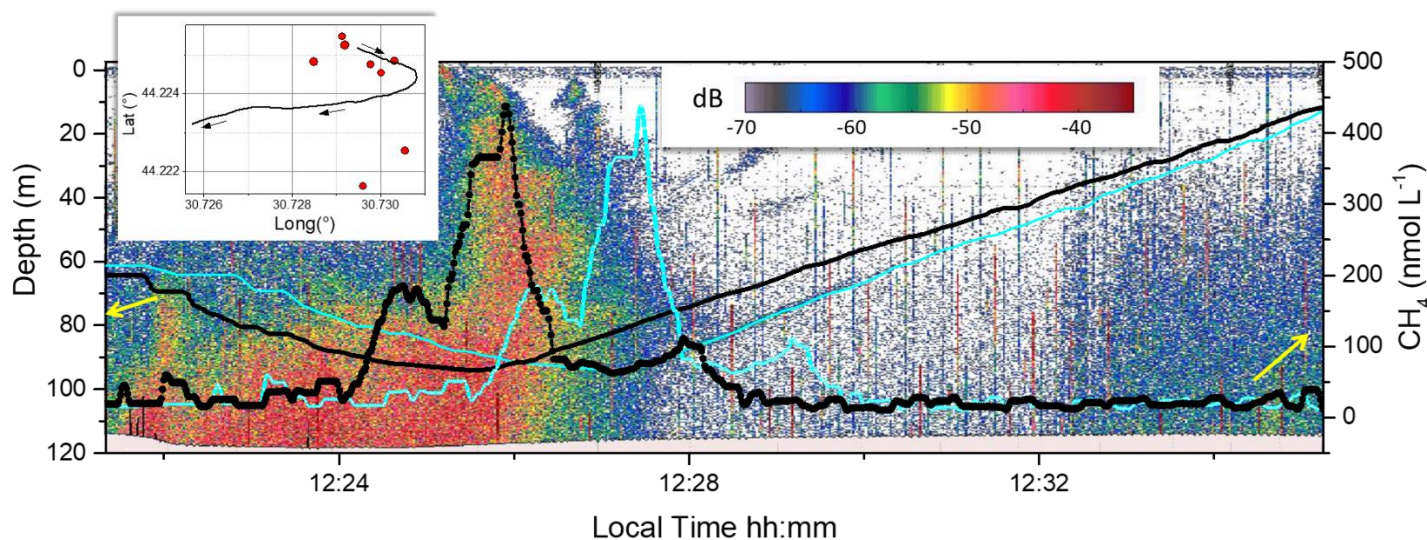
$$t = 23,27 \cdot Vt - 7,07 \quad , \quad (2)$$

With  $c$  the methane concentration ( $\mu\text{mol L}^{-1}$ ),  $t$  the gas temperature ( $^{\circ}\text{C}$ ),  $VCH4$  the methane concentration in voltage (V),  $Vt$  the temperature value in voltage (V).

## 2 Results: inter-comparison between the techniques

## 2.1 Qualitative comparison of MILS and echosounder data

In Figure S1-3, the two time-series of MILS and acoustic data are reported. The MILS data with the original timestamp is shown in light blue. The water depth profile matches well the acoustic trace produced by the backscattering from the instrument (dark blue scattering dots underneath the light blue trace), visible up to a 60 m water depth. At shallower depths, the MILS instrument was outside the lobe defining the insonified volume of the echosounder, and is therefore no longer acoustically visible. The concentration of dissolved methane determined by MILS, together with the depth of the probe, were dynamically corrected for the position of the instrument with respect to the vessel and reported in black. This correction allows to synchronize/match the two time-series, accounting for the fact that echosounder passed over a target area prior the towed MILS instrument.

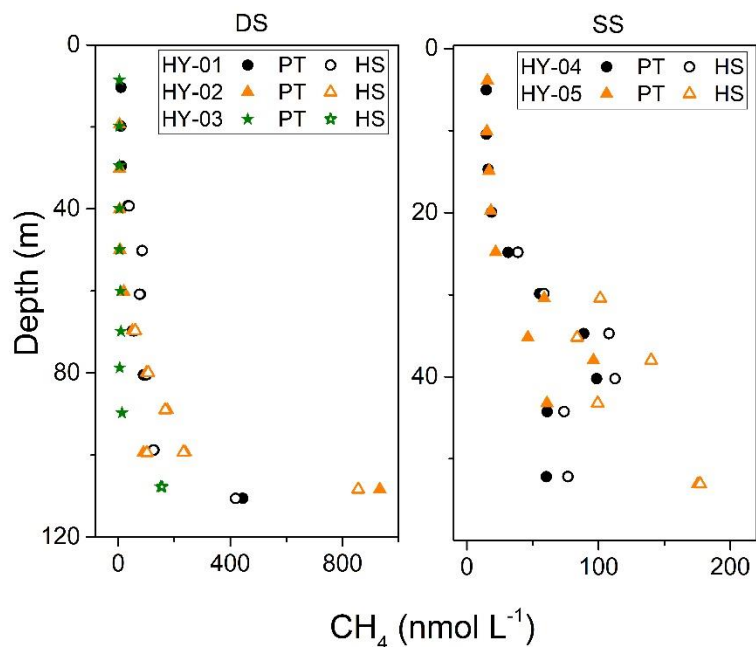


**Figure S1-3.** Qualitative comparison between the time series from the continuous concentration of dissolved methane measured by MILS and the acoustic signal from the echosounder. The data are from the VP03 profile performed on April 5th at the deeper site (44.224° N, 30.730° E) and are plotted against local time. The dissolved CH<sub>4</sub> and depth data with the original timestamp of the instrument are reported in light-blue, while in black the data were dynamically synchronized with the acoustic signal by accounting for the lag between the instrument and the vessel. Yellow arrows provide the link of the data with the axes. The water depth was measured by the MILS instrument as well as by the CTD. The echogram in the background shows the backscatter target strength values (color bar represents the intensity in dB). In the insert the trajectory of the MILS sensor during the transect with arrows showing the direction. Red dots indicate the position of identified flares.

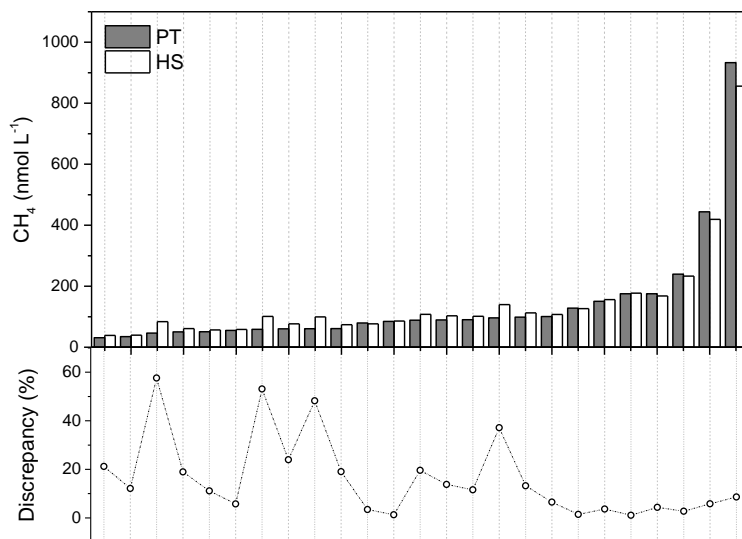
## 2.2 Inter-comparison between the two discrete measurement approaches

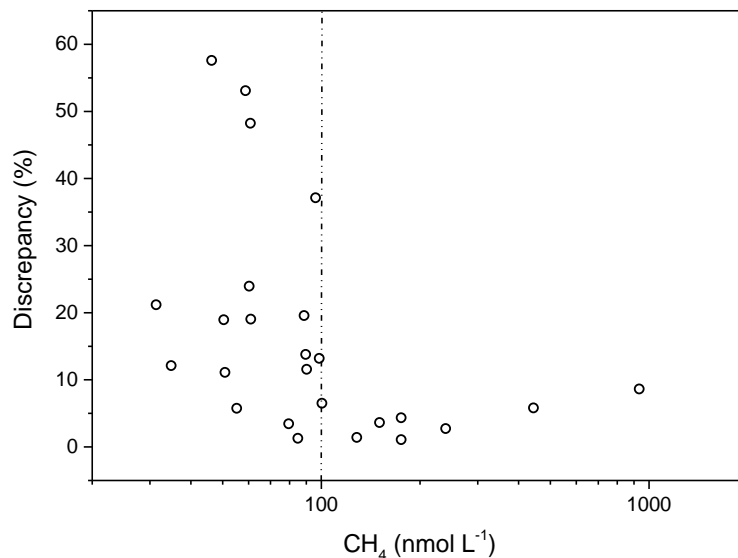
An inter-comparison between the two on-shore approaches (PT vs HS, Figure S1-4) for measuring dissolved CH<sub>4</sub> from the sampled water is proposed here. Three and two independent profiles were performed at different location in the DS and SS, respectively. The average discrepancy was 7.5 % and 27.3 % for the DS and SS, respectively, which translates into an agreement within 10% for concentrations higher than 100 nmol L<sup>-1</sup>, while at lower concentrations, the discrepancy increases up

to 58% (Figure S1-5). This has to be attributed to the lower precision of the HS since this method uses smaller amount of sample than the PT technique (Wilson et al., 2018).



**Figure S1-4.** Comparison between the data from purge and trap (PT) and the headspace (HS) technique for the deeper, DS and shallower, SS site. PT and HS analyses were performed on the same water samples, from five independent profiles.

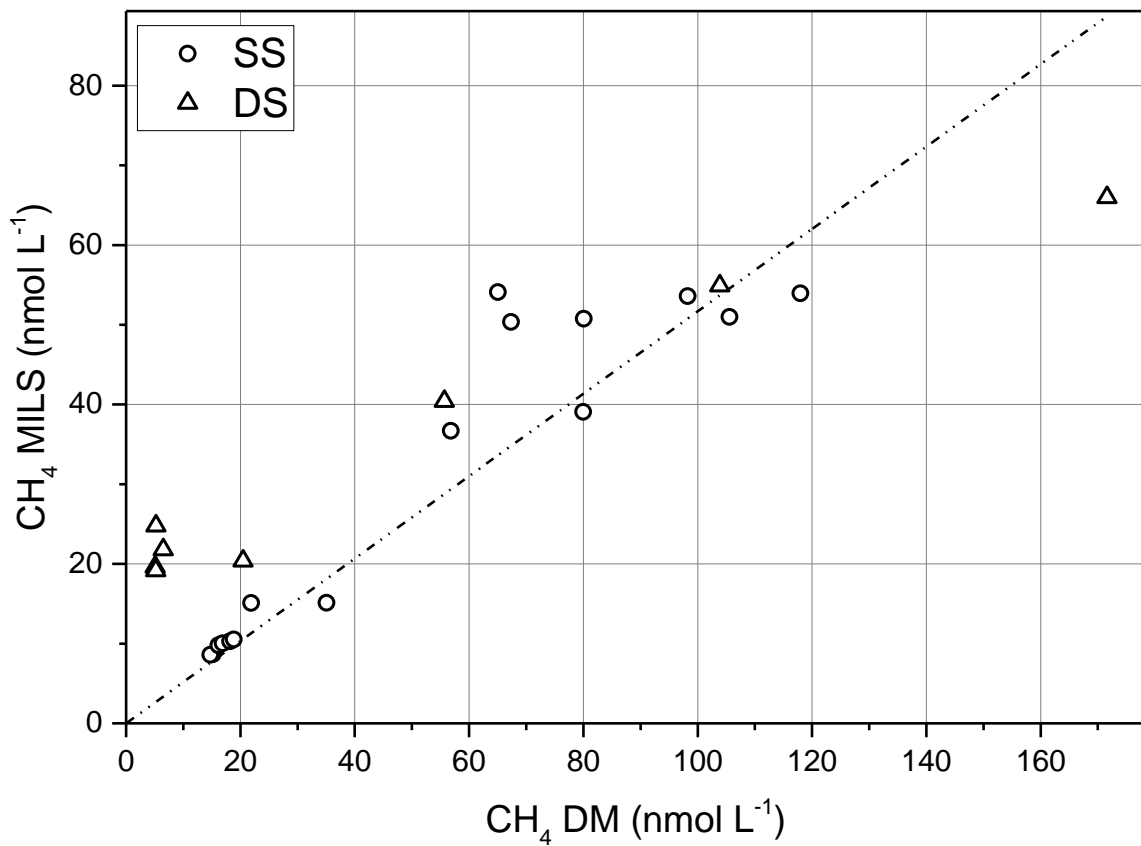




**Figure S1-5.** Comparison between the two on-shore methods for dissolved methane: purge and trap (PT) vs headspace (HS).

### 2.3 MILS vs discrete water sampling measurements at the deeper and shallower sites

The comparison between dissolved methane measurements performed by the *in situ* MILS and discrete water sampling followed by purge-and-trap and headspace measurements at the two sites is reported in Figure S1-6. Data from continuous MILS dataset was extracted at the depths of the discrete sampling, for a total of 24 measurements points at the two locations. By making a correlation, a slope of 0.52 was found, which in one hand may suggest a bias on the measurements. However, since the measurements were not conducted neither at the same time and exact location, by looking at the scattering of the data with some MILS data even higher or similar to the ones from discrete measurements, one can conclude as well that this comparison is strongly affected by spatio-temporal variability of the water masses and that it suffers from a number of observations ( $n_{\text{obs}} = 24$ ) insufficient for a consistent statistical analysis.



**Figure S1-6.** Comparison between dissolved methane measurements performed by the *in situ* MILS sensor and discrete water sampling followed by laboratory analysis (discrete measurements, DM). DM data are an average between the results from the two analytical techniques. Data from MILS were extracted at the corresponding discrete sampling depths. The slope (0.52) suggests a systematic bias on the measurements. However, the large discrepancy may be simply due to the fact that the measurements were not performed at the same time and location. This hypothesis is supported by the fact that there are data points where the MILS measurements are higher or closer to the concentration of discrete measurements.