



EGUsphere, referee comment RC1

<https://doi.org/10.5194/egusphere-2022-325-RC1>, 2022

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## Comment on egusphere-2022-325

Anonymous Referee #1

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Referee comment on "Seasonal study of the Small-Scale Variability of Dissolved Methane in the western Kiel Bight (Baltic Sea) during the European Heat Wave in 2018" by Sonja Gindorf et al., EGUsphere, <https://doi.org/10.5194/egusphere-2022-325-RC1>, 2022

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### General Comments

The present paper is dealing with an important scientific topic in marine science: the impact of heatwaves on methane fluxes from coastal waters. It presents a long term temperature and methane dataset combined with a dataset obtained during the summer season 2018 (data includes CH<sub>4</sub>, T, O<sub>2</sub>), a year in which northwestern Europe experienced a pronounced heatwave. Studies were conducted in the Kiel Bight and Eckernförde Bay (Baltic Sea) and compared with methane datasets from summer 2018 obtained in the North Sea and northern Baltic Proper. In contrast to the last two publications, the present manuscript could not find any significant water column methane enrichments related to the heatwave induced temperature increase (enhanced sedimentary methanogenesis). This makes in my opinion the dataset very valuable, even though the authors do not have any explanation for their differing observation.

The work is complemented by (1) the description of an improved Purge and Trap (P&T) method to measure methane concentrations in high quality and (2) high resolution surface water data to show the inhomogeneity in the distribution within the upper 2 m of the water column. Part (1) is quite interesting, whereas Part (2) is a bit disconnected from the main story (heatwave-CH<sub>4</sub>), but nevertheless quite interesting. I suggest discussing the high resolution CH<sub>4</sub> measurements in context to the methane distribution in the deeper water. Also some parts regarding the surface water sampling in the discussion section could maybe moved to the method section.

Altogether, the work addresses a relevant scientific topic and presents a novel and valuable dataset. The paper is well written, structured and clearly outlined (written in a focused way). The method section (especially the description of the new P&T method) is precisely described and the recent literature cited in the text. The abstract reflects the overall work, the summery seems to my opinion a bit too long and could be shortened (maybe a bit repetitive for such a short paper). The figures are excellent but the authors should take care with the size of the letters, they are sometime difficult to read (e.g. Fig. 10).

Overall, the paper is of good and solid quality and I recommend publication after minor revision.

AC: Thank you very much.

### Detailed comments

## Title

"Heat Wave" or Heatwave (as written I the following text)?

AC: corrected to 'Heatwave'.

## Introduction

Line 20

"with a significantly improved precision" Compared to what? Do you mean, compared to other P&T systems described so far in the literature. If so, a direct comparison is missing in the manuscript.

AC: compared to samples measured with static headspace equilibration that has been used in our lab before. A comparison is shown in the method section but we will add the information to this sentence.

Line 44

What about photochemical reactions that leads to the formation of CH<sub>4</sub> in surface waters?

AC: Thank you for pointing to the photochemical production. We will add 'A photochemical production of CH<sub>4</sub> in oxic surface layers of the coastal and open oceans was suggested only recently as an alternative, non-biological, production pathway (Li et al., 2020)'. Li, Y., Fichot, C. G., Geng, L., Scarratt, M. G., and Xie, H.: The Contribution of Methane Photoproduction to the Oceanic Methane Paradox, *Geophysical Research Letters*, 47, e2020GL088362, 2020.

Line 85

Florian Roth et al. (2022, *Global Change Biology*) showed in a recent paper that a high sampling intensity is required to capture coastal CH<sub>4</sub> variability. Do you think it is likely that you missed something with your sampling strategy?

AC: We agree. Indeed, a higher sampling/measurement frequency might have revealed small scale variabilities. Unfortunately, a high-resolution CH<sub>4</sub> measurement system (such as laser-based cavity enhanced absorption spectrometer) was not available at the time of our study.

Line 86

I could not find Ho et al. (2019) in the reference list.

AC: Thank you for pointing this out. Ho, D. T., Marandino, C. A., Friedrichs, G., Engel, A, Booge, D., Bange, H. W. , Barthelmess, E.T., Fischer, T., Koffman, T., Lange, F., Quack, B., Paulsen, M., Schlosser, P. and Zhou, L. (2019) Baltic Sea Gas Exchange Experiment (Baltic GasEx). Open Access [Poster] In: SOLAS Open Science Conference 2019. , 21.-25.04.2019, Sapporo, Japan .

Line 94

"higher resolution" What does it mean: mm scale? Not clear at this point.

AC: It is related to sampling the upper 1 m in 3 depths (10, 50 & 100 cm) which is a higher resolution compared to our usual 1 m sample for the surface. In order to avoid any misunderstanding we will delete 'in higher resolution'.

## Methods

Line 124

Can you be sure that no methane is left in the gas phase of the emptied bottle? Or will the gas phase also be transferred into the purge bottle with the gas stream. Was this tested?

AC: Different tests were performed. 1. We tested calibrations with different purge times between 2.5 and 15 minutes and found the best performance for 4 minutes. 2. We analysed 3 blanks after each standard measurement to make sure blanks were the same as before a standard injection and would not decrease in peak area. 3. On every measurement day we first purged a sample, then ran 3 blanks with that sample remaining in the purge chamber and then injected all our standards for calibration into the filled purge chamber.

Line 135

Why do you need a filter?

AC: Just a first step to stop water droplets from moving into the system

Line 170

You mentioned before that the new P&T is characterized by a "significantly improved precision". Do you mean in comparison to the headspace method? What is the main difference of the new system in comparison to already published systems?

AC: see reply above.

Line 217

„25m water depth" Here and elsewhere (see Fig. 8), please do not forget the space between „25 m".

AC: thank you for pointing this out. This will be corrected in the revised version.

Line 227ff

" $\Delta\text{CH}_4$  i, avg" is not described in the text.

AC: Thanks for pointing this out. We added the description of " $\Delta\text{CH}_4$  i, avg" in the text as follows: " $\Delta$  ( $\Delta\text{CH}_4$ ) is calculated similarly to  $\Delta T$  in the same time period using  $\Delta\text{CH}_4$  which is the monthly excess  $\text{CH}_4$  ( $\Delta\text{CH}_4$ , see above) in 1 (25) m depth.  $\Delta\text{CH}_4$  i, avg is the mean excess  $\text{CH}_4$  in 1 (25) m depth of the respective month i over this period at Boknis Eck."

Line 284

"oversaturation" is not displayed in Figure 5.

AC: you can see in figure 9 that the surface water  $\Delta\text{CH}_4$  values are positive most of the time which means the surface water was oversaturated with regard to the atmosphere. This would be very hard to read from figure 5 as it only shows concentrations. We will add a reference to figure 9.

## Discussion

Line 305

"However,..." I do not really understand this sentence. May this needs to be rephrased or your thoughts better explained.

AC: We will delete the sentence ('However, ...') and modify the previous sentence: 'It is rather the result of recent local  $\text{CH}_4$  release either at the BE site itself or advected to the BE site by the bottom waters.'

Line 320

Even if it is difficult from your dataset to explain the differences between the two published works and your own observations, it would be interesting to extend the

discussion here: What could be the reason for this discrepancy and the lack of methane enrichment in the Kiel Bight during the heatwave.

AC: We agree and will expand the discussion of the difference between our results and the other studies. We will include differences in the stratification regimes (Belgian coastal waters are well mixed throughout the year in contrast to Baltic Sea waters). Moreover, we will include a discussion on how warming will affect both CH<sub>4</sub> production and consumption processes which may have led to the low CH<sub>4</sub> concentration anomalies at BE.

Line 332ff

Do you mean that the increase in  $\Delta\text{CH}_4$  after 2013 is displayed by the three peaks in Figure 8 in 2014, 2016 and 2018? Or are these peaks related to storm events and the concurrent release of sedimentary methane by methane bubble emissions (Lohrberg et al. 2020, SRep)? Line 336

AC: Indeed, there are events with very high CH<sub>4</sub> concentrations which were attributed to major North Sea water inflow events and sedimentary CH<sub>4</sub> release. However, these events occurred in November 2013, March 2014 and December 2014 (see Ma et al., 2020, Lohrberg et al., 2020). The peaks of the CH<sub>4</sub> anomaly in the deep waters at BE in 2014, 2016 and 2018 (see Figure 8) do not seem to be related to storm events.

As I mentioned above, this part is interesting but a bit disconnected from the main story. The presented methane concentration data is not discussed in context to the heatwave and the methane data set presented in the deeper water (Figure 4 and 5). Not really sure if this is needed for the manuscript or if this could be better moved to the method section (or supplement).

AC: We agree. We will move Section 3.5 to become the new Section 3.3. With this the connection to the measurements described in Section 3.1 and 3.2 will be highlighted. Do you have any suggestion how the sampling of surface water should be performed in the future? What kind of process could drive the inhomogeneity of methane concentrations in the uppermost part of the water column (wind, temperature, oxidation,...)?

AC: Future measurements of the surface water should include high-resolution time series measurements of the physical, biological and chemical settings in the upper m of the water column (incl. the so-called surface microlayer). Moored buoys may be a suitable platform to carry sensor arrays for time-series measurements. We may speculate that temperature changes can induce small scale stratification events (see Fischer et al., 2019), whereas CH<sub>4</sub> production via photochemical production from CDOM may occur in the SML.

Line 346

Are the 2 m samples in Figure 10 taken with a Niskin bottle or UW ship sampling as mentioned in the figure caption?

AC: The 2 m samples were taken from the UW system.

Line 350

Might be good to explain what you mean with "carry over effect".

AC: We closed the bottles during the upcast. That means that while moving up we might bring bottom waters up a bit.

## Summary

Maybe a bit too long for such a short manuscript. I suggest a shortening of the conclusion.

AC: we will shorten it, see our reply below

Line 365

Is this paragraph really needed in a conclusion?

AC: We will delete the paragraph.

Line 417

„HB“ should be „HWB“

AC: Will be corrected.

## Figures

Figure 1

An overview map of the Baltic Sea is missing.

AC: We will add a map.

Figure 4 and 5

Station numbers are displayed for B but not for A. Why? It might be good to mention that the color scales in Figure 4 and 5 are different.

AC: Station numbers were only needed for methane discussion but will be added to the ancillary parameters as well. We will add one sentence about the different color scales.

Figure 9

Might be better to mention the months instead of the cruise name in the figure caption.

AC: We agree and we will modify the figure captions.

Figure 10

Not sure, if the samples at 2 m water depth were taken with the UW ship sampling and not with the Niskin bottle? The time lag between zodiac and UW sampling is relevant and might have a crucial impact on the methane concentrations. What you see is maybe not indicating a real gradient but rather variability as indicated by your error bars. Size of the letters is too small.

AC: Samples from 2 m water depth were taken with the UW system. The size of the letters will be increased. The time lag was always within one hour. We will take variability into consideration and rewrite the paragraph.