Author's response

Review 1

Title

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

Response: 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.

Response: we added “with a significantly improved precision for the CH4 concentration measurements compared to static headspace equilibration measurements” to the text (line 20-21, abstract). In chapter 2.3 this is discussed more detailed and figure 3 and table 1 show the comparison of the two methods and underline this statement.

Line 44

What about photochemical reactions that leads to the formation of CH4 in surface waters?

Response: line 46-48: We added a sentence ‘A photochemical production of CH4 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 CH4 variability. Do you think it is likely that you missed something with your sampling strategy?

Response: we included a statement on this issue and cite Roth et al. (2022) in the conclusion (see lines 438-440)

Line 86

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

Response: the reference list is updated and includes this reference now: Ho, D. T., Marandino, C. A., Friedrichs, G., Engel, A., Bange, H., Barthelmess, T., Fischer, T., Koffman, T., Lange, F., Quack, B., Paulsen, M., Schlosser, P., and Zhou, L.: Baltic Sea Gas Exchange Experiment (Baltic GasEx), https://oceanrep.geomar.de/id/eprint/53496/, 2019. (line 524-527)

Line 94

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

Response: we deleted '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?

Response: A reference to the Master Thesis by Gindorf, where all performed tests are described in detail, was included: "The materials that were used and all performance tests that were carried out are described in detail elsewhere (Gindorf, 2020)" in line 119-120.

Gindorf, S.: Development of a Purge + Trap System for the Quantification of Methane Variability in the Baltic Sea, 81 pp., https://oceanrep.geomar.de/id/eprint/51326, 2020.

Line 135

Why do you need a filter?

Response: We deleted the sentence but the full set up is described in a reference (see last comment).

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?

Response: see replies above.

Line 217

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

Response: all units in the MS were double-checked and corrected.

Line 227ff

“ΔCH4 i, avg” is not described in the text.

Response: We added “Δ (ΔCH4) is calculated similarly to ΔT in the same time period using ΔCH4 which is the monthly excess CH4 (ΔCH4, see above) in 1 (25) m depth. Δ CH4 i, avg is the mean excess CH4 in 1 (25) m depth of the respective month i over this period at Boknis Eck.” (lines 229-232).

Line 284

“oversaturation” is not displayed in Figure 5.

Response: we added a reference to figure 6 which shows that the surface water ΔCH4 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.

Discussion

Line 305

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

Response: We deleted the sentence (‘However, …’) and changed the previous sentence: ‘It is rather the result of recent local CH4 release either at the BE site itself or advected to the BE site by the bottom waters.’ (line 338-339)

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.

Response: an extended discussion of the differences between Boknis Eck, the Belgian coastal site and the Tvärminne coastal site was added (lines 364-392).

Line 332ff

Do you mean that the increase in ΔCH4 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

Response: Indeed, there are events with very high CH4 concentrations which were attributed to major North Sea water inflow events and sedimentary CH4 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 CH4 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).

Response: The old Section 3.5 is now Section 3.3 to highlight the connection to the measurements described in Section 3.1 and 3.2.

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,…)?

Response: our suggestions are summarized in line 436 ff.

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?

Response: The 2 m samples were taken from the UW system. This information is included in the figure caption (now figure 7).

Line 350

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

Response: we added the sentence “This can result from closing the Niskin bottles during the upcast, so that deeper waters might be brought up.” (line 306 f.)

Summary

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

Line 365

Is this paragraph really needed in a conclusion?

Response: We deleted the first paragraph of the conclusion.

Line 417

„HB“ should be „HWB“

Response: This has been corrected.

Figures

Figure 1

An overview map of the Baltic Sea is missing.

Response: We added an overview map of the Baltic sea and coastal North Sea and also included the research areas of Borges et al., 2019 and Humborg at al., 2019.

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.

Response: The figures have been updated and now include the same station numbers. The seasonal comparison now starts with the sentence “Please note that when comparing June and September data from figures 4 and 5, different colour schemes were used to emphasize gradients within each cruise.” (line 321 f.).

Figure 9 (now figure 6)

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

Response: All figure captions now include the months.

Figure 10 (now figure 7)

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.

Response: Samples from 2 m water depth were taken with the UW system. The size of the letters has been increased. The time lag was always within one hour. We agree that variability is important to take into consideration which is discussed in line 299 ff. and emphasized in the conclusion. However, as stated in the MS we observed “larger concentration differences between 0.1 and 1 m (0.2-2.7 nmol L-1) than between 1 and 2 m (0.1 -1.8 nmol L 1, mean difference between CH4 gradients: ~1 nmol L 1) during the AL 516 cruise” so the variability in between the zodiac samples is larger than between zodiac vs. UW.

Review 2

The authors report a valuable time-series of CH4 in Eckernförde Bay. Such a data-set is precious because long time-series of CH4 are very rare in marine environments. Yet, surprisingly, the data-set of CH4 concentrations shows little inter-annual variations and no clear response to the heat-wave of summer 2018

Is there a variability in salinity during the time-series from 2006 to 2018 (Figure 8) ? Could strong variability of water masses "obscure" signals due to other factors (e.g. heatwave) ?

Response: The CH4 concentration anomaly should be detectable in the surface (5 m water depth) layer. Changes of salinity in the surface layer are usually resulting from mixing events (by storms and/or upwelling). However, mixing of bottom waters brings CH4-enriched waters to the surface and thus results in a pronounced CH4 conc. anomaly in the surface layer (see Ma et al, 2020). However, we could not find a relationship between CH4 surface conc. anomalies and surface temperature anomalies. Therefore, changes in salinities (water masses) are unlikely to obscure the heatwave signals. We have extended the discussion of the differences between Boknis Eck, the Belgian coastal site and the Tvärminne coastal site in the revised manuscript (lines 364-392).

While the authors have analyzed inter-annual variations and response to the heatwave of 2018 for CH4 concentration they did not analyze the variability of the fluxes. Would it be possible to compute the fluxes and check if inter-annual changes in wind intensity lead to inter-annual changes of emissions of CH4, even if this is not the case of concentration as suggested by Figure 8 ?

Response: Time series of CH4 flux densities were computed for BE by Ma et al. (2020). Except for a few extremely high flux densities -which resulted from extremely high CH4 surface concentrations in November 2013, February/March 2014 and December 2014- there were no interannual changes (or trends) in the flux densities.

Ma, X., Sun, M., Lennartz, S. T., and Bange, H. W.: A decade of methane measurements at the Boknis Eck Time Series Station in Eckernförde Bay (southwestern Baltic Sea), 17, 3427–3438, https://doi.org/10.5194/bg-17-3427-2020, 2020.

Could it be possible to add information on air temperature close to study site and check if the heatwave of 2018 affected air temperature in the region ? If this is not the case, then it provides an explanation of the absence response of water temperature to the heatwave of 2018. If this is the case, however, it could be useful to try to figure out why the water temperature did not increase in response to a warmer air mass.

Response: There seems to be a misunderstanding. We do not claim to see an 'absence response of water temperature to the heatwave of 2018'. Indeed, we see a strong signal of the heatwaves in the surface water temperatures (e.g. for 2006 and 2018; see Figure 10 and line 341 ff.). ("[…]A pronounced temperature anomaly is visible in 1 m depth in August 2018 reflecting the heatwave which occurred from mid-July to August 2018 across northwestern Europe (Kueh and Lin, 2020)[…])

L110 : what was the delay before analysis ? There could be issues related to long storage of samples (Wilson et al. 2018).

Response: the samples from the Alkor cruises were taken in 2018 and analyzed in 2020. (the samples for the intercomparison of static headspace equilibration and the purge and trap system were analysed within a month after sampling.) The Boknis Eck time series samples were analysed within a few months after sampling. The fact that the CH4 concentrations were supersaturated does imply that there were no problems with contamination with ambient air (via leakage through septa) or preservation (samples have been poisoned and stored in the dark; and thus CH4 production/oxidation were prevented). Please note that the discussion of the storage time in Wilson et al. (2018) is valid for samples with extremely low CH4 concentrations which we did not encounter here.

L320 : Borges et al. also showed that water temperatures were distinctly higher in July 2018 than the previous 14 years. So there was a very distinct increase of water temperature during the 2018 heatwave off the Belgian coast. They also showed a very strong relationship between CH4 and water temperature. I'm unsure the reasoning of Borges et al. can be qualified as "speculation" as stated here. They hypothesized that the response of CH4 was related to higher temperature because it is well established in literature that methanogenesis strongly increases with warming.

Response: We changed the wording into" hypothesized" and included a discussion on the temperature-enhanced microbial processes (386 ff.)

However, I suggest to try to discuss the reasons for such a difference. The coastal area studied by Borges et al. is very shallow and does not stratify thermally even in summer (permanently mixed). This might explain the different behavior with Eckernförde Bay where thermal stratification occurs in summer. This leads to a strong physical decoupling between mixed layer and the bottom water and sediments. Such decoupling does not occur in the very shallow area off the Belgian coast, so that warming of surface water directly impact the bottom sediment, and conversily, enhanced CH4 production in sediments directly propagates to an increase of CH4 concentration in surface waters.

AC: We expanded the discussion of the differences between Boknis Eck, the Belgian coastal site and the Tvärminne coastal site (line 364-392)

I'm unsure that you can conclude that "Thus, CH4 emissions to the atmosphere at Boknis Eck does not seem to be affected by the heatwaves." The data show that there is no response to the heatwave of 2018. Based on your data you cannot conclude that the site is not affected by heatwaves in general.

Response: We disagree. We do not conclude that BE is not affected by heatwaves. Indeed, there is also a strong temperature anomaly signal for the heatwave in 2006 (see Figure 10). But this temperature anomaly is (as the signal in 2018) not reflected in the CH4 concentrations (see discussion in line 341 ff.). So, our conclusion is that heatwaves are visible in the temp. data set but the increased temperature does not affect CH4 concentrations and the subsequent CH4 fluxes to the atmosphere during the time period of our study (which spans 13 years).

In summer 2019, there was also a very strong heatwave in Europe that set all-time high temperature records in several EU countries including Germany (Sousa et al. 2020; Vautard et al. 2020). Any chance that CH4 was also measured in 2019 and to add this information to the analysis ?

Response: Monthly sampling for CH4 at Boknis Eck continues. Measurements of the samples from mid 2019 to present are currently ongoing. Please note, however, that the scope of our manuscript is focused on the results of our study in 2018.

There are several references missing from the reference list.

Response: We checked our reference list and found Ho et al., 2019 (see above) missing and found the two cruise reports were wrongly referenced. These have been corrected.

Booge, D.: Cruise Report AL510, 1–23 pp., https://doi.org/10.3289/CR_AL510, 2018a.

Booge, D.: Cruise Report AL516, 1–25 pp., https://doi.org/10.3289/CR_AL516, 2018b.

We could not find other missing references.

However, we added the following new references that were not included in the last version of the manuscript (ordered as appearing in the MS):

Li, Y., Fichot, C. G., Geng, L., Scarratt, M. G., and Xie, H.: The Contribution of Methane Photoproduction to the Oceanic Methane Paradox, Geophys. Res. Lett., 47, 1–10, https://doi.org/10.1029/2020GL088362, 2020.

Gindorf, S.: Development of a Purge + Trap System for the Quantification of Methane Variability in the Baltic Sea, 81 pp., https://oceanrep.geomar.de/id/eprint/51326, 2020.

Treude, T., Krüger, M., Boetius, A., and Jørgensen, B. B.: Environmental control on anaerobic oxidation of methane in the gassy sediments of Eckernförde Bay (German Baltic), Limnol. Oceanogr., 50, 1771–1786, https://doi.org/10.4319/lo.2005.50.6.1771, 2005.

Lohrberg, A., Schmale, O., Ostrovsky, I., Niemann, H., Held, P., and Schneider von Deimling, J.: Discovery and quantification of a widespread methane ebullition event in a coastal inlet (Baltic Sea) using a novel sonar strategy, Sci. Rep., 10, 1–13, https://doi.org/10.1038/s41598-020-60283-0, 2020.

Roth, F., Sun, X., Geibel, M. C., Prytherch, J., Brüchert, V., Bonaglia, S., Broman, E., Nascimento, F., Norkko, A., and Humborg, C.: High spatiotemporal variability of methane concentrations challenges estimates of emissions across vegetated coastal ecosystems, Glob. Chang. Biol., 28, 4308–4322, https://doi.org/10.1111/gcb.16177, 2022.

References

Sousa, P. M., D. Barriopedro, R. García-Herrera, C. Ordóñez, P. M. M. Soares, and R. M. Trigo, 2020: Distinct influences of large-scale circulation and regional feedbacks in two

exceptional 2019 European heatwaves. Commun. Earth Environ., 1, 48, https://doi.org/10.1038/s43247-020-00048-9.

Vautard, R., et al., 2020: Human contribution to the record-breaking June and July 2019 heatwaves in Western Europe. Environ. Res. Lett., 15, 094077, https://doi.org/10.1088/1748-9326/aba3d4.

Wilson et al. (2018). An intercomparison of oceanic methane and nitrous oxide 545 measurements. Biogeosciences, 15(19), 5891–5907. https://doi.org/10.5194/bg-15-5891-2018

List of changes:

- Title: Heat Wave was changed to Heatwave
- Abstract: we specified the improved precision if the purge and trap system "[…]compared to static headspace equilibration measurements." (line 20 f.)
- Introduction: we added the sentence "A photochemical production of CH4 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)." (line 46 f.)
- Line 90: reference Ho et al., 2019 was corrected
- Line 98 f.: the sentence "To examine potential CH4 concentration gradients in the very near-surface waters in higher resolution, additional samples from a zodiac were taken at selected stations." Was changed to "To examine potential CH4 concentration gradients in the very near-surface waters ~~in higher resolution~~, additional samples from a zodiac were taken at selected stations.".
- Line 119 f.: we added the sentence "The materials that were used and all performance tests that were carried out are listed in the supplementdescribed in detail in (Gindorf, (2020)."
- Chapter 2.7 Temperature and CH4 Anomalies has been shortened as some of the information was redundant with information in 2.5. We added the sentence "ΔCH4 i, avg is the mean excess CH4 in 1 (25) m depth of the respective month i over this period at Boknis Eck."
- Line 288 f.: we added a reference to figure 6.
- The order of figures 6-10 was changed accordingly with changing chapter 3.5 to 3.3
- Line 306 f.: we added an explanation to the "carry-over-effect" "This can result from closing the Niskin bottles during the upcast, so that deeper waters might be brought up."
- 3.3 was changed to 3.4 Seasonal Variability; we added a sentence "Please note that when comparing June and September data from figures 4 and 5, different colour schemes were used to emphasize gradients within each cruise." (line 321)
- Line 338f. we merged the last two sentences of that paragraph into "It is rather the result of recent local CH4 release either at the BE site itself or advected to the BE site by the bottom waters."
- In chapter 3.5 The 2018 European Heatwave Impact on CH4 we changed the wording of speculated into hypothesized (line 355) and concluded (line 360) and expanded the discussion about the differences between the different study sites (lines 364-392).
- The summary and conclusion was shortened and we added a sentence referring to the finding of Roth et al., 2022 emphasizing the high variability of coastal CH4 (438 f.)
- The author contributions were updated (HB was changed to HWB)
- Acknowledgements: we added the following two sentences:
    - We especially thank Tim Fischer for the deployment of the gradient pump system during the zodiack trips.
    - The Boknis Eck Time Series-Station is an endorsed project of the international Surface Ocean-Lower Atmosphere Study (SOLAS: www.solas-int.org) and Baltic Earth (www.baltic.earth).
- The reference list was updated with following new references:

- Li, Y., Fichot, C. G., Geng, L., Scarratt, M. G., and Xie, H.: The Contribution of Methane Photoproduction to the Oceanic Methane Paradox, Geophys. Res. Lett., 47, 1–10, https://doi.org/10.1029/2020GL088362, 2020.
- Gindorf, S.: Development of a Purge + Trap System for the Quantification of Methane Variability in the Baltic Sea, 81 pp., https://oceanrep.geomar.de/id/eprint/51326, 2020.
- Treude, T., Krüger, M., Boetius, A., and Jørgensen, B. B.: Environmental control on anaerobic oxidation of methane in the gassy sediments of Eckernförde Bay (German Baltic), Limnol. Oceanogr., 50, 1771–1786, https://doi.org/10.4319/lo.2005.50.6.1771, 2005.
- Lohrberg, A., Schmale, O., Ostrovsky, I., Niemann, H., Held, P., and Schneider von Deimling, J.: Discovery and quantification of a widespread methane ebullition event in a coastal inlet (Baltic Sea) using a novel sonar strategy, Sci. Rep., 10, 1–13, https://doi.org/10.1038/s41598-020-60283-0, 2020.
- Roth, F., Sun, X., Geibel, M. C., Prytherch, J., Brüchert, V., Bonaglia, S., Broman, E., Nascimento, F., Norkko, A., and Humborg, C.: High spatiotemporal variability of methane concentrations challenges estimates of emissions across vegetated coastal ecosystems, Glob. Chang. Biol., 28, 4308–4322, https://doi.org/10.1111/gcb.16177, 2022.

- Following references were corrected:
  - Ho, D. T., Marandino, C. A., Friedrichs, G., Engel, A., Bange, H., Barthelmess, T., Fischer, T., Koffman, T., Lange, F., Quack, B., Paulsen, M., Schlosser, P., and Zhou, L.: Baltic Sea Gas Exchange Experiment (Baltic GasEx), https://oceanrep.geomar.de/id/eprint/53496/, 2019. (line 524-527)
  - Booge, D.: Cruise Report AL510, 1–23 pp., https://doi.org/10.3289/CR_AL510, 2018a.
  - Booge, D.: Cruise Report AL516, 1–25 pp., https://doi.org/10.3289/CR_AL516, 2018b.
- Figures:
  - Figure 1 is now devided into A,B,C including an overview map of the Baltic and parts of the southeastern North Sea. In the overview map our study site is marked as well as the two comparison study sites.
  - Figures 4A and 5A now include the same station numbers as the cruise track and figures 4B and 5B
  - The order of figures 6-10 was changed according to the changes in text order.
  - Figure 10 now includes spaces between depths and units in the legend.
- We added the section “competing interests”.