Biogeosciences Discuss., 12, C3191–C3200, 2015
www.biogeosciences-discuss.net/12/C3191/2015/
© Author(s) 2015. This work is distributed under
the Creative Commons Attribute 3.0 License.

Biogeosciences
Discussions

Interactive comment on "Methane distribution, flux, and budget in the East China Sea and Yellow Sea" *by* M.-S. Sun et al.

Anonymous Referee #2

Received and published: 28 June 2015

GENERAL The paper by Sun et al. seeks to estimate methane fluxes in the East China Sea (ECS) and Yellow Sea (YS), with a special emphasis on the seasonality of the flux to the atmosphere and the development of a conceptual box model), addressing the fluxes by different water masses. The work is based on a very extensive data set of surface and bottom water concentrations and sections of vertical methane distributions based on flask sampling in connection to an established gas stripping technique. It is supplemented by some data on methane fluxes from the sediments based on the increase of CH4 concentration of ex situ methane incubations over time. The data, together with some data from the literature, are used to estimate the importance of various transport and production processes of methane in the ECS by adapting a box model previously used to address the salt balance of this marginal sea.

Unfortunately, there are several major issues which in my eyes have to be addressed before the paper can be published as a contribution within Biogeosciences or any peer reviewed journal, some of them really affecting the major conclusions of the paper. To highlight this, it might be best to summarize beforehand the main scientific statements of the paper:

a.) The study provides data on methane in an area heavily under-sampled. b.) Highest CH4 concentrations, fluxes and air-sea exchange (ASE) all occurred during summer c.) An estimate of the mean CH4 flux from the sediments is given d.) Major source of methane and driver of flux to the atmosphere is production in the water column.

The shortcomings in the, paper which need to be addressed are a more thorough introduction and discussion of knowledge from the literature, a better description of the methods used for the calculations and – in particular spatial integration, and a rough estimate of errors and shortcomings. In particular the finding d.) would be unexpected, but is not supported by any direct process measurements (subsurface maxima sampling, methanogenis rates, isotopic data), and I would suggest a very careful statement here.

On a formal side, the main figures of the mscpt. all suffer from not having the axis defined in a way which allows comparison of the parameters during the different times of sampling. To make the points in the interpretation intelligible, Fig 3-5 NEED TO BE REDRAWN WITH UNIFORM SCALES FOR THE SHOWN PARAMETERS ON ALL INDIVIDUAL PANELS.

MAJOR SCIENTIFIC ISSUES IN THE TEXT 1 INTRODUCTION: The mentioning of the history and development of the atm. growth rate over the last 2 decades is irrelevant for the paper and should be cut (Page 3, line 5 middle to line 9 end). The statement in line 13 is wrong! There is a wealth of literature on methane oxidation in sediments and the water column, both anoxic and oxic. Line 19: I think it would be more scientific to address the waters in the YS, ECS and SCS rather than the "coastal areas of

China". Most importantly, this 2nd paragraph should be extended. After all, there are several studies in the area, the majority of them involving one or several of the authors themselves, and this work should be briefly summarized (Yang et al., 2015, Zhang et al 2008ab&14, Ye et al., 2015) and incorporated in the considerations later on (including addressing discrepancies etc.). The work of Rehder and Suess (Mar. Chemistry 2001, 75, 89-108) already using the equilibration technique at an early stage is completely neglected, though providing a considerable data set for the Kuroshio-influenced surface waters in the ECS. The same is true for the work on the (methane emitting) hydrothermal activity in the Okinawa Trough, which would surely be worth consulting in the context of Fig. 5.

Also, the authors might consider to widen the context by briefly addressing some similar systems (marginal seas mainly fed by oceanic waters but with riverine imprints) under investigation (e.g the North Sea).

Formally it might be easier to start with a short paragraph on atmospheric methane and the role of the oceans, then followed by an introduction of the hydrography, then ALL work already done on methane in the area, and then specifying the new contribution of this paper (i.e. the paragraph starting page 4, line 14.

Other: Page 4 Line 6, "The production .... (Karl and Tilbrook, 1994). I do not understand this sentence at all, nor the context to the reference (which deals with relation of the methane subsurface methane maximum to other variables.

Page 4, line 12-13: Researchers ... CUT. This is more of a political statement, and it is also absolutely not clear what is meant by " beneficial effects of its biogeochemical cycles ...).

So in short: The introduction can be streamlined by keeping the focus on the content of the paper, but has to be extended by a comprehensive summary of what has been done with respect to the methane cycle in the area of investigation, and potentially comparable other regions.

Materials and Methods: 2.1 Page 5, line 19: check concentrations given for the standards: there are the digits behind 2 and 4 missing, I believe. Please quote accuracy of standard concentrations given by the RI-CNSM. 2.2 Page 6, line 9, what is meant by "at ambient temperature" Ambient in the lab or ambient in situ? Following: What was the difference between in situ and ambient. Please explicitly write down the equation used for T-adjustment "...calibrated by the Arrhenius empirical equation"?????

Methods and Figure S1: you refer to "water column control" in the text, "control" in the figure caption of S1 and "blank" in the legend of S1. Please be consistent.

2.3 Page 7, line 3-4 the concentration patterns of these stations, is quite unusal, with TAP and SDZ showing highest concentrations in summer and a clear land-influenced signal. I would expect the airborne mole fractions over the sea quite different. Though not really essential for the paper, the authors might want to add a sentence on this, as on the use of an annual mean in general of a gas which is know to show a seasonal cycle.

Page 7, last sentence of 2.3 "more representative and trustworthy" – than what? Please provide a scientific rationale (very easy for the most recent paper by W2014.

3 Results: 3.1 Line 17 "succession"? , => confluence

Fig 2: Figure Caption, last line, pls. extend: ".... CH4 sampling points, with concentration indicated by color code. Fig. 2: PLEASE ADJUST METHANE COLOR CODE TO BE ON THE SAME SCALE FOR ALL PLOTS

Page 7, Lines 22ff: from here on, you are also referring to Fig. 3 already, which has the spatial information, so insert a (Fig. 3) here. Page 8. Line15: It is odd to infer the mixing of the water masses from the methane pattern, with a.) lots of hydrographic parameters at hand and b.) a conclusion later on which suggests that most of the methane is produced in the water column. Skip or make the point from the physical parameters.

3.2, 3.3, 3.5 and Tables 2 and 3

Unfortunately, there are major issues with the (statistical) handling and interpretation of the data in these sections. Table 2, to my understanding, basically gives the ranges of data measured (so far so good), and the average and SD, where it should be stated that the SD gives the average difference between the average value and the individual values (and not any kind of uncertainty of the average, as suggestive from the $\pm$ sign). But what kind of average was chosen, given the fact that the measurement points were not evenly distributed. I assume just the linear) average. Moreover, there are strong variations in the areal coverage of the different surveys over the year. Later in the result and discussion, the differences in the mean values are then used to address seasonal changes. This is simply not scientifically sound. For instance, one of the findings of the paper is that the concentrations and fluxes were highest in summer. However, this cruise had a more limited spatial coverage, with a strong bias towards the mouth of the Chang Jiang river, which is –correctly – identified as the major hot spot of creating enhanced methane concentrations. At the other hand, the waters in the axis of the Kuroshio current were not sampled in summer at all. So a part of the summer maximum of surface and bottom methane concentrations is definitely a result of a sampling bias, and it is not intelligible how large this bias actually is. On the counterside, the lowest average concentrations were found in December, when the grid was heavily reduced towards the river mouth, but had lots of sampling stations in the Yellow Sea and the area south of 32 N, producing a bias towars a lower CH_4 concentration field. To be clear: I do not mean that the authors are not right in their conclusion about the annual behaviour; from the approach, I just cannot tell -at least not quantitatively- and the authors can't either, I fear. One possible approach to overcome this problem would be to use integrate over the gridded surface and bottom concentration fields (getting rid of the spatial inhomogeneity) and to compare results just from areas which are covered by all surveys.

In 3.6, the authors estimate the surface ASE fluxes. Here again, several things are unclear or potentially wrong. First of all, the boundary between the YS and ECS is not clearly defined, nor the total areas of the two seas indicated for which the approach is then followed. As the ASE flux is, under the assumption of common winds over the entire area, is proportional to the sea surface area, here at least a spatial weighting would be needed. This could for example – again – be extracted from the interpolated field data. Also, here again there is a problem with the spatial bias. For instant, how are the summer estimates given, with a strong oversampling near the River Mouth, no data coverage in the East, and basically no data in the Yellow Sea?

On top of this, there is again a huge problem in the understanding and use of statistics obvious in connection to Table 3. What is meant here be the $\pm$ values given behind the averages? Here, uncommented, a $\pm$ sign would suggest the uncertainty range of the average. But there are basically no data supporting an undersaturation, and in particular, the (unclear) error propagation gives raise to ASE flux estimates with an error margin allowing for considerable fluxes from air to sea.

I do not give any more specific comments to these sections at this point, as they need very major scientific reworking.

FIGURE 3: PLEASE ADJUST COLOR CODE TO BE ON THE SAME SCALE FOR ALL PLOTS OF T,S, AND CH4 (SURFACE AND BOTTOM) RESPECTIVELY (TOTAL OF 6 SCALES) 3.4

Line 11 : is section P not the same than section CJ?, you refer to this section as section P also for May in the Fig caption at some other places of the mscrpt.

Line 13. It is not true that the water is well mixed in the upper 100 m along the entire March Section. This is not true for the plume-affected west, but also for the very north.

Line 20: Correspondingly: be clear here. There are two processes involved: the annual development stratification, and the gradient (and run off induced permanent stratification) in the methane-rich coastal near part.

Line 26: “Surprinsingly” is not really scientific. It would be rather interesting to argue (in the discussion) whether this points to sedimentary sources feeding into the bottom layer.

In general, for the water column structure as a key control of the spreading of methane, a section of the density anomaly would be better suited than S and T separately.

FIGURE 4: PLEASE ADJUST COLOR CODE TO BE ON THE SAME SCALE FOR ALL PLOTS OF T,S, AND CH4 (TOTAL OF 3 SCALES), ALSO INCREASE SIZE OF DOTS INDICATING POSITION OF ACTUAL MEASURMENTS, CONSIDER ALSO NOT TO CHANGE THE DEPTH AND DISTANCE SCALE. Lastely, please check gridding result of the March situation, which for T and S appears very awkward, even for an unstratified water column.

Fig 5: I would again suggest using at least the same scales for depth and T, S; CH4 would maybe not work here. Also indicate these positions in Figure 1 (by arrows or surrounding circles. Else, one has to search quite a while.

As for the interpretation of the data shown in Fig. 5, it appears that the occurrence of the hydrothermal activity in the Okinawa Trough and its potential impact on the methane distribution of the deep water is completely neglected (and might be the reason for some of the observations (this should however be in Discussion).

Line : 9 Citations – make clear that the citations are on subsurface maxima at different places, but not at the pycnocline of the ECS and YS.

3.5 Sediment fluxes While the compiled sediment flux data are a nice data set, the spatial and temporal inhomogeneity are not really supporting a basin-wide extrapolation. Way more critical, however, is that in this case, the seasonal bias of sampling is too strong to allow the conclusion that fluxes are strongest in summer (though this might well be . . .). The summer sites are all on the western rim, in shallow waters

and relatively near to the outlet of the Chang Jiang, other than for any other sampling campaign. Is there a possibility to look at trends with respect to e.g. bottom water temperature and/or Oxygen, water depth, organic fraction of the sediment). Without thorough scientific thought, there is only very limited use of these data, and in particular the annual pattern of fluxes might be a mere sampling bias.

The authors state that (Page 13, lines 6-8) that the sediment fluxes are of limited certainty, which is surely right, but there is way better potential to interpret the data and do an extrapolation based on an understanding of influencing parameters. This part is more of a data report than a scientific analysis of the data.

4 Discussion 4.1 First sentence: again, while this might be true, severe problems in statistical analysis, spatio-temporal bias during the different campaigns and lack of scientific interpretation/analysis result in the fact that this “finding” is not really supported.

From the first paragraph of the discussion, one might argue that fluxes are even stronger correlated with driving parameters than concentrations. So what about checking on a correlation of CH4 sedimentary fluxes with T (and other parameters, see above) .

Page 15, line 3 : has been => have been More importantly, I have not seen any clear indication for subsurface maxima in the entire paper, neither in Figs 4 nor 5.

Page 15, lines 8-9 “microorganism and served as” => microorganismS and serve as Line 18-19: There is little to no indication for methane production in the deep water column. Even in anoxic waters (e.g. Black Sea, Baltic Sea) methanogenesis is mostly related to the sediments. If the authors want to make this point (which is a requirement for the reasoning on the box model results later on) they should reference this hypothesis well. There is no direct indication of methane production in the water column here, thought this is the main hypothesis based on the model approach.

Page 16, line 2-3: While I believe this argument, the modelling in 4.2 suggests a rather minor impact of transport and in situ production as a mean driver.

4.2

Page 16 Line 21-22 : Which might be problematic, as groundwater can be a major contribution to the methane sources, and will, when neglected, be counted as the only "missing source term", e.g. water column production.

Lines 13 ff: There is a major flaw in attributing the missing sink to in situ production in the water column. The authors neglected groundwater discharge due to a lack of existing data, and also did not consider methane from deep sources, e.g. the Okinawa Trough. In the following part of 4.2, they attribute the mismatch of sources and sinks in the model budget to production in the water column. However, they do not provide any support for this source. Neither there are any production rate measurements in the text, nor a spatial analysis of the water column data pointing to this kind of source. They cite del Valle and Karl 2014, but would need a larger production term and the process would definitely result in a very distinct surface layer maximum dominated production term in the subsurface layer.

In the last paragraph of 4.2 the authors state themselves where the shortcomings in the approach are. The problem of a missing quantification of the errors is obvious here. I thnk the main lesson to be learned here is that based on the data, there is a mismatch between sources and sinks, and it is likely that either there are too large gaps of knowledge, or the system has not been at steady state for the year 2011. The attribution to very strong in situ production is not supported. It would be a finding of major importance. That also means that without supporting data, it should not be allowed in a peer reviewed publication.

5 Conclusions In the conclusions, the problems with the data interpretation gets really obvious: - the seasonality in distribution and emission might be correct, but the approach does not really support this due to a scientifically unprecise handling of the problem of sampling bias, both for the water column data grid and the sediment flux

stations - the production of methane in the water column (attributed to amount for 70% here!!) is not supported by the content of this paper AT ALL. Rather, possible reasons are – uncertainty in the existing numbers; - importance of other external sources such as groundwater seepage or hydrothermal input in the deeper waters; - a problem with the assumption of a steady state for a single year, potentially others.

Interactive comment on Biogeosciences Discuss., 12, 7017, 2015.