

Interactive comment on “Effects of methane outgassing on the Black Sea atmosphere” by K. Kourtidis et al.

Anonymous Referee #2

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This paper presents the first comparison of indirect air-sea gas fluxes of methane from several sources in the Black sea, including thermogenic and biogenic sources. The largest sources were biogenic in shallow, presumably nutrient rich, harbor waters. Of intermediate strength were areas of active seepage, and lowest fluxes were calculated for deeper-water, biogenic sediment sources. Based on the air and water methane measurements and one of several air-sea exchange parameterizations. Methane fluxes were calculated and determined to negligibly affect atmospheric concentrations compared to variability for other reasons.

This conclusion raises a structural issue about the manuscript, which devotes almost the entire introduction to a discussion of the various literature parameterizations of air-sea gas exchange. References are needed for the statements that methane is

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an important greenhouse gas. Yet the data collected is not used to test the various flux parameterizations because the estimated flux is too small to change atmospheric concentrations. Thus, for the purposes of the data with respect to the main study conclusions, it is not particularly important which parameterization is used. The discussion of these parameterizations should be shortened. Also, wind speeds are not presented; however, the authors note a “high” wind speed was 6 m/s implying that winds were generally quite low. The authors should note that there is significant uncertainty in the parameterizations at very low wind speeds, particularly in the presence of slicks - a near certainty in a harbor.

The main goal of the study seems to be to evaluate the contribution from seep flux to the atmosphere with respect to other sources. However, it would be more accurate to state that the discussion is with respect to the indirect seep flux, rather than the bubble-mediated flux. Moreover, absent more specific location information of where samples were collected with respect to the bubble seep plumes - i.e., source(s) - and currents, it would be most accurate to state that the study is with respect to the far field, indirect contribution. Studies in the Coal Oil Point seep field, have shown enormous heterogeneity in the near-field dissolved methane plume (Clark et al., 2003). Thus, a proper evaluation of these results requires a better discussion of the sample locations, including the depth, and where appropriate, the depth of the mixed-layer.

There is a clear rise in atmospheric methane towards the end of the data set (day 15 to 17), with supersaturations particularly high on day 11, ~20:00. Do the authors have an explanation for this? Please state if it is from terrestrial sources or a cumulative air-sea exchange effect (i.e., was upwind onshore?)? This brings up a technical area for improvement of the manuscript. Specifically, the calculated air-sea exchanges are highly dependent on the wind speed; yet the wind data is not presented nor is its collection approach described. It would be highly useful to add to Figure 3 a plot of wind speed, either above or as a double-y plot. This would allow separation of the effect of wind speed from the effect of supersaturation. For example, one of the

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reasons for very high concentrations in the water column of methane could be very low wind speeds which prevented loss to the atmosphere, thereby causing an increase in the water concentration.

Also, further details on wind speed measurements should be provided. As is widely recognized, ships affect wind streamlines and can therefore alter the measured wind speed (unless a wind buoy is deployed). Also, for a non-linear parameterization, the averaging time scale affects the results. Thus, details on the location of the anemometer relative to the boat and the wind-speed averaging times need to be stated.

It is also noted that while there is extensive literature review of air-sea gas exchange; which as noted above was largely not relevant to the conclusion, the available and somewhat extensive literature on natural seepage is completely ignored. This is a shame for several reasons, one of which is that in order to show that seeps could contribute to atmospheric methane, the authors hypothesize an eruptive seepage event, based on data from a mud volcano (eruption??) in Azerbaijan, published in a conference abstract. Although this event is the basis of the final conclusion and an important calculation in the manuscript, there is no brief description of the data. This hypothesized event is then put into the model to show that it would produce a significant increase in methane atmospheric concentrations, one which the authors further argue that existing satellite-based platforms could detect such an event.

At issue to discuss is whether we learn anything by this calculation, and whether the calculation is sufficient to assert that satellite-based observation is a reasonable approach towards studying eruptive marine emission events. One could argue that this calculation does not inform us of anything new - i.e., namely that a (hypothesized) sufficiently large event affects atmospheric concentrations significantly. Most significant, are the numerous questions un-addressed and which cannot be easily answered at this time. First, how representative is the hypothesized event. Mud volcanism in Azerbaijan is on a scale not found anywhere else on the globe. Elsewhere smaller events are much more likely elsewhere - i.e., the black sea. However, it is fair to indicate that we do

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not know anything about the frequency-size distribution of such events. In such case, a more useful calculation would be how small an event could SCIAMACHY observe. And herein it is important to note that satellites do not observe concentrations, but column heights, which must be compared to the atmospheric column height of methane. Thus, Fig. 4 is not informative and should be shown as column height, not concentration, averaged over the satellite footprint, and then compared with the background atmospheric column height of methane to illustrate the signal to noise needed. Actual satellite footprints should be mentioned (and referenced), which are on the order of 100 km². Thus a very strong local deviation from atmospheric could be imperceptible when averaged over a pixel. And critical to Fig. 4 is the wind speed and horizontal mixing - vertical mixing does not affect column heights. Of equal importance is the time scale of an event. Thus a very short, extreme event, averaged over a “footprint pixel” could be less than instrument signal to noise and is very unlikely to be observed since the satellite would have to be overhead (and looking at the proper area) at the appropriate moment. Thus, a fair question, is whether there are any satellite observations of emissions from mud volcanism in Azerbaijan. If there are, they should be cited, although to my knowledge, there are not.

Overall, positioning the paper and significance of the study as arguing for satellite monitoring of seep areas is not supported by the data, and unconvincing given the extent of calculations performed. My suggestion is either to perform a more detailed calculation with respect to satellite observations - or reposition the manuscript.

More compelling arguments as to why seeps may contribute to atmospheric methane lie in the isotopic composition of atmospheric methane, which show that significant methane is carbon dead (i.e., thermogenic). This argument has been made in many papers in the seep literature, for example, see Kvenvolden 2001, with respect to atmospheric budgets. This literature should (as noted above) be cited and discussed. This suggests a better approach to placing the study results in perspective. Basically, if as numerous publications indicate, seeps contribute non-negligibly to atmospheric bud-

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gets, and the results of this study clearly indicate that the far-field indirect emissions are too small to explain the seep contribution, then another seep emission mechanism must be important - near field indirect, direct, and/or large explosive events.

With respect to the measurements, the results are important and merit publication, specifically that methane levels in areas of seepage are elevated above background in the Black sea. These results are not unique as other authors have noted similar elevation in other areas of seepage - which should be cited; however, noting that this elevation occurs in the black sea yields support for the idea that seeps are a non-negligible methane source to the upper water column in many regions. It is not surprising that methane concentrations in Danube fan were the largest; however, a discussion noting that they were only a factor of five larger (but what were the average concentrations?) and that the Danube fan is not a typical coastal environment due to the input of nutrients from the Danube river would be useful

It is confusing to try and identify where data on figure 1 was collected; thus, if regions were named on the figure, it would be easier to compare areas of seepage with deeper water (how deep?), the Danube fan, coastal/harbor, etc.

With respect to the calculated flux, how representative are the winds and water concentrations. Presumably, given the depth of the mixed layer and the light winds observed, gas evasion occurred very slowly and thus changes in aqueous concentration were also slow. For example, let us hypothesize a 1 month time scale for outgassing of the surface water layer. If the cruise happened to be in the area on a high wind day during a month that was relatively calm, it would appear to indicate an outgassing flux much larger than the monthly flux. Thus, for comparisons between the two cruises, it would be useful to calculate the emission flux for either the seasonal climatic values, or for the average winds over the evasion time scale. Alternatively, the authors could look at the variability in flux from day to day - i.e., the standard deviation for measurements in a region would be useful. This would allow evaluation as to whether there are statistically significant differences between flux values for different areas and with respect to the

earlier cruise

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