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Atmospheric Chemistry and Physics Discussions

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

K. Kourtidis et al.

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Response to comments by Referee #2

The comments are well-founded and addressing them contributes significantly to the improvement of the manuscript. Hence, all will be taken into account in the revised version. We give below in [brackets] the text that will be included in the revised version. The text given below is not the only addition to the revised version; here, only the text addressing more directly the referee's concerns is noted. In the revised version, Figures 1a, 1b and 2a are redrawn to indicate the location of the ship (i.e. seep area, Danube fan, Sevastopol harbor, station above active seeps), Fig. 1c with the wind measurements and bathymetry timeseries is added, Fig. 2b is redrawn to also indicate bathymetry and dates, while Fig. 3 is redrawn to include also a calculation of fluxes with the climatic wind speed value.

2nd paragraph of the comments:

Comment “References are needed for the statements that methane is an important greenhouse gas”: Reply: There are so many references on the importance of methane as a greenhouse gas, and this fact is so well for so long known that today it is almost a triviality in the atmospheric sciences community. Anyway, we added the following references in the revised version:[IPCC, 2001, Lelieveld et al., 1993, 1998]

2. Comment “with respect to the main conclusions, it is not particularly important which parameterisation (of air-sea gas exchange) is used”:

Reply: True. However, we believe these flux calculations are useful on their own merit, since they illustrate under field conditions the uncertainties introduced by the parameterisation. These are the only measurements of methane in the Black Sea with fluxes calculated with all three methods; hence, rather than shortening the part of the introduction that is referring to parameterisations of air-sea flux, we extended the other parts that the referee found meriting more attention (see below).

3. Comment “Wind speeds are not presented”

Reply: As mentioned above, in the revised version, wind speed will be included in Figure 1 as Fig. 1c:

[Figure 1c. Wind speed measurements during the BIGBLACK cruise. Shaded areas denote ship’s location, while areas with darker shading indicate measurements where vessel was anchored directly above active seeps. Areas denoted “Seep” are areas with active seeps. The bathymetry timeseries is also plotted.]

4. Comment “high wind speed was 6 m/s”, and ”uncertainty in parameterisations at very low wind speeds, particularly in the presence of slicks- a near certainty in a harbour”:

Reply: This was a typos in the manuscript, corrected in the revised version: [Wind speeds on the 11th and 12th of December were generally higher than 6 m/s and up to

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16 m/s (see Fig. 1c)]. Since winds were generally above 6 m/s, it would appear that our calculations are not influenced by the uncertainties of parameterisations at very low wind speeds. Also, comparison with the climatic value for December (8 m/s) has shown that the mean wind speed during the campaign was somewhat higher, but not very different from the climatic average of around 8 m/s for December (Sorikin, 2002; NEMOC, 2005). Slicks might well be present in the harbour of Sevastopol, where very high supersaturations were observed. However, due to the absence of wind speed measurements in the harbour, we have calculated fluxes there in the revised version only with the climatic wind value. Concentrations in the water and supersaturations are not influenced by either wind speed or slicks. Hence the comment about slicks has limited applicability to our data.

3rd paragraph of the comments:

Comment “The main goal of the study seems to be to evaluate the contribution from seep flux to the atmosphere with respect to other sources”:

Reply: This statement is almost correct; we would, however, prefer to phrase it a bit differently, namely that the main goal of this study is to evaluate the contribution of methane diffusion to the atmosphere compared with more violent events that might occur within the Black Sea basin. The latter effects are also applicable to other areas with submarine (or even land-based) mud volcanism.

Comment “it would be more accurate to state that the discussion is with respect to the indirect seep flux rather than the bubble mediated flux”

Reply: We would rather avoid making such a statement, because modelling and measurements of the bubble-mediated flux made by other partners in the CRIMEA project show that at shallow areas (as, e.g., the ones in the Danube fan)indicate that more research is needed to properly assess the relative contribution of these two processes. To quote the CRIMEA project Final Scientific Report: “Two sub-areas were chosen for a direct comparison of the two mechanisms of sediment-originated methane transfer to the atmosphere, both within shallow waters on the shelf where the strongest influence from the seeps was observed (Fig. 13.1A of the Report). Diffusive flux measurements, calculated after Wanninkhof (1992), estimate contributions of 1.18 mol/day for the sub-area in the 100 m deep seep site and 0.29 mol/day for the sub-area in the 250 m deep seep site, while bubble-transfer modelling estimates that the sub-area in the 100 m deep seep site contributes 21100 mol/day and the sub-area in the 250 m deep seep site contributes 1000 mol/day (Fig. 13.4 of the Report). Based on this comparison it appears that the direct transfer of bubble methane is four orders of magnitude higher than that from diffusive flux. This is an unexpected result when one considers that single-bubble modelling predicted only a limited methane-bubble transfer at the 100 m deep seep site and no transfer at the 250 m deep seep site. In addition, the 250 m deep seep site does not show any increased dissolved methane concentrations in the shallow waters or in the surface waters, as would be expected if bubbles with measurable methane concentrations reach the water/atmosphere interface. In theory, over a very limited area, there is the potential for an even greater difference between the contributions of these two processes. For example, when using the averaged measured diffusivity on the shelf (i.e. about K = 1 x 10-6 m2/s) and dividing it by the depth (i.e. 100 m), this yields a vertical transfer speed of 1 x 10-8 m/s (0.3 m/yr). On average, a bubble rises at about 0.25 m/s, which means that on a very local scale bubble migration may be as much as 7 orders of magnitude faster than diffusive transport. However, it must be clearly stated that while bubble migration is obviously much faster than diffusion, the final concentration of methane in the bubble just before it reaches the water/atmosphere interface will finally control the CH4 flux rate of this mechanism.

Regardless of these comparisons on a very local scale, diffusive transport is much more important than bubble transport when considered on the basin scale. More research and an inter-calibration of the various modelling approaches would be recommended to better understand the contribution of these two processes."

Comment "The study is with respect to the far-field, indirect contribution"

Reply: This is not correct. Measurements were also taken during two ship stations located above active seeps (Figures 1 and 2 are modified in the revised version to indicate this, see above, and this will be commented briefly). The measurements during the stations were made on two occasions, 13/12 from 8:00 to 20:05 and 14/12 from 8:10 to 17:30, when the vessel was anchored directly above seeps. While during the 13/12 station the CH4 concentration in water did not vary much (15-21 ppmv), during the 14/12 station there were variations of a factor of two (7-15 ppmv). Hence heterogeneity in the near-field dissolved methane plume will be discussed in the revised version and a reference to Clark et al., 2000, will be added.

Comment "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"

Reply: In the revised version, the sample locations are presented in figs. 1 and 2, figure 1c includes the bathymetry timeseries along with the wind data, while Fig. 2b is plotted on a bathymetric map of the Black Sea, with date indication. Also, the following text will be added: [The mixed layer depth, as determined from CTD measurements during the cruise, was generally between 20-50 m.]

4th paragraph of the comments:

Comment "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."

Reply: Probably the referee means methane in water, not atmospheric methane. As already mentioned in the text, on days 15-17 the ship was in the port of Sevastopol, which would explain the very high supersaturations observed during these days. As for day 11, 20:00, the ship was above an active seep area. The modifications in Figures 1 and 2 in the revised manuscript (mentioned above) will make the interpretation of the figures easier.

Comment "add to fig. 3 a plot of wind speed"

Reply: We added this in fig. 1, and wind speeds are now presented as fig. 1c (see above).

Comment "reasons for very high supersaturations could be very low wind speeds"

Reply: This was not the case, as wind speeds were generally above 6 m/s (see above). To our opinion, supersaturations were the result of methane flux from below. Figure 3 is redrawn in the revised version, to include also flux calculations with the climatic values of the wind speed. The mean of the measured wind values was near the climatic value of 8 m/s, hence low wind speeds cannot account for the high supersaturations.

5th paragraph of the comments:

Comment "Further details on wind speed measurements should be provided"

Reply: The following text is added in the revised version: [Wind measurements were made with the ship's anemometer, at 10.78 m height ASL, on a ship's mast of 4.75 m height, hence eliminating the need for corrections of the wind speed u to u10. These data were provided by the ship's operator, and consist of measurements of wind speed and direction provided twice an hour. No details on the averaging times were provided. The data were corrected for ship's movement, based on concurrent data on ship's velocity and heading. Clearly, no such correction was applied for the times the ship was anchored (these times are indicated in Figs. 1 and 2).]

6th paragraph of the comments:

Comment "extensive literature on natural seepage is completely ignored"

Reply: This will be addressed in the revised version, with a review of the existing literature in the introduction.

Comment criticising the use of mud volcano eruption in Azerbaijan (published in a conference abstract) as input data for the calculations:

Reply: At the time of the first submission, as stated in lines 20-29 of p. 3618, we

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started from a subsurface (at 2 km depth) emission rate of 22.5 million m3 gas, 90% CH4. This is in the lowest range of the amount of gas expelled during the first few hours from four prominent eruptions (1902-1961), 22.5-495 million m3, (Guliyev and Feizullayev, 1996, quoted extensively in the peer-reviewed literature, e.g. in Dimitrov, 2002; also Guliev, 1992, p. 7, quoted in Kopf, 2002, see also below). We note here that Guliev (1992) has performed the only extensive study on quantitative eruptive methane emissions from mud volcanoes; apart from this, only sporadic data are published in the literature (see below). Then, we used preliminary results from work done in the CRIMEA project on bubble-water column exchange of gases to assume that an upper limit of 0.1 % of the emitted methane would reach the surface, hence arriving at the 6.25 mmol/m2/s value for emission rate at the surface (at a 100 X 100 m2 rectangle). Since then, however, recent calculations by another group in the frame of the CRIMEA project, taking also into account newer findings about the formation of a bubble hydrate skin, indicate that for a substantially large eruption (larger than the one we simulated in the earlier manuscript version) a much larger percentage of the emitted gas reaches the surface (see below for details). Hence we have performed again our calculations using these recent bubble model results, and the following text will be added in the relevant discussion of the revised manuscript (taking also comments from reviewer #2 into account), while figure 5 will be updated accordingly:

[Guliev (1992), p. 7, quoted extensively in the western peer-reviewed literature, e.g. in Kopf (2002) and Guliyev and Feizullayev (1996), also quoted extensively, e.g. in Dimitrov (2002), states that for four prominent mud volcano eruptions between 1902-1961 (on land) the amount of gas expelled during the first few hours ranged from 22.5-495 million m3. We note here that Guliev (1992) has performed the only extensive study on quantitative eruptive methane emissions from mud volcanoes; apart from this, only sporadic data are published in the literature. These sporadic data (summarized in Dimitrov, 2002) yield estimates of methane expelled during the eruptive phase that range from 210 million m3 to 40 billion m3 CH4 over 1-2 days.

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If we assume a 4-hour, constant rate explosion, the upper estimate of 495 million m3 (Guliev, 1992) translates to 24,500,000 g/s, if the gas is 100% methane. For 70% methane this would still be 17,150,000 g/s. The amounts of methane that might rise to the atmosphere from a catastrophic methane release at depth have been estimated in the frame of the CRIMEA project (McGinnis et al., 2006) through a modified version of the Wuest et al. (1992) plume model. Some aspects of the model have been treated in McGinnis and Little (2002). The initial conditions of the model and the results are given in Table 1. It seems it would require a release of about 16,000,000 g/s (Scenario I) of methane in gas bubble form to reach the surface from 2000m. Of this, only roughly 30% reaches the atmosphere in both gaseous and dissolved form (50% gas, 50% dissolved). If we use 1,600,000 g/s then no methane reaches the surface. On the other hand, simulating a mud volcano gas release of 24,500,000 g/s (100% methane) at 2 km depth, all of the methane reaches the surface (about 20% gas, and 80% dissolved) (McGinnis, personal communication). The plume water when it reaches the surface is much denser, so it is difficult to estimate with certainty how much it will degass the dissolved fraction before settling back to the equilibrium depth. These simulations assume that a hydrate skin exists on the bubble in the stability zone (see, e.g., Rehder et al., 2002; Sauter et al., 2006). If no hydrate skin exists on the bubble, then the plume does not reach the surface.

Table 1 - Modelling results for two hypothetical scenarios of catastrophic mud volcano outbursts.

Initial Conditions (Source) Scenario I Scenario II

Initial plume radius (m) 100 100

Bubble diameter (mm) 8 8

Methane flux (mol/s) 1,000,000 1,531,000

Methane flux (kg/s) 16,000 24,496

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Depth (m) 2,000 2,000

Results

Flux methane in bubbles (mol/s) 143,600 319,073

Flux dissolved methane (mol/s) 158,400 1,218,613

Even the most intensive Black Sea bubble seep that was studied within the BIGBLACK and CRIMEA projects does not transfer methane into the atmosphere through bubble transport. Only at 90 m some of the methane can survive in the bubbles to reach the atmosphere, but this is very minor. At larger depths, all methane is stripped from the bubbles long before they reach the surface. The same holds also for a mud volcano (M/V Dvurechenskiy) gas eruption that was monitored during the CRIMEA project. So, in order to cause a significant methane input into the atmosphere, much more violent eruptions are needed. This seems rather unlikely for the shallower seep areas (100, 250, 600 m) given the nature of the seeping process there. On the other hand, it does not seem impossible for a really large mud volcano eruption to generate a much bigger methane bubble flux, with bigger bubbles and possibly even creating a bubble plume, which could eventually make it up to the atmosphere.

Results from the AERMOD atmospheric dispersion model in the case of a 4-hour explosion of a constant rate of 16,000,000 g/s gas at 2,000 m depth are presented. As mentioned above, bubble modelling estimates that 30% of the emitted gas reaches the atmosphere. The equivalent emission rate to the atmosphere would then be 2,400,000 g/s (here we assume that the direct bubble transfer is more efficient than the diffusion of dissolved methane, and hence neglect the latter in the calculation). Assuming the release takes place from an area source 100m x 100m, the maximum increases in the atmospheric levels of methane during the 4-hour eruption as estimated through dispersion modelling (ISC-AERMOD; The et al., 2002), are given in Figure 5.

Figure 5 (revised). Calculated increases in the atmospheric background of methane for

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the case of a catastrophic eruption under different atmospheric conditions. The wind speed used in the calculations was 3m/s, 8 m/s and 12 m/s, for stability classes A, D and F, respectively].

7th and 8th paragraph of the comments:

Comment: “how representative is the hypothesized event?”

Reply: We cannot add much to the statement of the referee, later on in the same paragraph “it is fair to indicate that we do not know anything about the frequency-size distribution of such events”, with which we partly agree. Indeed there are very limited data on the frequency-size distribution of such events. The following text will be added in the revised version:

[Jakubov (1971) provides statistics for 32 eruptions in Eastern Azerbaijan considering that 122 eruptions have occurred during the period 1840-1967. Ali-Zade (1984) states that 200 eruptions in 50 mud volcanoes have occurred in Eastern Azerbaijan from 1910 to 1980, while Ridd (1970) shows a time interval 1-22 years for mud volcanoes in New Zealand. Dimitrov (2002) summarises these and other data to infer, “with great skepticism” that about 30 mud volcanoes of Lokbatan type and 10 ones of the Schugin type erupt every year.]

We would argue that indeed we learn from our calculations; namely that at least certain events are observable from space (see our argumentation below), and this result might ultimately prove very useful in obtaining an idea, from spaceborne observations, about the frequency-size distribution of such events.

Comments on the positioning of the present study for satellite monitoring:

Reply: The modeled event causes a large enough perturbation, even of the columnar amounts, that persists for many hours after the eruption (see below the text that will be included in the revised version, commenting on the scale of the perturbation on an area grid 100 X 100 km2, comparable to the satellite spatial resolution):

[The plume dispersion modelling results show that the spatial average of the methane perturbation during the eruption over a square receptor area with dimension 100km x 100km centered in the source (assuming a 4h release) is approximately 4 ppmv for unstable conditions (A), 10 ppmv for neutral conditions (D) and 20 ppmv for stable conditions (F), which represent increases of the average background methane mixing ratio of 1.86 ppmv over the Black Sea of 315%, 640% and 1175%, respectively.

Assuming that above the mixing height the concentrations of methane remain unaffected at 1.86 ppmv, a tropopause height of 10 km and negligible methane concentrations above the tropopause, these correspond to columnar increases of atmospheric methane of 146%, 216%, and 331% for these three stability classes, respectively.

Similarly, the spatial 24h-average of the methane perturbation over a square receptor area with dimension 100km x 100km centered in the source (also assuming a 4h release) is approximately 0.7 ppm for unstable conditions (A), 2.7 ppm for neutral conditions (D) and 6.5 ppm for stable conditions (F). The wind velocity field was 3, 8 and 12 (m/s) for the stability classes A, D and F, respectively (the perturbation amount will be generally higher for lighter winds). Hence, given an average background methane mixing ratio of 1.86 ppmv over the Black Sea, the calculated increase (%) of the 24-hr average mixing ratio of methane over the 100 km X 100 km area ranges from 35% for unstable conditions to 350% for stable conditions. Again, these correspond to columnar increases of atmospheric methane of 108%, 131%, and 175% for these three stability classes, respectively.]

Clearly, these perturbations of the columnar amounts over the eruption time (4 hr) and over the next 24 hrs following the eruption are fairly larger than the few percent perturbations required for the detection of emissions by the SCIAMACHY instrument. Given the steady improvement of algorithms for the detection of methane from space (e.g. Buchwitz et al., 2000, Buchwitz et al., 2005, Meirink et al., 2006) we do think that we present a case for the detection of either fairly large underwater mud volcano eruptions or modest ones over land.

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Regarding the existing satellite capabilities, the following text will be added in the revised version:

[Generally, the typical spatial resolution of the SCIAMACHY instrument onboard ENVISAT is 30 km by 60 km. Each horizontal scan of the atmosphere in limb covers 960 km in the horizontal (across track direction), and global coverage is achieved after 6 days (Bovensmann et al., 1999). SCIAMACHY consists of eight main spectral channels and seven spectrally broad band Polarization Measurement Devices (PMDs) (details are given in Bovensmann et al., 1999). Observations of channel 8 (from a small spectral fitting window 2265-2280 nm) and PMD number 1 (320-380 nm) have been used in the detection of CH4 (Buchwitz et al., 2000, 2005). In addition, channel 4 has been used to determine the mass of dry air from oxygen (O2) column measurements using the O2 A band (Buchwitz et al., 2000, 2005). Channel 8 spectral resolution is 0.2 nm. For SCIAMACHY the spatial resolution, i.e., the footprint size of a single nadir measurement, depends on the spectral interval and orbital position. For channel 8 the spatial resolution is 30Œ120 km2 corresponding to an integration time of 0.5 s, except at high solar zenith angles, where the pixel size is twice as large (30Œ240 km2). The main scientific application of the methane measurements of SCIAMACHY is to obtain information on the surface sources of methane (e.g. Frankenberg et al., 2005). The modulation of methane columns due to methane sources is only on the order of a few percent. Typically, the weak methane source signal is difficult to be clearly detected with single overpass SCIAMACHY data, unless the variations in atmospheric methane exceed a few percent. Using various bias corrections improved methane data products have been generated (e.g. Buchwitz et al., 2005); their comparison with model simulations shows agreement within a few percent (mostly within 5%). Applications of existing algorithms have shown that SCIAMACHY can detect elevated methane columns resulting from emissions from surface sources such as rice fields and wetlands over India, southeast Asia and central Africa (Buchwitz et al., 2005, Frankenberg et al., 2005).

Hence, considering also the modelling results of the present study, it appears that certain events of mud volcano explosions should be distinguishable from satellite instruments such as SCIAMACHY. Although the present study does neither offer a complete assessment study for the extend of the applicability of satellite monitoring of mud volcano eruptions, nor fully constrain these, it offers nevertheless results that show that such an assessment study might prove very useful. Properly assessing the fraction of the time that an event of various magnitudes might be observable (i.e. both within the limits of temporal coverage and instrument performance], might offer in the near future a means not only to observe such events from space, but also to obtain a size-frequency distribution of these events.]

The latter, is, we believe, a very useful result, and to our knowledge, the first indication in the literature that satellite monitoring of mud volcanoes might be possible. The referee is right that it would be useful to constrain the applicability of satellite sensors for this, but clearly such an extensive assessment study would exceed the purpose of the present manuscript.

9th paragraph of the comments:

Since at the observed supersaturation levels the contribution to atmospheric methane is found to be negligible, we believe that large explosive events are the only mechanism that could add significantly to the atmospheric budget. A discussion on this will be included in the revised version, together with relevant references.

10th paragraph of the comments:

The proposed discussion and references will be included in the revised version.

11th paragraph of the comments, “it is confusing to try to identify in Fig. 1 where data were collected”:

As stated in the beginning, in the revised version, Figures 1a, 1b and 2a are redrawn to indicate the location of the ship (i.e. seep area, Danube fan, Sevastopol harbor, station above active seeps), Fig. 1c with the wind measurements and bathymetry timeseries

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is added and Fig. 2b is redrawn to indicate bathymetry and dates

12th paragraph of the comments:

Fig. 3 has been redrawn to include also a calculation of fluxes with the climatic wind speed value. In general, there are no significant differences in the fluxes, since the climatic value for December is 8 m/s (Sorokin et al., 2002; NEMOC, 2005), very close to the mean of our wind data.

References (these, too, will be included in the revised manuscript, as well as the ones listed in the response to referee #1)

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