

**Response of the  
Black Sea methane  
budget to inputs of  
methane**

O. Schmale et al.

# Response of the Black Sea methane budget to massive short-term submarine inputs of methane

O. Schmale<sup>1</sup>, M. Haeckel<sup>2</sup>, and D. F. McGinnis<sup>2</sup>

<sup>1</sup>Leibniz Institute for Baltic Sea Research Warnemünde (IOW), Rostock, Germany

<sup>2</sup>Leibniz Institute of Marine Sciences (IFM-GEOMAR), Kiel, Germany

Received: 27 October 2010 – Accepted: 2 December 2010 – Published: 15 December 2010

Correspondence to: O. Schmale (oliver.schmale@io-warnemuende.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

A steady state box model was developed to estimate the methane input into the Black Sea water column at various water depths. Our model results reveal a total input of methane of  $4.7 \text{ Tg yr}^{-1}$ . The model predicts that the input of methane is largest at water depths between 600 and 700 m (7% of the total input), suggesting that the dissociation of methane gas hydrates at water depths equivalent to their upper stability limit may represent an important source of methane into the water column. In addition we discuss the effects of massive short-term methane inputs (e.g. through eruptions of deep-water mud volcanoes or submarine landslides at intermediate water depths) on the water column methane distribution and the resulting methane emission to the atmosphere. Our non-steady state simulations predict that these inputs will be effectively buffered by intense microbial methane consumption and that the upward flux of methane is strongly hampered by the pronounced density stratification of the Black Sea water column. For instance, an assumed input of methane of  $179 \text{ Tg CH}_4 \text{ d}^{-1}$  (equivalent to the amount of methane released by 1000 mud volcano eruptions) at a water depth of 700 m will only marginally influence the sea/air methane flux increasing it by only 3%.

## 1 Introduction

For about 30 years the Black Sea methane cycle has been in the focus of international studies (e.g. Hunt, 1974; Kessler et al., 2006; Reeburgh et al., 1991). The Black Sea water column stratification plays a key role in this complex cycle. Its structure is strongly influenced by the inflow of highly saline water via the Bosphorus and freshwater from rivers, mainly Danube, Dnepr and Dnestr, resulting in a permanent pycnocline located at water depths between 100 and 150 m. The lack of sufficient downward supply of dissolved oxygen to counter organic matter fluxes from the highly productive surface waters into the deep waters has resulted in the present anoxic conditions below the

**BGD**

7, 9117–9136, 2010

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

pycnocline and has made the Black Sea the world's largest anoxic basin with CH<sub>4</sub> concentrations of up to 13 μM (Naqvi et al., 2010).

Recent hydroacoustic investigations have shown that active seep sites releasing gas bubbles (consisting mainly of methane) into the water column are widely distributed along the coast, the shelf, shelf edge, and upper slope of the Black Sea (Fig. 1; Dimitrov, 2002; Naudts et al., 2006; Greinert et al., 2006; Nikolovska et al., 2008). Methane is also emitted from submarine mud volcanoes (MVs; Fig. 1). Until today, about 65 MVs have been discovered in the Black Sea. They are located on the Kerch-Taman shelf, the slope off Bulgaria, Ukraine, Russia, Georgia, and Turkey, as well as in the central part of Black Sea (Kruglyakova et al., 2002). The contribution of seeps and MVs to the total Black Sea methane budget, however, is poorly constrained and needs further investigation.

The first Black Sea methane budget by Reeburgh et al. (1991) determined the total water column methane inventory to be 96 Tg. Thus, the Black Sea represents the largest marine water reservoir of dissolved methane. According to Reeburgh et al. (1991), the major methane sources are shelf and slope sediments, which are balanced by anaerobic oxidation of methane as the major sink in the anoxic deep water (4.6 Tg yr<sup>-1</sup>). The second most important sink is the methane flux across the sea/air interface with 0.07 Tg yr<sup>-1</sup>. The total oxidation rate (oxic and anoxic) of 4.6 Tg yr<sup>-1</sup> of CH<sub>4</sub> suggests a residence time of about 20 years for methane. Reeburgh's Black Sea methane budget was modified by Kessler et al. (2006) who estimated the input of methane from seeps and dissociating gas hydrates into the intermediate and deep waters (below 150 m) to be 3.6–5.65 Tg yr<sup>-1</sup>.

Here, we present a steady state box model with a structure similar of that of Kessler et al. (2006) to determine the Black Sea methane budget. Based on this model we establish a non-steady state model to study the response of the Black Sea methane cycle to massive methane inputs (e.g. caused by MV eruptions or submarine landslides), i.e. we analyse how this would affect the methane water concentrations and the fluxes across the air/sea interface.

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2 Model description

Two different models were developed: a steady state box model (Model A) to analyse the recent magnitudes of methane inputs into the Black Sea water column and a non-steady state box model (Model B) to explore the effects of methane injections into different water depths (e.g. by deep-water MV eruptions and landslides at intermediate water depths) on the amount and vertical distribution of methane in the water column as well as on the methane efflux into the atmosphere.

Both box models consist of 20 well-mixed boxes integrating a depth interval of 100 m. Box volumes and areas were calculated based on the GEBCO 1-min global bathymetric grid (<http://www.gebco.net/>). Both models exchange methane with the atmosphere and include the oxic and anoxic parts of the Black Sea water column with an oxic/anoxic interface located 100 m below the sea surface. The shelf and coastal waters (water depth <100 m) are not included in our model because the distribution and intensity of methane sources (e.g. river plumes and shallow seep areas) and sinks (e.g. water column methane oxidation and evasion to the atmosphere) are very complex. At the present time, these are poorly constrained in these regions. Methane emitting areas in these shallow areas show only regional influences on the water column methane distribution and are not affecting the open water body of the Black Sea (Schmale et al., 2010).

Water fluxes into and out of the Black Sea were adopted from Özsoy and Ünlüata (1997), but ignore the negligible effects of evaporation, rain, and river inflow on the Black Sea open ocean methane budget. Our model considers a Bosphorus inflow of  $300 \text{ km}^3 \text{ yr}^{-1}$  and a similar outflow of  $300 \text{ km}^3 \text{ yr}^{-1}$  into the Sea of Marmara. The influx of Bosphorus water is mainly restricted to a water depth between 100 and 500 m (Oguz and Rozman, 1991), which is balanced by upwelling that is represented by an advective transport (Özsoy and Ünlüata, 1997).

In addition to advection of solutes, the model includes the vertical transfer of methane by eddy diffusion (i.e.  $K_z$ ). In the nearly stagnant Black Sea deep waters (500–2000 m)

**BGD**

7, 9117–9136, 2010

### Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the transport of methane is restricted to turbulent diffusion. Eddy diffusion coefficients ( $K_z$ ) were calculated on the base of CTD profiles to estimate turbulent overturns (Galbraith and Kelley, 1995).

For the non-steady state Model B, which is used to analyze the response of the Black Sea methane cycle to massive methane injections, the methane input into different water depths was calculated by a gas bubble dissolution model (McGinnis et al., 2006), i.e. a rate-depth profile for the dissolution of rising methane gas bubbles is prescribed. This function predicts the evolving bubble size, gas composition, total bubble rise distance, and dissolution/stripping of five gases (Ar, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>). The model is adapted for the hydrographic conditions of the Black Sea and considers the formation of a hydrate rim around the methane gas bubble within the hydrate stability zone (i.e., below 700 m; Vassilev and Dimitrov, 2002).

To study the sea-air gas exchange in our box model, the surface water box is also connected to the atmosphere. The methane flux across the sea surface ( $F_{CH_4}$ ) is calculated based on the sea-air gas exchange model of Wanninkhof (Wanninkhof, 1992) for long-term wind averages.

$$F_{CH_4} = kw(C_A - C_1)A_1 \quad (1)$$

where  $kw$  represents the gas transfer velocity across the sea surface,  $C_1$  is the dissolved methane concentration in the surface water box (Box 1; depth interval 0–100 m),  $C_A$  is the theoretical thermodynamic equilibrium concentration between surface waters and the ambient atmosphere, and  $A_1$  is the surface area. Methane solubility in seawater was calculated following Wiesenburg and Guinasso (Wiesenburg and Guinasso, 1979). Averaged values for salinity, temperature, wind speed, and atmospheric methane concentration were taken from the literature (Table 1 in the Supplement).

Methane oxidation rates were calculated based on the dataset published by Reeburgh et al. (1991). They have been shown to depend linearly on the dissolved methane concentration (Ward et al., 1987). Consequently, we applied a first order rate

**BGD**

7, 9117–9136, 2010

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

law, assuming that electron acceptors (i.e.,  $\text{SO}_4^{2-}$  and  $\text{O}_2$ ) are not limiting the microbial methane oxidation rates to derive depth-specific kinetic constants.

$$R_{\text{ox}} = k [\text{CH}_4] \Rightarrow k = \frac{R_{\text{ox}}}{[\text{CH}_4]} \quad (2)$$

where  $k$  is the kinetic constant for methane oxidation,  $R_{\text{ox}}$  the methane oxidation rate, and  $[\text{CH}_4]$  the dissolved methane concentration ( $R_{\text{ox}}$  and  $[\text{CH}_4]$  were taken from Reeburgh et al., 1991). The data from Reeburgh et al. (1991) contain a high-quality dataset with the densest sampling interval available for the central Black Sea.

The detailed parameter values, notations, and references used in the model as well as the transport-reaction equations for each box are listed in the Supplement.

### 3 Results and discussion

#### 3.1 Model A: input of methane into the Black Sea water column

A steady state box model was applied to quantify a depth-dependent input of methane to the Black Sea water column. The recent Black Sea methane distribution shows methane concentrations in the nanomolar range (average of 8.7 nM; Table 1 in the Supplement) at water depth between 0 and 100 m. At intermediate water depths of 100 to 600 m the methane concentration increases linearly with depth. The deep waters (600–2200 m) are characterized by uniform methane concentrations of around 11  $\mu\text{M}$  (Reeburgh et al., 1991).

The methane inputs in each box of our Model A were varied until the modelled methane concentrations agreed with the averaged measurements published by Reeburgh et al. (1991; modelled versus measured concentrations are listed for each box in Table 1 in the Supplement). Similar to the results published by Kessler et al. (2006) the modelled results displayed in Fig. 2 indicate that most  $\text{CH}_4$  is entering the Black Sea waters between 600–700 m water depth ( $0.33 \text{ Tg CH}_4 \text{ yr}^{-1}$ , i.e. 7%

**BGD**

7, 9117–9136, 2010

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of the total input). The lower boundary of this depth range is close to the stability boundary of methane hydrates (670–700 m; Vassilev and Dimitrov, 2002). Poort et al. (2005) have modelled the regional response of the gas hydrate stability zone to the post glacial flooding and resulting bottom water temperature increase in the Black Sea.

5 They predict that at present a widespread dissociation of gas hydrates is expected to occur at the minimum water depth for hydrate stability. The model results imply that gas hydrate dissociation at the Black Sea continental slopes may take place and serve as an important methane source to intermediate waters. However, so far only a few active seep sites influencing the methane concentrations in the water column have been discovered in this specific depth range (Fig. 1). Hydroacoustic seep detection along the slope of the NW Black Sea indicates that the minimum depth of gas hydrate stability is not characterized by a higher-than-average number of seep sites (Naudts et al., 2006).

10 In contrast to previously published Black Sea methane models, our model also describes the methane cycle in the upper 100 m of the Black Sea water column. The model predicts that diffusive and advective transports are not sufficient to maintain the average surface water methane concentration of 8.7 nM observed by Reeburgh et al. (1991); the modelled concentration without additional surface water input is 5.9 nM. An additional input of  $0.009 \text{ Tg yr}^{-1}$  of  $\text{CH}_4$  is needed to reach a surface water methane concentration similar to the one published by (Reeburgh et al., 1991). This open ocean methane source at shallow water depths is provided by microbial subsurface methane generation taking place in zooplankton guts, the oxygen-deficient interior of particles (e.g. fecal pellets), or under phosphate limiting conditions (Damm et al., 2010; Karl et al., 2008). Subsurface methane maxima together with light  $^{13}\text{C}\text{CH}_4$  anomalies have been observed in the upper water column of the Black Sea by Schmale et al. (2010) indicating that this methane production occurs in the oxygenated water column. The limited methane transport across the pycnocline by eddy diffusion and upwelling stresses that the subsurface methane generation is crucial for the methane flux across the sea surface in Black Sea open waters. However, the subsurface methane production rate is poorly constrained by our model, because the methane source term in the upper

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



100 m is highly correlated to rate of sea-air gas exchange. Depending on the approach used to parameterize the gas transfer velocity ( $kw$ ) the sea-air flux estimates can show large variations (Wanninkhof et al., 2009).

Overall, the basin-wide  $CH_4$  input of  $4.7 \text{ Tg yr}^{-1}$  calculated by our Model A is similar to the estimate published by Kessler et al. (2006; i.e.  $3.6\text{--}5.65 \text{ Tg yr}^{-1}$ ) and identical with the sediment production calculated by Reeburgh et al. (1991). The good agreement between these different datasets represents an indirect validation of our steady state model.

### 3.2 Model B: influence of massive short-term methane injections on the Black Sea methane budget

Based on the structure of Model A a non-steady state model was applied to predict the effects of massive short-term methane injections on the methane distribution in the Black Sea water column. Two scenarios are discussed: (Model B1) the release of methane from numerous of Black Sea MVs in the abyssal plain at about 2000 m water depths (Fig. 1), and (Model B2) the injection of methane at the gas hydrate stability boundary where hydrate dissociation may take place and submarine landslides could be expected (670–700 m; Vassilev and Dimitrov, 2002; Poort et al., 2005).

The approach was to separately increase the methane input to these two water depths (represented by boxes 7 and 20; i.e. depth intervals of 600–700 m and 1900–2000 m, respectively) and to simulate the evolution of methane concentration in the Black Sea water column and the resulting flux of methane across the sea surface until a steady state was reached.

It is difficult to constrain the methane release from MV eruptions or submarine landslides since no direct gas flux measurements are available from these events. In terms of MV eruptions a few estimates exist implying that gas fluxes are on the order of  $10^7$  to  $10^{10} \text{ m}^3$  (STP = at standard pressure and temperature conditions, i.e.,  $25^\circ\text{C}$  and 1 bar) over several days (Milkov et al., 2003, and references therein). In our model, we use a number which is based on gas flux records during strong eruptions of onshore mud

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





volcanoes in Azerbaijan ( $2.5 \times 10^8 \text{ m}^3 \text{ CH}_4$  (= 179 Gg or  $1.1 \times 10^{10}$  mol) per eruptive MV event; Dadashev, 1963; a number also used by Milkov et al., 2003) to estimate the global gas flux from eruptive MVs. To model the effect of massive short-term methane inputs we use a fictive number of 179 Tg  $\text{CH}_4$  (equivalent to the amount of methane released by 1000 MV eruptions) released within a day. We also assume that these kinds of massive sedimentary gas inputs will be characterized by the release of free gas (i.e. gas bubbles). To describe the input of methane into different water depths by ascending gas bubbles, we applied the gas bubble dissolution model of McGinnis et al. (2006). The largest bubbles observed in the Black Sea are around 18 mm in diameter (McGinnis et al., 2006, and references therein). This most likely represents the upper size limit, as larger bubbles may have a tendency to break apart during their rise and are transported as smaller bubbles with faster dissolution and gas exchange (McGinnis et al., 2006). For our model run we use an initial bubble diameter of 20 mm, hypothesizing that an eruptive gas release would rather result in the liberation of large bubbles.

### 3.2.1 Model B1: methane input at 2000 m water depth

The simulation of Model B1 was initiated with the steady state methane concentrations obtained with Model A. Further, we assume a methane release of 179 Tg of  $\text{CH}_4$  at 2000 m water depth over an eruptive phase of one day (e.g. eruptions of 1000 MVs). Proposing that the gas exclusively consists of methane, the eruptions will increase the input of methane in box 20 (depth interval 2000–1900 m) at a rate of  $10.9 \text{ Gg km}^{-3} \text{ d}^{-1}$ . The bubble model of McGinnis et al. (2006) predicts that within the hydrate stability zone (i.e., below 700 m water depth) the bubble dissolution rate is slowed down by the formation of a gas hydrate rim around the bubble (Fig. 3a). After passing the stability boundary of gas hydrates, the model assumes that the hydrate skin disappears instantly, resulting in faster bubble dissolution rates and increasing methane inputs.

**BGD**

7, 9117–9136, 2010

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

For this massive methane input the model results suggest that it takes about 200 years to return to the previous steady state methane concentrations. In this run the initial methane input in box 20 (1900–2000 m) results in a concentration increase within this box which is about fivefold higher than the concentration derived from our steady state calculations (Model A, Fig. 4a). The methane input caused by the rapid dissolution of gas bubbles above the hydrate stability zone leads to a concentration increase in box 7 (600–700 m) which is about seven times higher than the steady state concentration. However, the large methane input is effectively buffered by microbial methane consumption and pronounced water column stratification leading to a constantly decreasing influence on the methane concentrations in the overlying boxes. The model shows that the influence of such a major event on the surface water methane concentration is negligible and only leads to a 2-% increase in the sea/air methane flux.

To test if the concentrations of  $\text{SO}_4^{2-}$  in the anoxic Black Sea waters are high enough to compensate for the high  $\text{CH}_4$  input of the MV eruption scenario (i.e.  $1.1 \times 10^{13}$  mol of  $\text{CH}_4$  for 1000 MV eruptions), we calculated the total amount of sulfate below 100 m water depth. The balance shows that the total amount of sulfate of about  $9 \times 10^{18}$  mol can easily compensate for the maximum methane injections. The annual sulfate input from the Bosphorus ( $0.95 \times 10^{13}$  mol) is already of the same order of magnitude.

### 3.2.2 Model B2: methane input at 700 m water depth

Our second case study focused on the inspection of a methane release to intermediate water depths (e.g. catastrophic submarine landslide) and its influence on the water column methane distribution and the subsequent atmospheric emission. Also, this model run was initiated with steady state methane concentrations calculated in Model A and assumes a methane release of 179 Tg of  $\text{CH}_4$  at 700 m water depth over a time span of one day. Such an event will increase the input of methane to box 7 (depth interval 600–700 m) to  $6.2 \text{ Gg km}^{-3} \text{ d}^{-1}$ . In contrast to Model B1 methane is released above the hydrate stability zone resulting in a constantly decreasing bubble size and methane input during the bubble ascent (Fig. 3b).

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



After the injection of gas, the initial methane concentration in box 7 increases up to 200 000 nM (about 20 times higher than the steady state concentration calculated in Model A). The relaxation time needed for the system to return to previous steady state concentrations is about 200 years. Also, this study shows that methane is efficiently consumed microbially and that the exchange between individual boxes is strongly hampered, resulting in a limited transport of methane towards the sea surface (Fig. 4b). The slightly elevated surface water methane concentration increases the methane emission across the sea surface by only 3%.

#### 4 Conclusion and outlook

Our model predicts that massive short-term injections of methane will be effectively buffered in the Black Sea water column. Even if the gas is liberated at intermediate water depths methane transport to the surface and thus emission across the sea/air interface is strongly reduced by microbial methane consumption and the hydrographic stratification of the Black Sea. However, we have to take into account in our model approach, that violent eruptions in spatially limited regions will probably be characterized by the creation of a focused two-phase plume consisting of methane gas bubbles and methane saturated ambient seawater (Leifer and Patro, 2002). These conditions reduce the bubble dissolution rates and increase the bubble life-time as well as its vertical rise velocity in the water column. Violent eruptions may thus have the capacity to transfer methane from deep waters into shallow water depths. However, our box model is not able to take these rapid localized transport features into account since it assumes well-mixed boxes.

**BGD**

7, 9117–9136, 2010

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

*Acknowledgements.* We thank Gregor Rehder, Robin Keir and Christian Holzner for comments and suggestions which considerably helped to improve the manuscript.

## References

- Dadashev, F. G.: Hydrocarbon gases of mud volcanoes of Azerbaijan, Azerneshr, Baku, 1963 (in Russian).
- Damm, E., Helmke, E., Thoms, S., Schauer, U., Nöthig, E., Bakker, K., and Kiene, R. P.: Methane production in aerobic oligotrophic surface water in the central Arctic Ocean, *Biogeosciences*, 7, 1099–1108, doi:10.5194/bg-7-1099-2010, 2010.
- Dimitrov, L.: Contribution to atmospheric methane by natural seepages on the Bulgarian continental shelf, *Cont. Shelf Res.*, 22, 2429–2442, 2002.
- Galbraith, P. S. and Kelley, D. F.: Identifying overturns in CTD profiles, *J. Atmos. Ocean. Tech.*, 13, 688–702, 1995.
- Greinert, J., Artemov, Y., Egorov, V. N., De Batist, M., and McGinnis, D.: 1300-m-high rising bubbles from mud volcanoes at 2080 m in the Black Sea: Hydroacoustic characteristics and temporal variability, *Earth Planet. Sc. Lett.*, 244, 1–15, 2006.
- Hunt, J. M.: Hydrocarbon Geochemistry of Black Sea, in: *The Black Sea – Geology, Chemistry, and Biology*, edited by: Degens, E. T. and Ross, D. A., The American Association of Petroleum Geologists, 499–504, 1974.
- Karl, D. M., Beversdorf, L., Bjorkman, K. M., Church, M. J., Martinez, A., and Delong, E. F.: Aerobic production of methane in the sea, *Nat. Geosci.*, 1, 473–478, 2008.
- Kessler, J. D., Reeburgh, W. S., Southon, J., Seifert, R., Michaelis, W., and Tyler, S. C.: Basin-wide estimates of the input of methane from seeps and clathrates to the Black Sea, *Earth Planet. Sci. Lett.*, 243, 366–375, 2006.
- Kruglyakova, R., Gubanov, Y., Kruglyakov, V., and Prokoptsev, G.: Assessment of technogenic and natural hydrocarbon supply into the Black Sea and seabed sediments, *Cont. Shelf Res.*, 22, 2395–2407, 2002.
- Kruglyakova, R. P., Byakov, Y. A., Kruglyakova, M. V., Chalenko, L. A., and Shevtsova, N. T.: Natural oil and gas seeps on the Black Sea floor, *Geo-Mar. Lett.*, 24, 150–162, 2004.
- Leifer, I. and Patro, R.: The bubble mechanism for transport of methane from the shallow

**BGD**

7, 9117–9136, 2010

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

seabed to the surface: a review and sensitivity study, *Cont. Shelf Res.*, 22, 2409–2428, 2002.

McGinnis, D. F., Greinert, J., Artemov, Y., Beaubien, S. E., and Wüest, A.: Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere?, *J. Geophys. Res.*, 111, C09007, doi:10.1029/2005jc003183, 2006.

Milkov, A. V., Sassen, R., Tatiyana, V., Apanasovich, V., and Dadashev, G.: Global gas flux from mud volcanoes: A significant source of fossil methane in the atmosphere and the ocean, *Geophys. Res. Lett.*, 30, 1037, doi:10.1029/2002GL016358, 2003.

Naqvi, S. W. A., Bange, H. W., Farías, L., Monteiro, P. M. S., Scranton, M. I., and Zhang, J.: Marine hypoxia/anoxia as a source of CH<sub>4</sub> and N<sub>2</sub>O, *Biogeosciences*, 7, 2159–2190, doi:10.5194/bg-7-2159-2010, 2010.

Naudts, L., Greinert, J., Artemov, Y., Staelens, P., Poort, J., Van Rensbergen, P., and De Batist, M.: Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea, *Mar. Geol.*, 227, 177–199, 2006.

Nikolovska, A., Sahling, H., and Bohrmann, G.: Hydroacoustic methodology for detection, localization, and quantification of gas bubbles rising from the seafloor at gas seeps from the eastern Black Sea, *Geochem. Geophys. Geosy.*, 9, Q10010, doi:10.1029/2008gc002118, 2008.

Oguz, T. and Rozman, L.: Characteristics of the Mediterranean underflow in the southwestern Black Sea continental shelf/slope region, *Oceanol. Acta*, 14, 433–444, 1991.

Özsoy, E. and Ünlüata, Ü.: Oceanography of the Black Sea: a review of some recent results, *Earth-Sci. Rev.*, 42, 231–272, 1997.

Poort, J., Vassilev, A., and Dimitrov, L.: Did postglacial catastrophic flooding trigger massive changes in the Black Sea gas hydrate reservoir?, *Terra Nova*, 17, 135–140, 2005.

Reeburgh, W. S., Ward, B. B., Whalen, S. C., Sandbeck, K. A., Kilpatrick, K. A., and Kerkhof, L. J.: Black Sea methane geochemistry, *Deep-Sea Res.*, 38, 1189–1210, 1991.

Schmale, O., Beaubien, S. E., Rehder, G., Greinert, J., and Lombardi, S.: Gas seepage in the Dnepr paleo-delta area (NW-Black Sea) and its regional impact on the water column methane cycle, *J. Marine Syst.*, 80, 90–100, 2010.

Vassilev, A. and Dimitrov, L.: Spatial and quantity evaluation of the Black Sea gas hydrates, *Russ. Geol. Geophys.*, 43, 637–649, 2002.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373–7382, 1992.

Wanninkhof, R., Asher, W., Ho, D. T., Sweeney, C., and McGillis, W. R.: Advances in quantifying air-sea gas exchange and environmental forcing, *Annual Review of Marine Science*, 1, 213–244, 2009.

5 Ward, B. B., Kilpatrick, K. A., Novelli, P. C., and Scranton, M. I.: Methane oxidation and methane fluxes in the ocean surface layer and deep waters, *Nature*, 327, 226–229, 1987.

Wiesenburg, D. A. and Norman L. Guinasso, J.: Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water, *J. Chem. Eng. Data*, 24, 356–360, 1979.

## BGD

7, 9117–9136, 2010

### Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Response of the Black Sea methane budget to inputs of methane**

O. Schmale et al.

**Table 1.** Parameter values, notations, and references.

Parameter/Symbol/Unit	Value										Reference
Box <i>n</i>	1	2	3	4	5	7	8	9	10		
Volume <i>V</i> , km <sup>3</sup>	31 400	31 400	30 614	30 143	29 660	29 188	28 704	28 266	27 748	27 234	GEBCO
Area <i>A</i> , km <sup>2</sup>	322 267	322 267	308 795	303 703	298 924	294 217	289 350	284 887	280 079	275 008	GEBCO
Bosphorus inflow <i>B</i> <sub>in</sub> , km <sup>3</sup>	–	75	75	75	75	–	–	–	–	–	Özoy and Ünlüata (1997)
Bosphorus outflow <i>B</i> <sub>out</sub> , km <sup>3</sup>	300	–	–	–	–	–	–	–	–	–	Özoy and Ünlüata (1997)
Bosphorus CH <sub>4</sub> concentration <i>C</i> <sub>BIn</sub> , nM	–	8.5	8.5	8.5	8.5	–	–	–	–	–	steady st. CH <sub>4</sub> conc. in box 1
Upwelling <i>u</i> <sub>up</sub> , km <sup>3</sup>	–	300	225	150	75	–	–	–	–	–	Oguz and Rozman (1991)
Eddy diffusion <i>K</i> <sub><i>e</i></sub> , m <sup>2</sup> s <sup>-1</sup>	2.1 × 10 <sup>-6</sup>	4.3 × 10 <sup>-6</sup>	8.2 × 10 <sup>-6</sup>	1.5 × 10 <sup>-5</sup>	2.9 × 10 <sup>-5</sup>	4.0 × 10 <sup>-5</sup>	5.5 × 10 <sup>-5</sup>	7.5 × 10 <sup>-5</sup>	1.0 × 10 <sup>-4</sup>	1.4 × 10 <sup>-4</sup>	This study
Box thickness Δ <i>z</i> , km	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Kinetic const. aerobic CH <sub>4</sub> oxidation <i>k</i> <sub>OM</sub> , yr <sup>-1</sup>	0.043	–	–	–	–	–	–	–	–	–	Reeburgh et al. (1991)
Kinetic const. anaerobic CH <sub>4</sub> oxidation <i>k</i> <sub>ADM</sub> , yr <sup>-1</sup>	–	0.442	0.154	0.096	0.072	0.060	0.055	0.055	0.055	0.055	Reeburgh et al. (1991)
Wind speed <i>u</i> <sub>wind</sub> , m s <sup>-1</sup>	4.8	–	–	–	–	–	–	–	–	–	Reeburgh et al. (1991)
Surface water temperature <i>t</i> , °C	15	–	–	–	–	–	–	–	–	–	Sorokin (2002)
Surface water salinity <i>S</i> , g kg <sup>-1</sup>	17.9	17.9	–	–	–	–	–	–	–	–	Sorokin (2002)
Atmospheric methane concentration <i>C</i> <sub>A</sub> , ppmv	1.86	1.86	–	–	–	–	–	–	–	–	Schmale et al. (2005)
Measured CH <sub>4</sub> concentration (mean), nM	8.7	1359	3899	6232	8293	9929	10 904	10 904	10 904	10 904	Reeburgh et al. (1991)
Modelled CH <sub>4</sub> concentration, nM	8.5	1365	3860	6240	8290	9919	10 900	10 904	10 906	10 907	This study, Model A
Box <i>n</i>	11	12	13	14	15	16	17	18	19	20	
Volume <i>V</i> , km <sup>3</sup>	26 611	26 026	25 324	24 640	23 770	22 862	21 635	20 505	18 604	32 398	GEBCO
Area <i>A</i> , km <sup>2</sup>	269 058	263 266	256 771	249 987	242 186	233 355	222 496	210 737	197 443	175 593	GEBCO
Eddy diffusion <i>K</i> <sub><i>e</i></sub> , m <sup>2</sup> s <sup>-1</sup>	1.9 × 10 <sup>-4</sup>	2.6 × 10 <sup>-4</sup>	3.5 × 10 <sup>-4</sup>	4.8 × 10 <sup>-4</sup>	6.6 × 10 <sup>-4</sup>	8.5 × 10 <sup>-4</sup>	8.5 × 10 <sup>-4</sup>	8.5 × 10 <sup>-4</sup>	8.5 × 10 <sup>-4</sup>	8.5 × 10 <sup>-4</sup>	This study
Box thickness Δ <i>z</i> , km	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Kinetic const. anaerobic CH <sub>4</sub> oxidation <i>k</i> <sub>ADM</sub> , yr <sup>-1</sup>	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	Reeburgh et al. (1991)
Measured CH <sub>4</sub> concentration (mean), nM	10 904	10 904	10 904	10 904	10 904	10 904	10 904	10 904	10 904	10 904	Reeburgh et al. (1991)
Modelled CH <sub>4</sub> concentration, nM	10 908	10 908	10 908	10 908	10 908	10 908	10 908	10 908	10 908	10 908	This study, Model A

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.

**Table 2.** Differential equations for each box (abbreviations are listed in Table 1).

Box	Differential equations
1	$\frac{\partial C_n}{\partial t} = \frac{kW(C_A - C_n)A_n}{V_n} - k_{OM} \cdot C_n + \frac{B_{up,n} \cdot C_{n+1}}{V_n} - \frac{B_{out} \cdot C_n}{V_n} - \frac{Kz_n(C_n - C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in,n}$
2–4	$\frac{\partial C_n}{\partial t} = \frac{Kz_{n-1}(C_{n-1} - C_n)A_n}{\Delta z_n \cdot V_n} - k_{AOMn} \cdot C_n + \frac{B_{in} \cdot C_{Bin}}{V_n} - \frac{u_{up,n} \cdot C_n}{V_n} + \frac{u_{up,n+1} \cdot C_{n+1}}{V_n} - \frac{Kz_n(C_n - C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in,n}$
5	$\frac{\partial C_n}{\partial t} = \frac{Kz_{n-1}(C_{n-1} - C_n)A_n}{\Delta z_n \cdot V_n} - k_{AOMn} \cdot C_n + \frac{B_{in} \cdot C_{Bin}}{V_n} - \frac{u_{up,n} \cdot C_n}{V_n} - \frac{Kz_n(C_n - C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in,n}$
6–19	$\frac{\partial C_n}{\partial t} = \frac{Kz_{n-1}(C_{n-1} - C_n)A_n}{\Delta z_n \cdot V_n} - k_{AOMn} \cdot C_n - \frac{Kz_n(C_n - C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in,n}$
20	$\frac{\partial C_n}{\partial t} = \frac{Kz_{n-1}(C_{n-1} - C_n)A_n}{\Delta z_n \cdot V_n} - k_{AOMn} \cdot C_n + R_{in,n}$

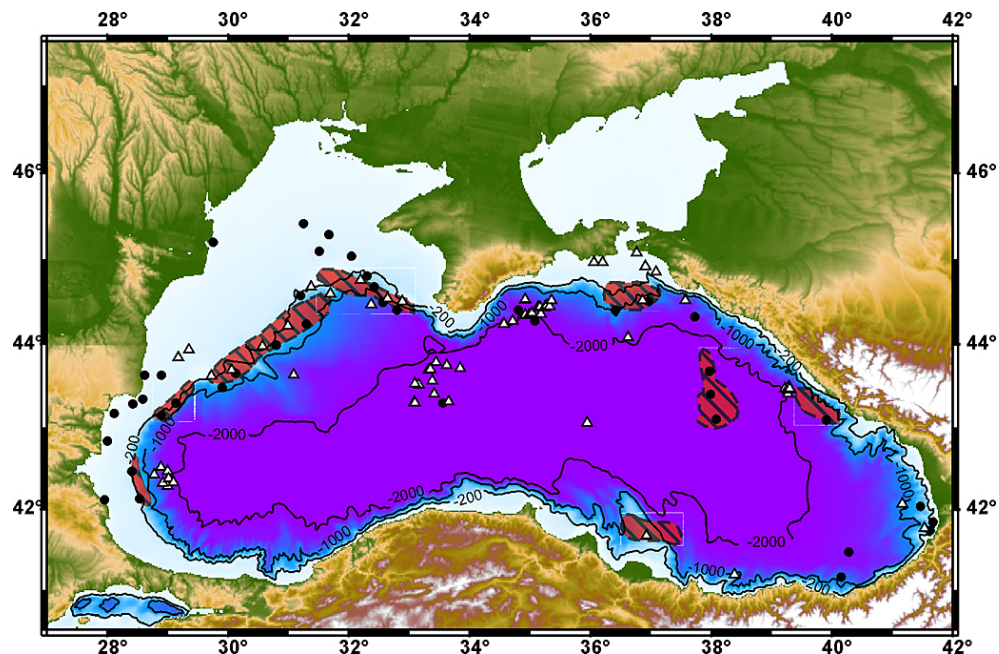
$R_{in,n}$  represents the methane flux into each box.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)



## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.



**Fig. 1.** Map of gas and fluid discharge in the Black Sea. Triangles and dots represent locations of submarine mud volcanoes and areas of intense fluid discharge, respectively. Red areas represent regions of gas seepage and seabed pockmarks. Map is based on a data compilation from Kruglyakova et al. (2004) and Vassilev and Dimitrov (2002).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

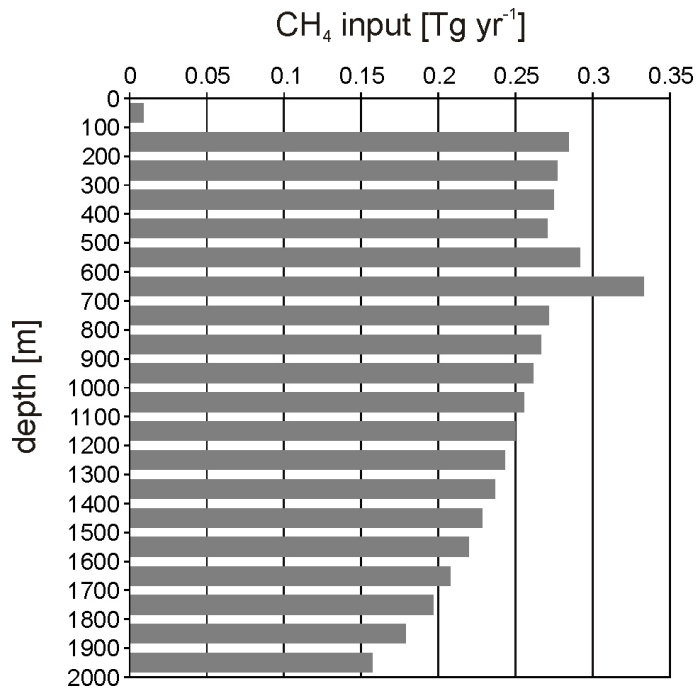
Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Fig. 2.** Methane inputs into different water depths based on steady state Model A.

**Response of the Black Sea methane budget to inputs of methane**

O. Schmale et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

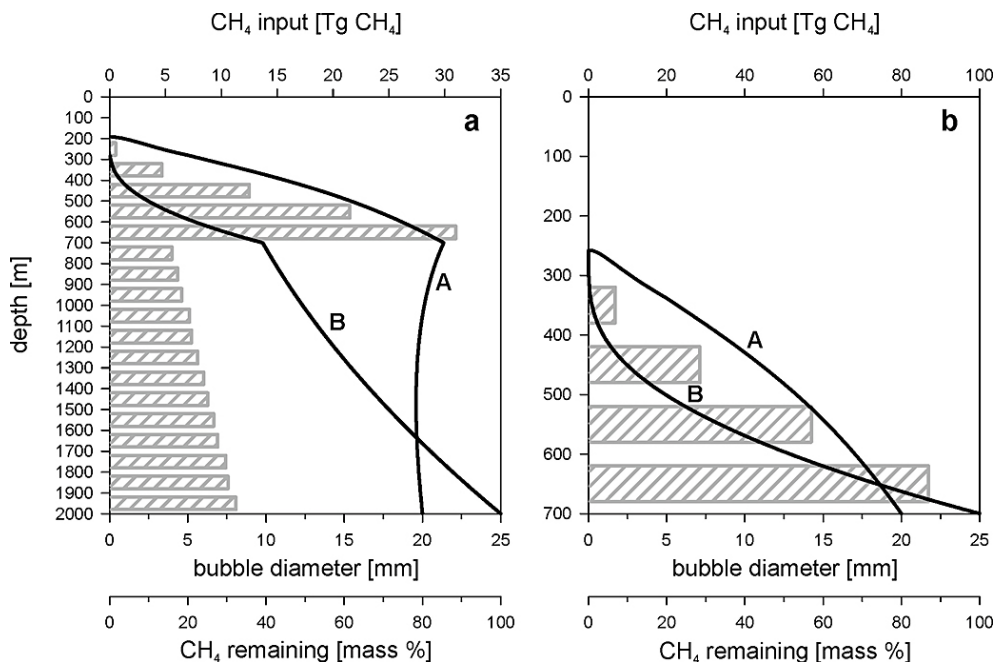
Printer-friendly Version

Interactive Discussion



Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.



**Fig. 3.** Inputs of methane into different water depths after a release of  $179 \text{ Tg d}^{-1}$  of  $\text{CH}_4$  at **(a)** 2000 m and **(b)** 700 m water depth. The input function is based on a bubble model predicting the (A) evolution of the bubble size and (B) the fraction of methane remaining in the uprising bubble (McGinnis et al., 2006). Note the different depth scales.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

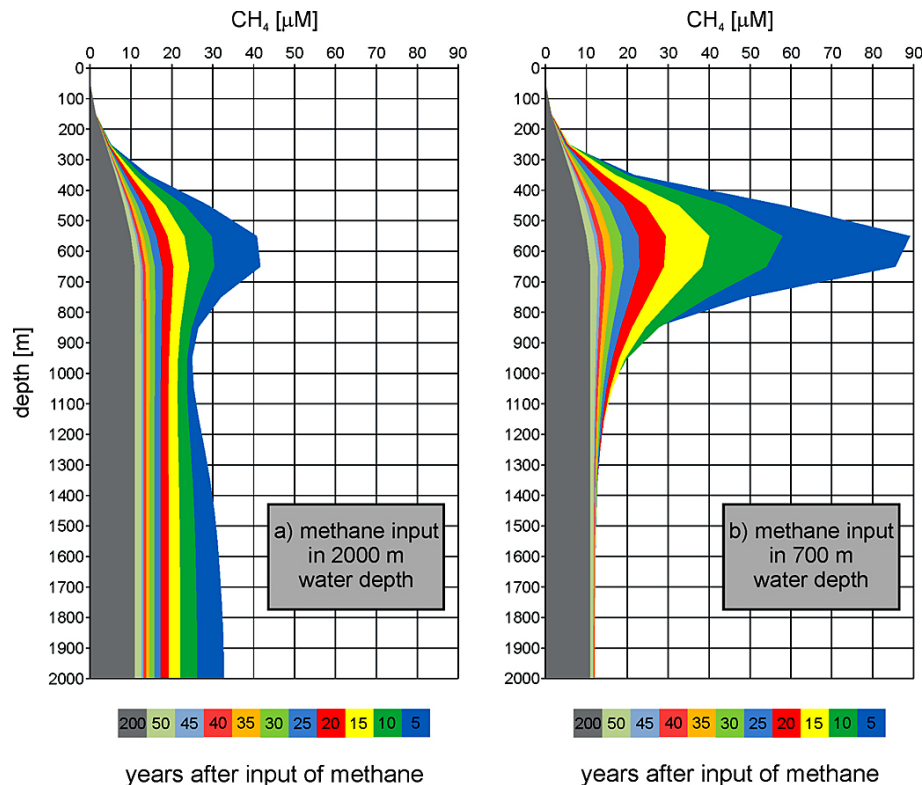
Printer-friendly Version

Interactive Discussion



## Response of the Black Sea methane budget to inputs of methane

O. Schmale et al.



**Fig. 4.**  $\text{CH}_4$  evolution over time after an initial input of 179 Tg of  $\text{CH}_4$ . The left panel **(a)** represents the dissolved methane distribution after an input at 2000 m water depth. The right panel **(b)** shows the distribution after an input at 700 m water depth. The colour scale indicates the years after the input event. The gray area represents the final steady state methane concentration in the Black Sea water column.