

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

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**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 yr 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

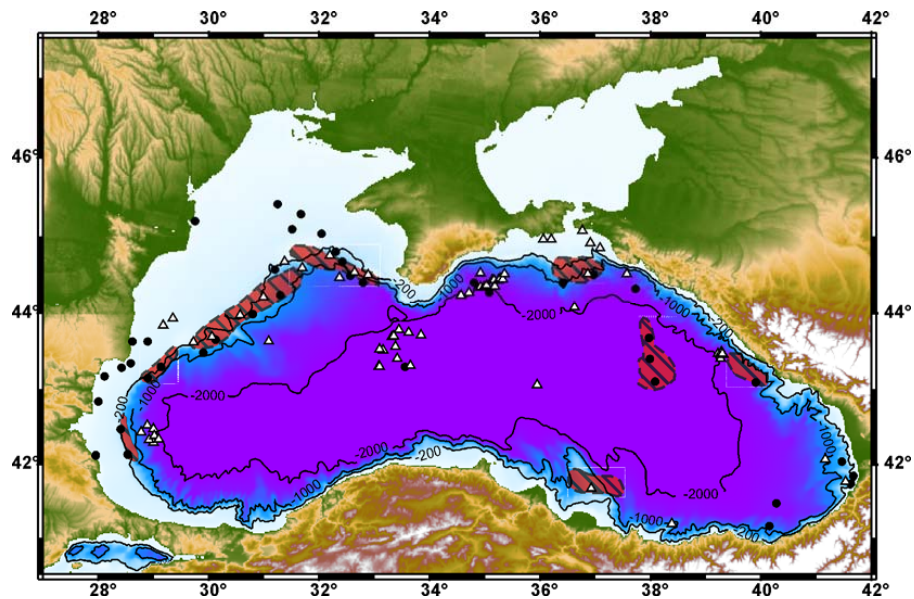
pycnocline located at water depths between 100 and 150 m. The lack of sufficient downward supply of dissolved oxygen to counter organic matter fluxes from the highly productive surface waters into the deep waters has resulted in the present anoxic conditions below the pycnocline and has made the Black Sea the world's largest anoxic basin with  $\text{CH}_4$  concentrations of up to  $13 \mu\text{M}$  (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  $96 \text{ Tg}$ . 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 ( $4.6 \text{ Tg yr}^{-1}$ ). The second most important sink is the methane flux across the sea/air interface with  $0.07 \text{ Tg yr}^{-1}$ . The total oxidation rate (oxic and anoxic) of  $4.6 \text{ Tg yr}^{-1}$  of  $\text{CH}_4$  suggests a residence time of about 20 yr 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  $3.6\text{--}5.65 \text{ Tg yr}^{-1}$ . The regional influence of focused methane gas emissions



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**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).

on the atmospheric methane budget caused by massive methane inputs (e.g. MV eruptions) is studied by Kourtidis et al. (2006), but ignores any effects from the well-documented microbially mediated oxidation of methane in the oxic and anoxic part of the Black Sea water column.

Here, we present a steady state box model with a structure similar to 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.

## 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) 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 ( $F_{\text{CH}_4}$ ) is calculated based on the sea-air gas exchange model of Wanninkhof (Wanninkhof, 1992) for long-term wind averages.

$$F_{\text{CH}_4} = kw(C_{\text{AE}} - C_1)A_1 \quad (1)$$

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),  $C_{\text{AE}}$  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).

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 law, assuming that electron acceptors (i.e., SO<sub>4</sub><sup>2-</sup> and O<sub>2</sub>) 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. Inhomogeneous oxidation rates within the upper 500 m result in decreasing  $k$  values (box 1–5, Table 1). Below 500 m water depth (box 6–20) the oxidation rates are homogeneous leading to constant  $k$  values.

The detailed parameter values, notations, and references used in the model as well as the transport-reaction equations for each box are listed in Tables 1 and 2.

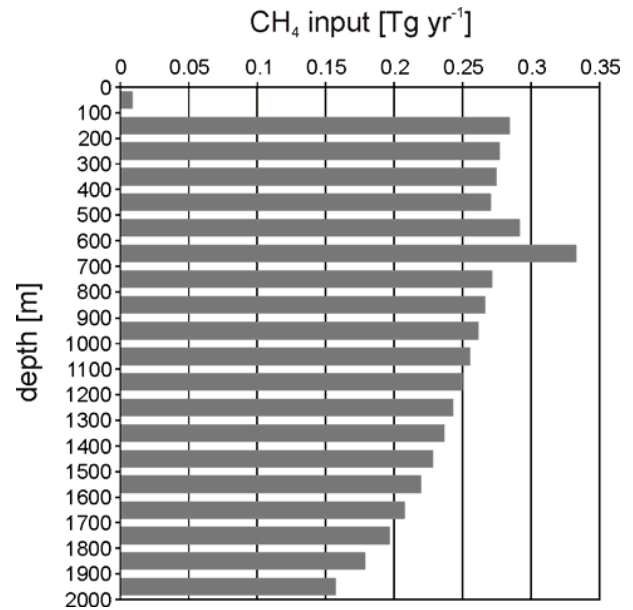


Fig. 2. Methane inputs into different water depths based on steady state Model A.

### 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) 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 μM (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). Similar to the results published by Kessler et al. (2006) the modelled results displayed in Fig. 2 indicate that most CH<sub>4</sub> is entering the Black Sea waters between 600–700 m water depth (0.33 Tg CH<sub>4</sub> yr<sup>-1</sup>, i.e. 7% 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. They predict that at present a widespread dissociation of gas hydrates is expected to occur at the minimum water depth for

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

Parameter/Symbol/Unit	Value										Reference
Box $n$	1	2	3	4	5	6	7	8	9	10	
Volume $V$ , 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 $A$ , 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 $B_{in}$ , km <sup>3</sup>	–	75	75	75	75	–	–	–	–	–	Özsoy and Ünlüata (1997)
Bosphorus outflow $B_{out}$ , km <sup>3</sup>	300	–	–	–	–	–	–	–	–	–	Özsoy and Ünlüata (1997)
Bosphorus CH <sub>4</sub> concentration $C_{Bin}$ , nM	–	8.5	8.5	8.5	8.5	–	–	–	–	–	steady st. CH <sub>4</sub> conc. in box 1
Upwelling $u_{up}$ , km <sup>3</sup>	–	300	225	150	75	–	–	–	–	–	Oguz and Rozman (1991)
Eddy diffusion $K_z$ , m <sup>2</sup> s <sup>-1</sup>	$2.1 \times 10^{-6}$	$4.3 \times 10^{-6}$	$8.2 \times 10^{-6}$	$1.5 \times 10^{-5}$	$2.9 \times 10^{-5}$	$4.0 \times 10^{-5}$	$5.5 \times 10^{-5}$	$7.5 \times 10^{-5}$	$1.0 \times 10^{-4}$	$1.4 \times 10^{-4}$	This study
Box thickness $\Delta z$ , 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 $k_{OM}$ , yr <sup>-1</sup>	0.043	–	–	–	–	–	–	–	–	–	Reeburgh et al. (1991)
Kinetic const. anaerobic CH <sub>4</sub> oxidation $k_{AOM}$ , 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 $w_{wind}$ , m s <sup>-1</sup>	4.8	–	–	–	–	–	–	–	–	–	Sorokin (2002)
Surface water temperature $t$ , °C	15	–	–	–	–	–	–	–	–	–	Sorokin (2002)
Surface water salinity $S$ , g kg <sup>-1</sup>	17.9	17.9	–	–	–	–	–	–	–	–	Sorokin (2002)
Atmospheric methane concentration $C_A$ , 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 $n$	11	12	13	14	15	16	17	18	19	20	
Volume $V$ , 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 $A$ , 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 $K_z$ , m <sup>2</sup> s <sup>-1</sup>	$1.9 \times 10^{-4}$	$2.6 \times 10^{-4}$	$3.5 \times 10^{-4}$	$4.8 \times 10^{-4}$	$6.6 \times 10^{-4}$	$8.5 \times 10^{-4}$	$8.5 \times 10^{-4}$	$8.5 \times 10^{-4}$	$8.5 \times 10^{-4}$	$8.5 \times 10^{-4}$	This study
Box thickness $\Delta z$ , 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 $k_{AOM}$ , 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

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

Box	Differential equations
1	$\frac{\partial C_n}{\partial t} = \frac{kw(C_{AE}-C_n)A_n}{V_n} - k_{OM} \cdot C_n + \frac{B_{upn} \cdot C_{n+1}}{V_n} - \frac{B_{out} \cdot C_n}{V_n} - \frac{Kz_n(C_n-C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in n}$
2–4	$\frac{\partial C_n}{\partial t} = \frac{Kz_{n-1}(C_{n-1}-C_n)A_n}{\Delta z_n \cdot V_n} - k_{AOMn} \cdot C_n + \frac{B_{in} \cdot C_{Bin}}{V_n} - \frac{u_{upn} \cdot C_n}{V_n} + \frac{u_{upn+1} \cdot C_{n+1}}{V_n} - \frac{Kz_n(C_n-C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in n}$
5	$\frac{\partial C_n}{\partial t} = \frac{Kz_{n-1}(C_{n-1}-C_n)A_n}{\Delta z_n \cdot V_n} - k_{AOMn} \cdot C_n + \frac{B_{in} \cdot C_{Bin}}{V_n} - \frac{u_{upn} \cdot C_n}{V_n} - \frac{Kz_n(C_n-C_{n+1})A_{n+1}}{\Delta z_n \cdot V_n} + R_{in n}$
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.

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).

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 Tg yr<sup>-1</sup> of CH<sub>4</sub> 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 <sup>13</sup>CH<sub>4</sub> 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 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  $\text{CH}_4$  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 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; Vasilev 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 volcanoes in Azerbaijan ( $2.5 \times 10^8 \text{ m}^3 \text{ CH}_4$  (=  $179 \text{ Gg}$  or  $1.1 \times 10^{10} \text{ mol}$ ) 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  $179 \text{ Tg CH}_4$  (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

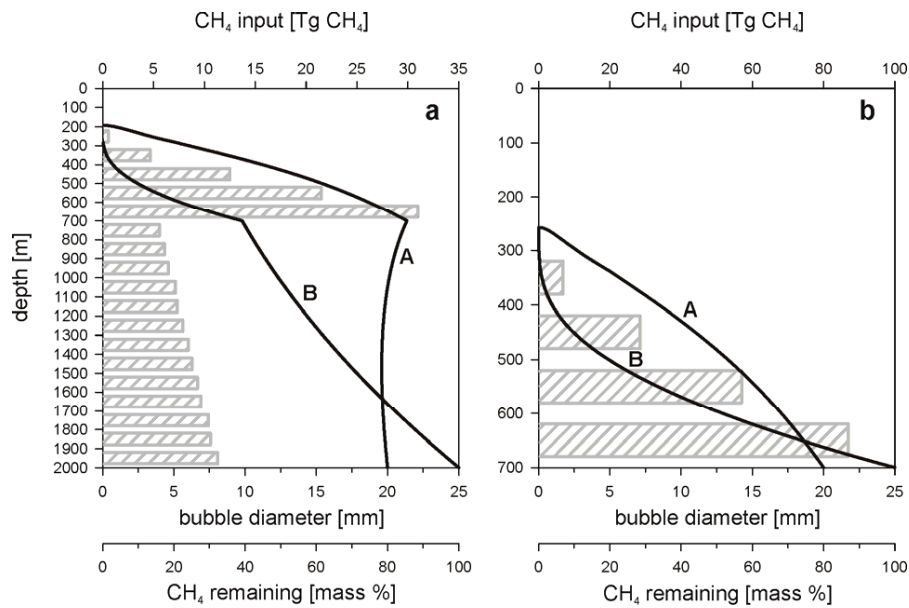
The simulation of Model B1 was initiated with the steady state methane concentrations obtained with Model A. Further, we assume a methane release of  $179 \text{ Tg}$  of  $\text{CH}_4$  at 2000 m water depth over an eruptive phase of one day (e.g. eruptions of 1000 MVs). Proposing that the gas exclusively 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.

For this massive methane input the model results suggest that it takes about 200 yr 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.

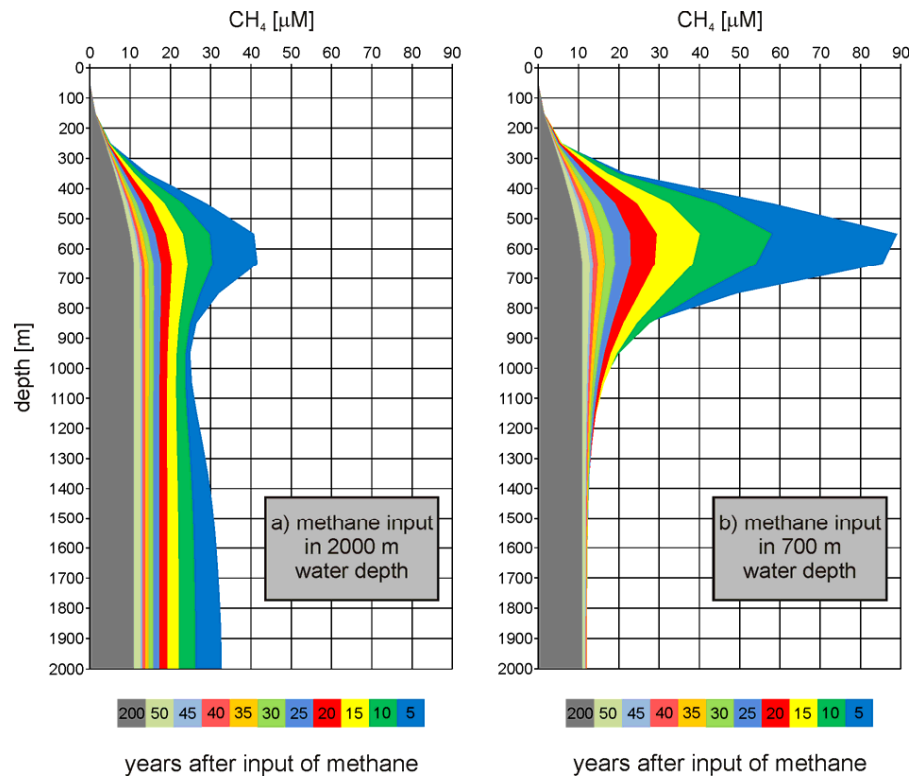
To test if the concentrations of  $\text{SO}_4^{2-}$  in the anoxic Black Sea waters are high enough to compensate for the high  $\text{CH}_4$  input of the MV eruption scenario (i.e.  $1.1 \times 10^{13} \text{ mol}$  of  $\text{CH}_4$  for 1000 MV eruptions), we calculated the total amount of sulfate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



**Fig. 3.** Inputs of methane into different water depths after a release of  $179 \text{ Tg d}^{-1}$  of CH<sub>4</sub> 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.



**Fig. 4.** CH<sub>4</sub> evolution over time after an initial input of  $179 \text{ Tg}$  of CH<sub>4</sub>. The left panel (a) represents the dissolved methane distribution after an input at 700 m water depth. The right panel (b) shows the distribution after an input at 2000 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.

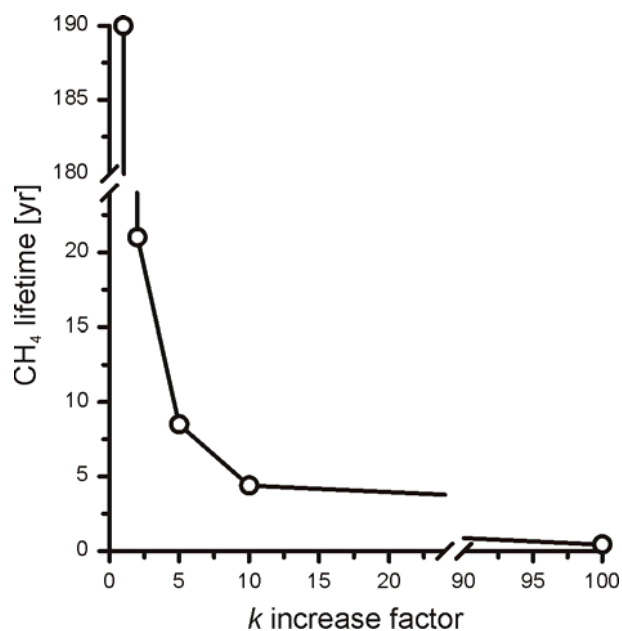
a methane release of 179 Tg of CH<sub>4</sub> at 700 m water depth over a time span of one day. Such an event will increase the input of methane to box 7 (depth interval 600–700 m) to 6.2 Gg km<sup>-3</sup> d<sup>-1</sup>. In contrast to Model B1 methane is released above the hydrate stability zone resulting in a constantly decreasing bubble size and methane input during the bubble ascent (Fig. 3b).

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 yr. 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%.

Kessler et al. (2011) studied the response of the water column methane cycle after the Deepwater Horizon oil spill in the Gulf of Mexico in the year 2010. The authors registered a rapid feedback of aerobic methanotrophic bacteria indicated by an increase in population size and methane oxidation rate constant ( $k_{OM}$  amplification by a factor of 100). Such a bloom in the anoxic waters of the Black Sea is rather unlikely because of the slow growth rate of methane oxidizing consortia (doubling time in the order of several months, Nauhaus et al., 2007). However, over the predicted 200 yr lifetime of this methane perturbation, a doubling time of several months would be viewed as a relatively instantaneous bloom. Thus, to simulate the lifetime of methane perturbation under different rate constants we increased  $k$  by a factor of 2, 5, 10 and 100 in each box. We examined the lifetime of methane perturbation in box 6 (500–600 m water depth), which shows the strongest increase in methane concentration (Fig. 4b). The results displayed in Fig. 5 indicate that the lifetime of methane decreases from 190 to 0.4 yr using  $k$  values reported by Reeburgh et al. (1991; Table 1) and an assumed increase of  $k$  by a factor of 100.

#### 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. It should be highlighted that we employ a vertical 1-dimensional box model which inherently assumes homogenous methane emission over each depth interval. Further investigation is required for the appropriate extrapolation of intense localized emissions (such as pure methane emissions producing focused two-phase plumes (Kourtidis et



**Fig. 5.** Lifetime of methane perturbation as a function of the increase factor of  $k$ . Model runs were performed for factors of 2, 5, 10, and 100. The results of box 6 are displayed from simulations with Model B2.

al., 2006; Leifer and Patro, 2002) as well as gas and oil emissions forming deepwater and mid-depth plumes (Socolofsky and Adams, 2005) to these larger integrated spatial scales.

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