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Methane discharge into the Black Sea and the global ocean via fluid flow through submarine mud volcanoes

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Abstract

During the MARGASCH cruise M52/1 in 2001 with RV Meteor we sampled surface sediments from three stations in the crater of the Dvurechenskii mud volcano (DMV, located in the Sorokin Trough of the Black Sea) and one reference station situated 15 km to the northeast of the DMV. We analysed the pore water for sulphide, methane, alkalinity, sulphate, and chloride concentrations and determined the concentrations of particulate organic carbon, carbonate and sulphur in surface sediments. Rates of anaerobic oxidation of methane (AOM) were determined using a radiotracer ($^{14}CH_4$) incubation method. Numerical transport-reaction models were applied to derive the velocity of upward fluid flow through the quiescently dewatering DMV, to calculate rates of AOM in surface sediments, and to determine methane fluxes into the overlying water column. According to the model, AOM consumes 79% of the average methane flux from depth ($8.9 \cdot 10^{+6}$ mol a^{-1}), such that the resulting dissolved methane emission from the volcano into the overlying bottom water can be determined as $1.9 \cdot 10^{+6}$ mol a^{-1}. If it is assumed that all submarine mud volcanoes (SMVs) in the Black Sea are at an activity level like the DMV, the resulting seepage represents less than 0.1% of the total methane flux into this anoxic marginal sea. The new data from the DMV and previously published studies indicate that an average SMV emits about $2.0 \cdot 10^{+6}$ mol a^{-1} into the ocean via quiescent dewatering. The global flux of dissolved methane from SMVs into the ocean is estimated to fall into the order of 10^{+10} mol a^{-1}. Additional methane fluxes arise during periods of active mud expulsion and gas bubbling occurring episodically at the DMV and other SMVs.

Keywords: submarine mud volcanoes; Black Sea; methane fluxes; numerical modelling; anaerobic oxidation of methane

1. Introduction

The Black Sea is the world's largest anoxic basin and the largest surface reservoir of dissolved methane, with concentrations of up to 11 μmol/l, and an inventory of $6 \cdot 10^{12}$ mol [1]. The total oxidation rate of $2.9 \cdot 10^{11}$ mol a^{-1} [1] implies a residence time of methane in the Black Sea of about 20 a. Seeps on the shelf and slope of the main deep anoxic basin and methanogenesis in anoxic sediments are an important source for methane in the water column

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[2,3]. Methane is also released at SMVs [4]; however, methane fluxes from these have not yet been quantified.

The emission rates of methane from SMVs are very uncertain [5], as is the number of SMVs in the Black Sea. Kruglyakova et al. [6] reported about 65 known SMVs in the Black Sea, which are located on the Kerch–Taman shelf and on the slope in the waters of Bulgaria, Ukraine, Russia, Georgia, and Turkey. Recent estimates of the total number of SMVs worldwide range from 840 to 5000 [7–9]. SMVs originate from the ascent of under consolidated sediment, which consists of fluids and semi-liquid mud breccias, forming characteristic morphological features in sharp contrast to the surrounding host sediment [8]. Generally, the volcanoes are connected to deep fluid and methane reservoirs and methane is discharged into the bottom water in dissolved form or as gas bubble.

Most of the methane produced in marine sediments is consumed by anaerobic oxidation of methane (AOM) before it reaches the upper oxic zone of the sediment according to the following equation [10–12]:

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \quad (1)$$

Therefore, significant methane fluxes into the bottom water are produced only at places where high methane fluxes from below push the sulphate–methane boundary to the seafloor [13]. The reduction of methane discharge from SMVs by AOM was not considered in earlier studies [14], except for the Kazan mud volcano in the Mediterranean Sea, where calculations by Haese et al. [15] have shown that almost all of the methane flux from depth is consumed by AOM.

While the first part of our detailed study of the Dvurechenskii mud volcano (DMV) discussed the ascending fluids, their composition, and their origin [16], the main objective of this paper is the calculation of the flux of methane from the DMV, taking into account the consumption of the methane by anaerobic oxidation. Both measured and modelled oxidation rates are reported. A numerical transport-reaction model is used to estimate fluid seepage rates and benthic methane fluxes. Based on their estimated abundance, we also assess the importance of SMVs for the methane budget of the Black Sea. Methane seepage of other well known SMVs are compared to those of the DMV and it is shown that SMVs emit dissolved methane at an average rate of $2 \cdot 10^{+6}$ mol a^{-1}.

2. Study area

2.1. Mud volcanism in the Sorokin Trough

The Sorokin Trough, located SE of the Crimean peninsula at water depths of 800–2200 m, is considered to be the fore-deep of the Crimean Alpine range. It was formed in Oligocene/Early Miocene times and appears as a large SW–NE oriented depression 150 km long and 45–50 km wide [17]. The area is subject to a N–S oriented compressive regime generated between the buried Tetyaev and Shatskii rises. These structural highs act as rigid buttresses against which clays of the Maikopian formation (Oligocene–Lower Miocene) become over-pressured and rise diapirically [18]. As a result, the sedimentary succession in the Sorokin Trough is pierced by numerous SE–NE oriented diapiric ridges which have roots several kilometres deep [19]. A multitude of SMVs is located on the culmination of these, suggesting a genetic link between mud diapirism and mud volcanism.

2.2. The Dvurechenskii mud volcano

The DMV lies on the culmination of an E–W trending sector of a diapiric ridge. A multi-channel seismic survey across the DMV shows that the underlying diapiric intrusion is most likely fault-controlled and extends below the maximum penetration depth of the seismic data, which is about 3.5 km [20]. Morphologically, the DMV is a round, flat-topped elevation of 800 m in diameter and 80 m in height (Fig. 1). Echo sounder and deep-tow side scan sonar surveys proved that the uppermost 30 m are composed of acoustically homogeneous sediments with no relief and low reflectivity, which provides an indication of a very fluid mud of low viscosity [18]. Images from these surveys show mud flows from the summit down-slope the volcano's flanks. During a deep-tow video survey, several indications for mud flow activity were observed

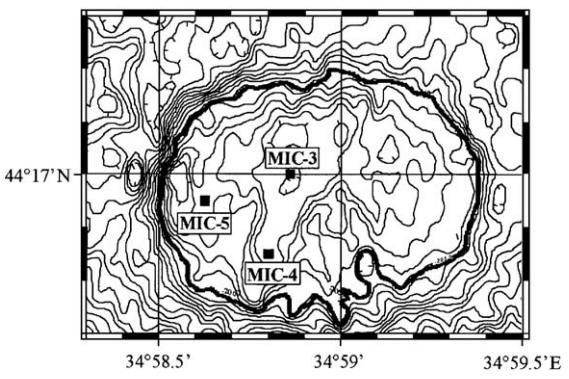

Fig. 1. Bathymetric map of the Dvurechenskii mud volcano, showing MIC stations and the crater area, which is marked by the black continuous line. Isobars are at 5 m intervals. Bathymetric data were retrieved during the MARGASCH cruise.

in the crater [19]. Also, fresh mud flows could be seen on video images and colour slides near to its rim. A small area of approximately 50–70 m in diameter with high seepage activity could be located in the central part of the mud volcano. Here, also several small round spots were seen, which are to be interpreted as active gas or fluid expulsion sites. The flat shape of the DMV summit is due to the fluidity of the expelled mud [21]. SMVs of similar shape, termed diatremes or mud pies, have been described from the Barbados Accretionary Prism, where they are associated to gas hydrates, high fluid flow rates, and dissolved methane emissions [14].

During our MARGASCH cruise gas bubbles were not observed to emanate from the seafloor above the DMV while acoustic flare imaging showed evidence of gas bubbles above the DMV during the CRIMEA cruise in 2002. Therefore, bubble emission seems to occur episodically at the DMV. Methane measurements in surface waters above the DMV showed no significant enrichments indicating that methane released at the seafloor is consumed by AOM on its way through the water column [3]. Surface sediments taken from the DMV during the MARGASCH cruise contained abundant dissolved methane and small crystals of solid hydrate. The gas extracted by dissociation of the hydrate samples was dominantly methane with low amounts of ethane and propane. The isotopic composition of hydrate-bound methane (−62 to −66‰ PDB in $\delta^{13}C$ and −185 to −209‰ SMOW in δD) indicates a mainly biogenic origin with an admixture of thermogenic gas [22].

3. Methods

Surface sediments were taken with the German research vessel RV Meteor during the MARGASCH cruise M52/1 in January 2001. Here, we report the results obtained at three stations located within the crater of the DMV and an additional reference station located 15 km to the northeast of the DMV (Table 1).

3.1. Sampling and chemical analysis

The samples were taken with two different multicorers. One of these instruments (MUC) was equipped with 8 plastic tubes while the other instrument (MIC) contained only 4 tubes. The tubes used in the MUC and MIC had the same design being 50 cm long and having an inner diameter of 10 cm. They were applied to take sediment cores with a length of up to 45 cm and a very well preserved sediment/water interface. Retrieved sediments were cut into slices and pore water was extracted in the on-board laboratory at 6–9 °C.

Table 1
Sampling sites included in this study

Core	Region of DMV	Latitude (°N)	Longitude (°E)	Water depth (m)
MUC-1	15 km NE of DMV, Reference	44° 22.49′	35° 08.62′	1889
MIC-3	DMV summit, centre	44° 16.99′	34° 58.81′	2070
MIC-4	DMV summit, SW	44° 16.88′	34° 58.80′	2085
MIC-5	DMV summit, W	44° 16.97′	34° 58.61′	2089

Still on board, we analyzed the pore water for total dissolved sulphide ($TH_2S = [H_2S] + [HS^-] + [S^{2-}]$), using the standard photometric procedure; total alkalinity (TA) was determined by titration immediately after pore water separation [23]; finally the pore water methane concentration was measured with the headspace method by gas-chromatography [24]. The remaining pore water was analyzed in the shore-based laboratory for dissolved anions (SO_4^{2-}, Cl^-) by ion chromatography. Porosity was calculated from the water content under the assumption of a dry solid density of 2.6 g cm^{-3}. The concentrations of particulate organic carbon (POC), inorganic carbon ($CaCO_3$) and total sulphur (S) were determined using an element analyzer (Carlo Erba). All analytical procedures applied on board and in our IFM–GEOMAR laboratories are documented in detail at: http://www.ifm-geomar.de/index.php?id=1858 and L=1.

3.2. Measurement of AOM rates

Rates of AOM in DMV surface sediments were determined by the $^{14}CH_4$-radiotracer method [10]. Parallel sediment sub-samples were placed in cut off glass syringes sealed with gas-tight rubber stoppers. Subsequently, 50 µl of a gas mixture containing 0.2% ^{14}C-methane in hydrogen gas (specific activity 1.029 MBq) was injected into each syringe through the rubber stopper with another gas-tight syringe. Samples were incubated in the dark at 7–8 °C under an anaerobic argon atmosphere for 12 to 24 h. After fixation with sodium hydroxide (1 N) on board, the amount of $^{14}CO_2$ produced by AOM was determined in the home laboratory by acidifying the sediment and trapping the released CO_2 with ethanolamine. To determine also the portion of the ^{14}C which was incorporated (i.e. assimilated as $^{14}CO_2$ in bacterial biomass) during incubation, the retained CO_2- and carbonate-free sediment slurry was dried and ground with mortar and pestle. Following Bussmann et al. [25] aliquots were combusted in a biological oxidizer and the escaping $^{14}CO_2$ was sampled for radioactivity measurements. Empirical

AOM rates were then calculated using the activity of the $^{14}CO_2$ directly formed by AOM [$^{14}CO_2$], ^{14}C incorporated in the sediment [$^{14}C_{incorp}$], the measured methane concentration [CH_4], and the known radioactivity of the added methane [$^{14}CH_{4\ injected}$] according to the following equation:

$$\mathrm{AOM} = \frac{([^{14}CO_2] + [^{14}C_{incorp}]) \cdot [CH_4]}{[^{14}CH_{4\ injected}] \cdot t} \quad (2)$$

where t is the incubation time. The radioactive methane used in the incubations was supplied by R. Schmaljohann (IFM–GEOMAR). It was biologically prepared by *Methanobacterium thermoautotrophicum* and purified according to [26] to completely remove ^{14}CO and $^{14}CO_2$. The amount of injected $^{14}CH_4$ [$^{14}CH_{4\ injected}$] was determined by measuring the activity of control samples (3 replicates for each measurement). These samples were produced by injecting 50 µl of the $^{14}CH_4$-bearing gas mixture into a gas-tight Hungate vial containing 5 ml of NaOH. It is important to notice that most of the methane which is contained in the sediment under *in situ* conditions is lost prior to the incubation due to the decrease of pressure during core retrieval and sampling.

3.3. Set-up of the numerical transport-reaction model

Fluid seepage rates, AOM rates and benthic methane fluxes at the DMV were calculated based on numerical modelling of pore water profiles in short cores MIC-3, MIC-4, and MIC-5. Rates of upward fluid flow were determined by applying a transport model to the inert tracer chloride, which is dissolved in the pore fluids. The model considers molecular diffusion and advection of dissolved chloride and is based on the following differential equation:

$$\Phi \cdot \frac{\partial [Cl^-]}{\partial t} = \frac{\partial \left(\Phi \cdot \frac{D_{Cl}}{\Theta^2} \cdot \frac{\partial [Cl^-]}{\partial x} \right)}{\partial x} + \frac{\partial (\Phi \cdot v \cdot [Cl^-])}{\partial x} \quad (3)$$

where t is time, x is sediment depth, [Cl^-] is the concentration of dissolved chloride, D_{Cl} is the molecular diffusion coefficient of Cl^-, Φ and Θ are sediment porosity and tortuosity, and v is the velocity of vertical fluid flow (seepage rate). Sediment porosity changes with depth due to sediment compaction. The depth profile is approximated using the following exponential function [27]:

$$\Phi = \Phi_f + (\Phi_0 - \Phi_f) \cdot e^{-p \cdot x} \quad (4)$$

where the parameter values for Φ_f (porosity at infinite depth), Φ_0 (porosity at zero depth), and p (attenuation coefficient for the exponential decrease of porosity with depth) are determined by fitting the porosity model to the corresponding porosity data. Sediment tortuosity is calculated from porosity using the following empirical relation [28]:

$$\Theta^2 = 1 - \ln(\Phi^2) \quad (5)$$

The interstitial fluid flow velocity v induced by upward fluid advection is calculated as:

$$v = \frac{v0 \cdot \Phi_0}{\Phi} \quad (6)$$

It is scaled with the depth-dependent porosity since v is reduced in unconsolidated surface sediments [13]. The burial of pore water by sedimentation and the fluid flow induced by compaction of surface sediments are both neglected since the vertical water displacement induced by these processes is orders of magnitude smaller than the fluid advection caused by the ascent of deep fluids through the DMV. The velocity of upward fluid flow at the sediment/water interface ($v0$) driven by the ascent of deep fluids is determined by fitting the model to the chloride pore water profile measured in the recovered sediment cores.

A transport-reaction model was applied to calculate AOM rates and benthic methane fluxes from dissolved sulphate concentration profiles in surface sediments. The model considers molecular diffusion and advection of dissolved sulphate and methane and the anaerobic oxidation of methane. It is based on a system of two coupled differential equations:

$$\Phi \cdot \frac{\partial [SO_4^{2-}]}{\partial t} = \frac{\partial \left(\Phi \cdot \frac{D_S}{\Theta^2} \cdot \frac{\partial [SO_4^{2-}]}{\partial x} \right)}{\partial x} + \frac{\partial (\Phi \cdot v \cdot [SO_4^{2-}])}{\partial x} - \Phi \cdot R_{AOM} \quad (7)$$

$$\Phi \cdot \frac{\partial [CH_4]}{\partial t} = \frac{\partial \left(\Phi \cdot \frac{D_M}{\Theta^2} \cdot \frac{\partial [CH_4]}{\partial x} \right)}{\partial x} + \frac{\partial (\Phi \cdot v \cdot [CH_4])}{\partial x} - \Phi \cdot R_{AOM} \quad (8)$$

where t is time, x is sediment depth, [CH_4] and [SO_4^{2-}] are concentrations of dissolved methane and sulphate in sediment pore waters, D_S and D_M are molecular diffusion coefficients of sulphate and methane, and R_{AOM} is the AOM rate.

A second order kinetic rate law was used to model AOM rates [13]:

$$R_{AOM} = k_{AOM} \cdot [CH_4] \cdot [SO_4^{2-}] \quad (9)$$

where the value of the kinetic constant k_{AOM} is derived by fitting the model to the sulphate pore water data.

Sulphate might also be reduced by the microbial degradation of organic matter and higher hydrocarbons. The ancient Maikopian muds transported to the surface at the DMV have, however, rather low concentrations of particulate organic carbon (Fig. 2). Considering also that the reactivity of sedimentary organic matter decreases with age, these old sediments should not drive any significant sulphate consumption. Oil and higher hydrocarbons that probably induce additional sulphate reduction in the seepage areas located in the Gulf of Mexico [29] were not observed at the DMV. The pivotal role of methane as the major driver of sulphate consumption at the studied mud volcano is confirmed by the strong contrast in metabolite concentrations between the DMV sediments and a nearby reference station not affected by the ascent of methane-charged fluids (Fig. 3). It is thus reasonable to assume that sulphate consumption in the DMV is driven by AOM rather than by the degradation of sedimentary organic matter and hydrocarbons.

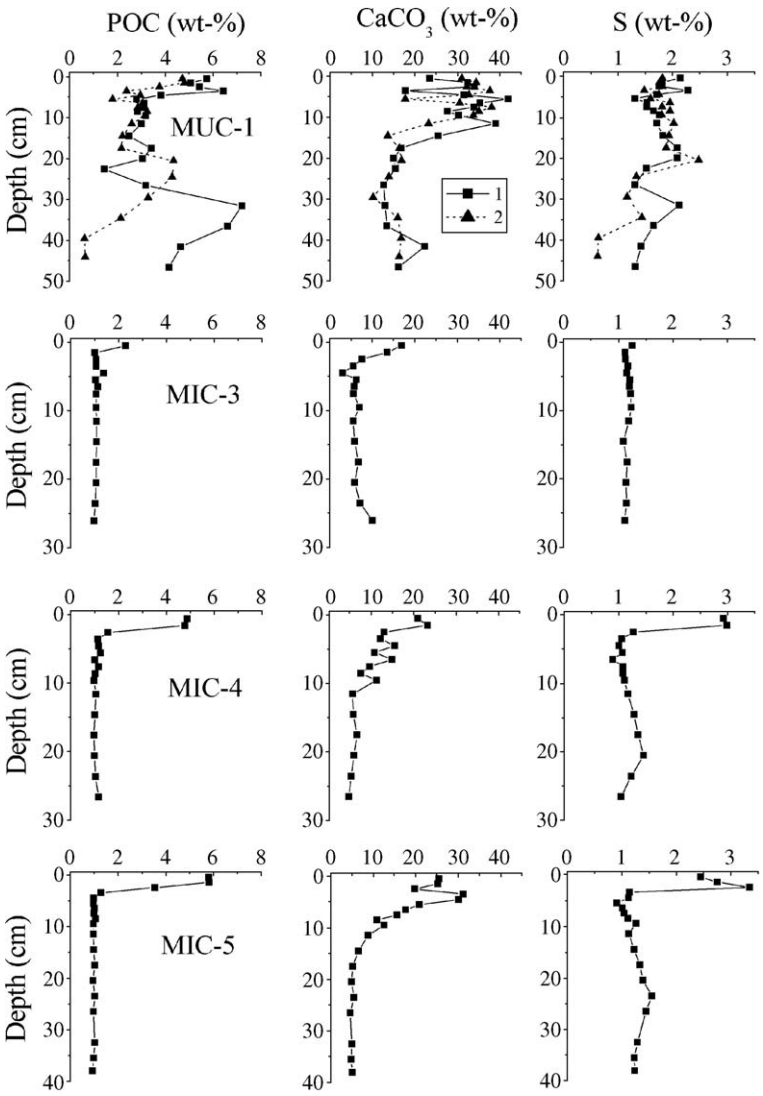

Fig. 2. Concentrations of particulate organic carbon (POC), inorganic carbon (expressed as $CaCO_3$ in wt.%), and sulphur (S) in surface sediments from the Black Sea. MUC-1 was taken at a reference station not affected by mud volcanisms while the MIC samples were taken from the DVM crater. Two different cores were retrieved at the reference station during one multi-corer deployment (MUC-1). They were both analyzed for dissolved and solid constituents.

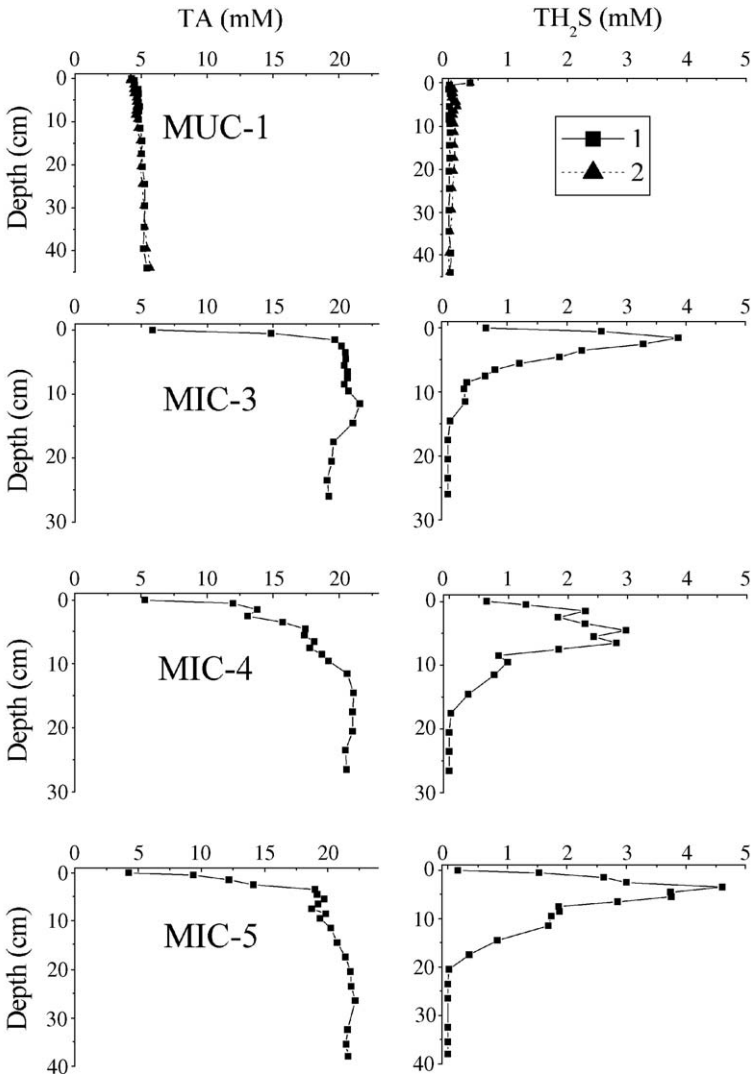

Fig. 3. Total alkalinity (TA) and total dissolved sulphide (TH_2S) in sediment pore waters.

Benthic fluxes of methane across the upper boundary of the model column, F_{M0}, are calculated applying the following equation [28]:

$$F_{M0} = -\Phi_0 \cdot \frac{D_M}{\Theta_0^2} \cdot \left(\frac{\partial [CH_4]}{\partial x}\right)_0 - \Phi_0 \cdot v_0 \cdot [CH_4]_0 \qquad (10)$$

where the subscript "0" refers to the upper boundary of the model column ($x=0$).

Boundary conditions were defined at the sediment surface ($x=0$) and at the base of the model column ($x=L=26$–38 cm), corresponding to the deepest pore water sample in the different short cores. The methane concentration at the upper boundary (M0) was set to 0.01 mM [1] and the sulphate concentration (S0) to 16.8 mM, equal to the sulphate concentration in ambient bottom waters. The rising fluids were assumed to be in equilibrium with gas hydrates due to the occurrence of hydrates in shallow DMV sediments. The equilibrium methane concentration applied at the lower boundary (ML = 85 mM) was calculated after [30] as the saturation value under the pressure and temperature conditions prevailing at the DMV. The seeping fluids are sulphate free. Thus, the sulphate concentration at the lower boundary (SL) was set to zero.

The model was run into steady state starting from arbitrary initial conditions. Due to the high reaction rates and flow velocities, steady state was usually attained within a few years. MATHEMATICA version 5.0 was used to implement the model and MATHEMATICA's NDSolve object was applied for the numerical integration of the differential equations. NDSolve uses the

Method-of-Lines code for integration, a finite difference procedure which has been frequently applied in the modelling of early diagenetic processes [13,31]. Table 2 summarizes the parameter values which were used for the modelling of upward fluid flow and AOM rates in short core sediments.

4. Results

We analysed three up to 45 cm long cores from the DMV summit (MIC-3, central; MIC-4 and MIC-5, peripheral), and two cores from a reference site (MUC-1), 15 km northeast of the DMV (Fig. 1, Table 1).

4.1. Composition of surface sediments and pore fluids

Surface sediments from the Black Sea floor deposited below the redox-cline are usually laminated and rich in particulate organic carbon (POC). Since the invasion of *E. huxleyi* into the Black Sea at about 1500–3000 years ago, laminated coccolith oozes have been deposited [11]. The reference cores (MUC-1) show high carbonate values in the top 10 cm (Fig. 2) marking the thickness of the coccolith layer. The local sedimentation rate may thus be estimated as 3–5 cm ka^{-1}. In one of the two reference cores, very organic-rich sediments are found below the carbonate-rich section. This sapropel layer is observed at many sites throughout the Back Sea and was deposited over the last 7500 years when anoxic conditions prevailed. Total sulphur concentrations are in the order of 1–2 wt.% due to the formation of sedimentary pyrite. Sediment cores taken from the DMV crater have a different composition (Fig. 2). Here, POC concentrations fall into a very narrow range of only 0.9–1.3 wt.%. These values are significantly lower than the POC concentrations observed at the reference station and reflect the composition of the ascending mud. The carbonate contents decrease with sediment depth towards a value of about 5 wt.% while the total S concentrations decrease to about 1 wt.% in the underlying mud. The mud is covered with a thin layer of sediments enriched in POC, $CaCO_3$ and S. This layer represents young pelagic sediment deposited on top of the mud extrusions. The average thickness of this layer (2 cm) indicates that the outer area of the crater sampled with MIC-4 and MIC-5 did not receive mud flows over several hundred years. However, the pelagic apron is not clearly seen in the core taken close to the centre of the crater (MIC-3) indicating more recent mud flow activities in this area.

Aloisi et al. [16] characterised nature and amount of the fluids which are expelled from the DMV. They ascend from a depth of at least 3 km, where they are heavily

Table 2
Parameter values used in the modelling

Parameter	Symbol	Value
Length of the model column (cm)	L	26–38
Average surface sediment temperature (°C)	T	10
Chloride concentration at zero depth (mM)	Cl0	350
Chloride concentration at depth L (mM)	ClL	760–815
Sulphate concentration at zero depth (mM)	S0	16.8
Sulphate concentration at depth L (mM)	SL	0
Methane concentration at zero depth (mM)	M0	0.01
Methane concentration at depth L (mM)	ML	85
Molecular diffusion coefficient of chloride at T (cm^2 a^{-1})	D_{Cl}	441
Molecular diffusion coefficient of sulphate at T (cm^2 a^{-1})	D_S	227
Molecular diffusion coefficient of methane at T (cm^2 a^{-1})	D_M	394

The methane concentration at depth (ML) was calculated after [30] assuming equilibrium with gas hydrates under ambient conditions (T=10 °C, P=205 bar, S=47 psu). Molecular diffusion coefficients were taken from [28].

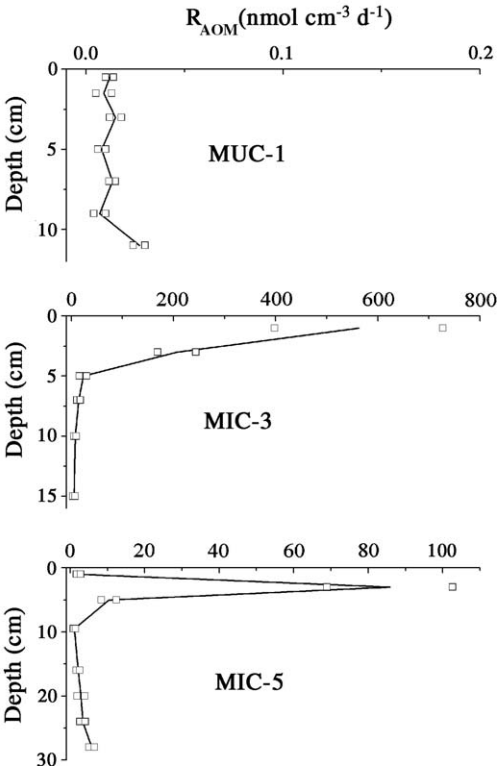

Fig. 4. Rates of anaerobic oxidation of methane (AOM) measured in surface sediments with the radio-tracer incubation method. MUC-1 was taken at a reference station, located 15 km to the northeast of the DMV. Measured rates are shown as symbols while the solid line indicates the average value of the two replicate measurements performed in each depth interval.

altered by organic matter and silicate diagenesis at temperatures of about 100 °C. Therefore the fluids are particularly enriched in geochemically important species, such as Li, B, I^-, Ba^{2+}, Sr^{2+}, and NH_4^+. The depth profiles of total alkalinity (TA) and total dissolved sulphide (TH_2S) shown in Fig. 3 indicate that the ascending fluids are essential sulphide-free (<0.1 μM) and enriched in alkalinity (20–23 mM). A strong sulphide maximum is observed close to the surface. The sulphide enriched in these surface layers is produced by the anaerobic oxidation of ascending methane (Eq. (1)) and the strong interfacial gradients in alkalinity are maintained by the same process. The much lower alkalinity and sulphide concentrations at the reference site confirm that the pore fluids sampled within the DMV crater are strongly affected by fluid flow and AOM (Fig. 3).

4.2. Anaerobic oxidation of methane measured by radio-tracer incubation

AOM rates were measured in surface sediments of the DMV summit and at the reference station. In the centre of the crater (MIC-3) extremely high AOM rates of more than 500 nmol cm^{-3} d^{-1} are observed within the top centimetre of the sediment (Fig. 4). The other investigated core located more towards the rim of the crater (MIC-5) shows a strong AOM maximum at 2 cm depth where the rate approaches 86 nmol cm^{-3} d^{-1} (Table 3). AOM rates were not measured in MIC-4 and AOM rates are smaller than 0.03 nmol cm^{-3} d^{-1} at the reference station (Fig. 4). The strong difference between the DMV and the adjacent reference site confirms that high AOM rates can only be attained by methane being transported to the surface by ascending fluids.

4.3. Model results

Chloride and sulphate data are reproduced satisfactorily by the model (Fig. 5). The obvious discrepancy between modelled and measured CH_4 concentrations is due to the loss of methane from the sediment which degasses during sample retrieval. At the centre of the DMV the value of the kinetic constant k_{AOM} (100 dm^3 $mmol^{-1}$ a^{-1}; core MIC-3) is five times higher than at the other sites (20 dm^3 $mmol^{-1}$ a^{-1}; cores MIC-4 and MIC-5). Higher k_{AOM} values reflect a greater abundance and activity of the AOM microbial community at the central DMV site (Table 4). The density of microbial consortia and thus the rate of methane oxidation may increase towards the centre due to the higher methane supply rate

Table 3
Rates of anaerobic oxidation of methane oxidation measured with the radiotracer technique in sediments of the Dvurechenskii mud volcano (DMV) and at other locations

Location	Water depth (m)	Depth-integrated AOM rate (mmol m^{-2} d^{-1})	Rate maximum (nmol cm^{-3} d^{-1})	Reference
DMV (Black Sea) MIC-3	2070	16.7 (0–18 cm)	563 (1 cm)	This study
DMV (Black Sea) MIC-5	2070	2.6 (0–18 cm)	86 (2 cm)	This study
Core MUC-1 (reference, non seep site)	1889	0.002 (0–12 cm)	0.03 (11 cm)	This study
Green Canyon (Gulf of Mexico), core 4315	540	4.61 (0–10.5 cm)	120 (8.5 cm)	[29]
Green Canyon (Gulf of Mexico), core 4324	560	11.6 (0–13.5 cm)	500 (13.5 cm)	[29]
Hydrate Ridge cold seeps (NE Pacific)	777	98.8 (0–10 cm)	5500 (7 cm)	[39]
Eckernförde Bay cold seeps (Baltic Sea)	25	6.8 (0–50 cm)	49 (25 cm)	[25]
Southern Skagerrak cold seep (North Sea)	332	76.8 (0–42 cm)	900 (40 cm)	[52]
Håkon Mosby mud volcano, (Norwegian Sea)	1250	0.55[b] (0–80 cm)[c] 6.7[d] (0–20 cm)	0.8[a] (20–30 cm)	[44] [53]
Odessa MV (Black Sea)	1840	55.7 (0–360 cm)	45 (37.5 cm)	Drews, unpublished data

Rates were integrated over the given depth intervals. The highest rates (rate maximum) were observed at the indicated sediment depth. Notes: (a) Calculated from 9.9 μg C dm^{-3} d^{-1}. (b) Calculated from 6600 μg C m^{-2} d^{-1}. (c) Read from the diagram. (d) Calculated from 0.15 *L* CH_4 m^{-2} d^{-1}.

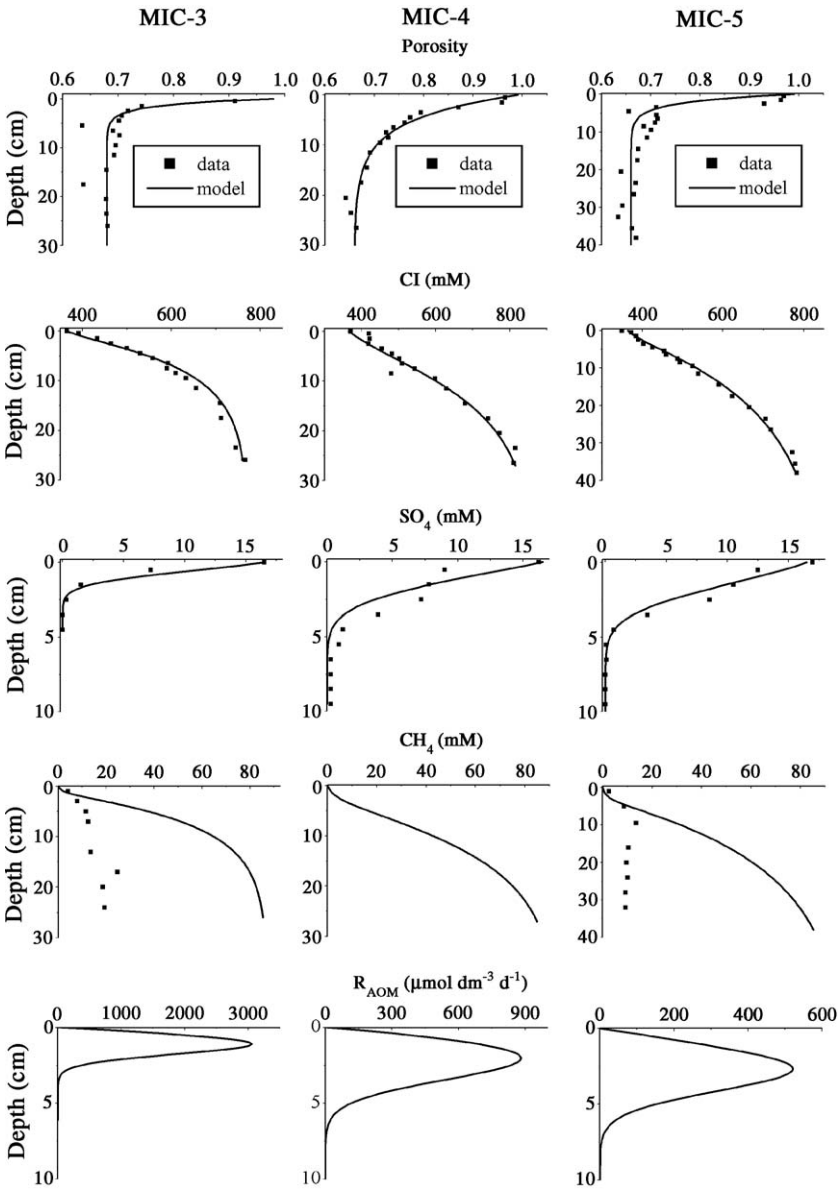

Fig. 5. Pore water profiles and modelling results for the DVM crater. Data are indicated as solid squares while model results are plotted as solid lines. The cores are positioned at increasing distance from the centre (MIC-3) to the rim (cores MIC-4 and MIC-5) of the crater.

since modelled methane fluxes from depth are higher at the centre of the DMV summit than at the rim (Table 4). The AOM rates showed pronounced peaks within the sulphate-bearing surface layers (Fig. 5). Strong peaks of dissolved sulphide were observed at the same depth level (Fig. 3) confirming that the modelling approach correctly describes the AOM processes at the DMV. The depth-integrated rate of AOM calculated with the model ranges from 47.2 mmol m^{-2} d^{-1} at the DMV centre (core MIC-3) to 18.2 mmol m^{-2} d^{-1} at site MIC-5 (Table 4).

The total methane flux from depth is calculated as $8.9 \cdot 10^{+6}$ mol a^{-1} by multiplying the average methane flux at the base of the investigated sediment cores (39.4 mmol m^{-2} d^{-1}, Table 4) and the area of the DMV crater (0.62 km^2, [16]). The methane emission, calculated by multiplying the average methane flux at the sediment/water interface (8.3 mmol m^{-2} d^{-1}, Table 4) and the crater area results as $1.9 \cdot 10^6$ mol a^{-1}. This flux does not include the release of gaseous methane and the methane fluxes during mud eruptions at the DMV. It rather gives the methane discharge into the overlying bottom water during

Table 4
Results of the transport-reaction modelling applied to MIC data

Parameter	Station			
	MIC-3	MIC-4	MIC-5	Average
Velocity of fluid flow at zero depth $v0$ (cm a^{-1})	25	15	8	16
AOM kinetic constant k_{AOM} (dm^3 $mmol^{-1}$ a^{-1})	100	20	20	47
Methane flux from depth (mmol m^{-2} d^{-1})	58.3	38.3	21.6	39.4
Depth-integrated AOM rate (mmol m^{-2} d^{-1})	47.2	28.0	18.2	31.1
Percentage of methane flux from depth consumed by AOM (%)	81	73	84	79
Methane flux into the bottom water (mmol m^{-2} d^{-1})	11.1	10.3	3.4	8.3

the current period of quiescent dewatering considering both fluid flow and molecular diffusion (Eq. (10)).

5. Discussion

Methane seepage from the seabed (SMVs, pockmarks, seeps, other features associated with fluid flow) is widespread and contributes significantly to the global methane budget of the hydrosphere and possibly also to the atmosphere [32]. Only recently the process of benthic AOM acting as a filter to reduce the amount of methane which is released into the water column at SMVs has come into focus. For the DMV we found that AOM consumes about 80% of the rising methane. Using a similar modelling approach, Haese et al. [15] found an even higher efficiency of AOM for the Kazan mud volcano (Mediterranean Sea).

5.1. Spatial distribution of methane seepage at the DMV and other mud volcanoes

The distribution of seepage on SMVs and other vent areas is often quite irregular [13,33,34]. The strong patchiness and lateral gradients in fluid composition, fluid flow, and AOM observed at these sites indicates that most of the methane is delivered by focussed fluid flow through small active vents. Shallow convection systems driven by the density contrast between low-salinity fluids and overlying bottom waters [35,36], bio-irrigation [37], and bottom currents interacting with the bottom topography add further complexity to the shallow hydrologic regime and may enhance lateral heterogeneity. However, sediment cores taken at 8 different positions within the DMV revealed that pore fluids and sediments are very homogenous in their composition throughout the entire crater area [16]. The low degree of patchiness at the DMV indicates that fluids are expelled over the entire crater area and points towards a broad feeder channel delivering fluids over a wide surface area. Moreover, the ascending fluids have a very high salinity and density clearly exceeding the density of the low-salinity bottom waters. This stable density layering probably prevents the penetration of bottom waters into the crater area. Large vent fauna which could pump bottom water into the sediments are also not present since the bottom waters covering the DMV are completely anoxic. A gradual decrease of methane emissions from the centre to the rim of the crater is observed in the data. However, the rates of fluid flow and methane release fall into the same order of magnitude over the entire crater area (Table 4). Hence, the DMV is an almost ideal system to quantify the methane emission from SMVs.

5.2. Anaerobic oxidation of methane at the DMV and other vent sites

AOM rates measured with the radio-tracer technique in surface sediments of the DMV are amongst the highest rates previously measured with the same technique at other locations (see Table 3). Depth-integrated AOM rates measured by sediment incubations at sites MIC-3 (16.7 mmol m^{-2} d^{-1}) and MIC-5 (2.6 mmol m^{-2} d^{-1}) are, however, much lower than the corresponding rates obtained by transport-reaction modelling (Table 4). During sampling and sample preparation methane degasses very quickly so that the methane concentrations in the incubation vials were much lower than the *in situ* methane concentration. According to experimental results of Nauhaus et al. [38], AOM rates increase at higher methane partial pressures. Hence, the in-situ turnover of methane at the seafloor may be strongly underestimated during on-board incubations.

Model studies showed that the fraction of dissolved methane escaping into the bottom water depends on the fluid flow rate [13]. At high rates of upward fluid flow, the penetration depth of sulphate is diminished because sulphate diffusing into the sediment from above is transported back into the overlying bottom water by fluid advection. In response to the upward advection of fluids, the thickness of the AOM layer is reduced and a larger fraction of the ascending methane escapes oxidation to be emitted into the bottom water [13].

Numerical experiments were performed to further quantify the release of methane at different fluid flow rates applying the parameter values used in the previous modelling of methane turnover in DMV sediments (Table 2). In these experiments, it was assumed that

methane concentrations at the base of the model column (30 cm) approach saturation with respect to gas hydrates (85 mM) and the kinetic constant for AOM (k_{AOM}) was set to a value of 50 dm^3 $mmol^{-1}$ a^{-1} representing the average activity of AOM at the investigated sites (Table 4). The model was run into steady state at various fluid flow velocities covering a range of 0–300 cm a^{-1}. Methane fluxes into the overlying water were calculated for each of these model runs and are expressed as fraction of the inflowing methane in Fig. 6. The model showed that less than 1% of the ascending methane escapes into the bottom water at fluid flow rates of up to 1 cm a^{-1} while more than 99% are consumed by AOM. The methane flux into the bottom water increases to 9% at a fluid flow rate of 10 cm yr^{-1} and reaches a value of 66% at advection rates of 100 cm a^{-1} (Fig. 6). These numbers are confirmed by other field studies. Thus, Treude et al. [39] calculated that 79% to 96% of the ascending dissolved methane is oxidized anaerobically within surface sediments at an advection rate of 10 cm a^{-1} and calculations by Haese et al. [15] for the Kazan mud volcano showed that AOM is responsible for consuming up to 100% of the deep methane flux at advection rates of 3–5 cm a^{-1}. It may thus be concluded that dissolved methane is only released into the bottom water at high fluid flow velocities whereas slow seepage of methane charged fluids (<5 cm a^{-1}) does not contribute significantly to the overall methane emission.

5.3. Contribution of mud volcano emissions to the methane inventory of the Black Sea

Reeburgh et al. [1] provided a methane budget for the Black Sea which has recently been updated by Kessler et al. [40]. Using ^{14}C-measurements and various mass balance approaches Kessler et al. [40] estimate the basin-wide flux of methane from gas and fluid seepage to the water column as $2–3 \times 10^{+11}$ mol a^{-1}. Kruglyakova et al. [6] reported the coordinates of 65 SMVs in the Black Sea. Assuming that all of these are at the same activity level as the DMV ($1.9 \cdot 10^6$ mol a^{-1}), SMVs would emit about $1.2 \cdot 10^8$ mol CH_4 a^{-1} into the Black Sea via quiescent dewatering, which is less than 0.1% of the total methane input [40]. However, large regions of the continental margins and of the deep Black Sea remain unexplored to the present day; so further research may show that SMVs are widespread elsewhere, with their contribution to the methane budget becoming more noteworthy. Moreover, the methane emission of SMVs during mud eruptions is still unknown and the release of methane gas bubbles occurring episodically at the DMV and possibly at other SMVs may add further methane to the water column. Nevertheless, it can be concluded that methane fluxes induced by fluid flow through SMVs play only a minor role in the methane budget of the Black Sea.

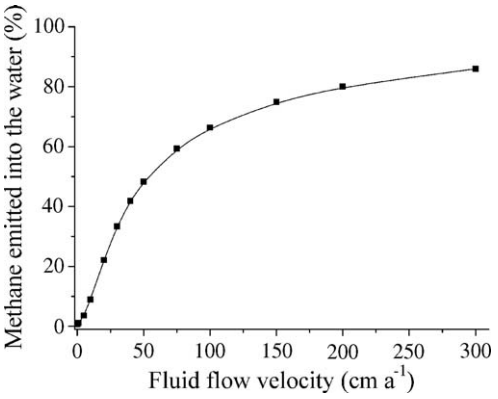

Fig. 6. Results of numerical experiments. Dissolved methane is transported to the surface by upward fluid flow and is consumed within the surface sediment by AOM. The fraction of the inflowing methane which is not oxidized but emitted into the overlying water is plotted as a function of the vertical fluid flow velocity.

5.4. Modes and rates of methane emission at submarine mud volcanoes

SMVs are three phase systems transporting solids, fluids and gases from the deep underground to the surface. Methane ascends either as free gas (gas bubbling) or in dissolved form via fluid flow (dewatering) and mud extrusion.

Methane is not an inert species but is rapidly oxidized by aerobic and anaerobic microorganisms using oxygen and sulphate as terminal electron acceptors. These methane consuming organisms are located at the SMV surface where the oxidizing agents are available. Hence, a “microbial filter” is established at the surface which may consume a large portion of the ascending methane. This filter is, however, selective because it can only consume methane delivered by the slow ascent of fluids (Fig. 6). Gaseous methane is not taken-up by microorganisms so that gas bubbles by-pass the microbial filter to transport methane into the overlying bottom water. Mud flows originating from the deep subsurface are usually devoid of methane-oxidizing microorganisms because oxidizing agents are not available in the deep underground. Hence, most of the methane in fresh mud flows is not oxidized but released into the bottom water. The microbial filter thus acts selectively on methane being transported to the surface by the slow ascent of methane-charged fluids.

Up to now, methane emissions from SMVs via fluid flow have been investigated only at a few locations. Henry et al. [14] studied the methane fluxes from two SMVs (Atalante, Cyclops) located seaward of the Barbados accretionary wedge at a water depth of approximately 5000 m. In the centre of these flat "mud pies" lies a pond of warm and low salinity mud with a diameter of about 200 m. Heat flow measurements and strong vertical gradients in pore water composition were used to constrain the rates of upward fluid flow as 100–160 cm a^{-1} and 10–36 cm a^{-1} for the mud ponds of Atalante and Cyclops, respectively. Fluid flow also occurs in the surroundings of the mud lakes albeit at much lower rates. The total water flux into the overlying bottom water was calculated as 40,000 m^3 a^{-1} and 9000 m^3 a^{-1} for the Atalante and Cyclops mud lakes. Assuming that the strong freshening of the fluids was entirely due to gas hydrate destabilization, the authors estimated maximum release rates of methane in the order of $185 \cdot 10^{+6}$ mol a^{-1} and $14 \cdot 10^{+6}$ mol a^{-1} for Atalante and Cyclops, respectively. Considering, however, that other processes such as smectite/illite transformations in the deep source area of the fluids could release freshwater [41], these estimates might be too high. A more realistic value can be obtained assuming that the fluids were saturated with respect to gas hydrates. The solubility of pure methane gas hydrate can be calculated as 160 mmol CH_4 kg^{-1} for Atalante (500 bar, 21 °C, 200 mM Cl^-) and 60 mmol CH_4 kg^{-1} for Cyclops (500 bar, 5 °C, 400 mM Cl^-) applying the thermodynamic approach of [30]. Using these methane concentrations and the water fluxes given above, the methane emission rates result as $6.5 \cdot 10^{+6}$ mol a^{-1} and $0.6 \cdot 10^{+6}$ mol a^{-1} for Atalante and Cyclops, respectively.

Ginsburg et al. [42] investigated the methane emissions at the Håkon Mosby mud volcano (HMMV) on the Norwegian continental slope in the Arctic (72 °N) at 1250 water depth. This flat shaped SMV is 1.5 km in diameter and 10 m high. Dissolved methane is released through the 200 m wide central part of the SMV [43] where the fluid flow rate may be as high as 250 cm a^{-1} [42]. The total water flux through the central part of the structure amounts to 80,000 m^3 a^{-1} and the methane emission rate was estimated as $5.4 \cdot 10^{+6}$ mol a^{-1} [42]. Rates of anaerobic methane oxidation were found to be very low within the central part of the HMMV [44] suggesting that most of the methane emitted in the central zone is not oxidized but released into the water column.

Haese et al. [15] studied the methane release from the Kazan mud volcano, one of several SMVs located in the Anaximander Mountains, west of Cyprus at a water depth of approximately 2000 m. Using pore water modelling, they derived an upward fluid flow rate of 4± 1 cm a^{-1} and determined the methane concentration in the ascending fluids as 130 mM. The modelling and additional data revealed that the ascending methane was almost completely oxidized by AOM in surface sediments so that essentially no methane was released into the overlying water column. The fluid flow rate was significantly smaller than the range of values observed at the DMV and it seems to be likely that the low flow rate was responsible for the lack of any significant methane emission into the overlying bottom water.

Mau et al. [45] investigated methane emissions at three outcropping mud diapirs and SMVs situated along the Pacific coast of Costa Rica. These mound-shaped structures discovered off Costa Rica have diameters of about 1000 m and are 20 m to 150 m high. They are covered with carbonate crusts and nodules formed by the anaerobic oxidation of methane [46]. Mau et al. [45] determined the methane fluxes by mapping the methane plume situated above the mounds and by measuring the bottom current velocities. They determined the methane inventory in the plume and determined a clearance time from the current measurements to derive the methane emission into the water column. Large methane fluxes were found at Mound Culebra ($0.6 \cdot 10^{+6}$ mol a^{-1}) and at Mound 12 ($0.4 \cdot 10^{+6}$ mol a^{-1}) whereas much lower emissions were calculated for Mound 11 ($0.07 \cdot 10^{+6}$ mol a^{-1}). Seafloor observations with a video sledge showed that fluid flow occurred only within small patches characterized by the occurrence of dense bacterial mats and clam colonies while most of the remaining mound surface was inactive. Fluid flow rates ranging in between 10 cm a^{-1} and 300 cm a^{-1} were determined for the most active sites [34,47]. Free gas was not released into the water column as clearly demonstrated by the regular distribution of methane in the water column and by acoustic measurements which failed to detect any "flares" or other anomalies related to gas bubbling [45].

The dissolved methane emissions listed in Table 5 show that large fluxes ($0.6–6.5 \cdot 10^{+6}$ mol a^{-1}) are obtained for flat-shaped SMVs with a pool of warm mud located in the centre of the volcano (Atalante, Cyclops, Håkon Mosby, Dvurechenskii). These mud pies [7] are characterized by high fluid flow velocities and extensive water discharge. They release water and methane over the entire area of the central mud pool so that large emission rates of methane can be obtained. Other SMVs and mud extrusions (Kasan, Culebra, Mound 11, Mound 12) have lower emission rates ($0–0.6 \cdot 10^{+6}$ mol a^{-1}). In these structures, fluid flow and methane discharge is focussed to small active patches (vents) with a diameter in the order of 1 m or less [34]. The diffuse fluid seepage through the remaining surface area of these mud extrusions does not

Table 5
Emissions of methane from SMVs into the overlying bottom water via quiescent dewatering (n.d.: not determined, 1 Mmol $a^{-1} = 10^6$ mol a^{-1})

Mud volcano	Water depth	Fluid flow rate	Water discharge	Methane flux
	(m)	(cm a^{-1})	(m^3 a^{-1})	(Mmol a^{-1})
Dvurechenskii	2050	8–25	94,000	1.9
Atalante	5000	100–160	40,000*	6.5
Cyclops	5000	10–36	9000*	0.6
Håkon Mosby	1250	250	80,000	5.4
Kazan	2000	3–5	n.d.	<0.1
Culebra	1650	n.d.	n.d.	0.6
Mound 11	1000	10–300	n.d.	0.07
Mound 12	1000	10–300	n.d.	0.4

*The water discharge at Atalante and Cyclops refers to the mud lakes situated in the centre of these mud pies. Significantly larger rates of water discharge were obtained considering the entire mud volcanoes and their immediate surroundings [14].

allow for significant methane emissions because methane is almost completely oxidized within the surface sediments at low fluid flow rates (Fig. 6).

For most of the SMVs included in Table 5 the oxidation of methane in surface sediments is considered so that the listed values represent emission rates into the overlying water column (Dvurechenskii, Kazan, Culebra, Mound 11, and Mound 12). Very high rates of fluid flow were observed for the Atalante and Håkon Mosby mud volcanoes. Numerical modelling of the methane turnover in surface sediments indicates that only a small fraction of the ascending methane is oxidized at fluid flow rates greater than 100 cm a^{-1} (see Fig. 6). Hence, it can be assumed that the methane fluxes through these very active SMVs are only slightly reduced by methane oxidation so that the values listed in Table 5 can be regarded as true emission rates. This conclusion is supported by measurements in the crater of the Håkon Mosby mud volcano were AOM rates were found which are considerable lower than those measured in the DMV (Table 3). Only at Cyclops, the methane emission is probably overestimated because a large fraction of the ascending methane may be oxidized at the moderate level of fluid flow prevailing at this SMV.

Gaseous methane fluxes at SMVs have only recently been quantified [48]. The pioneering study of Sauter et al. [48] at the HMMV showed that methane gas bubbles rapidly released into the water column from this SMV produce methane emissions in the order of 10^{+7} mol a^{-1}. It might, thus, be possible that gas bubbling is a major pathway for the emission of methane through SMVs. Up to now, gas bubbles have, however, not been detected at most SMVs located at the continental slope and rise.

Methane emissions from mud flows have not been measured so far. It is, however, possible to derive the order of magnitude of these fluxes from the volume and age of SMVs. Kopf [49] investigated the Milano and Napoli mud volcanoes located on the Mediterranean Ridge at a water depth of approximately 2000 m. He determined the age of these volcanoes as 1.0–1.5 Myr and the mud volumes as 3.4–7.8 km^3 and 9.5–14.6 km^3 for the Milano and Napoli, respectively. Taking these numbers, the rate of mud discharge at these volcanoes can be estimated as 2000–8000 m^3 yr^{-1} for the Milano and 6000–15,000 m^3 yr^{-1} for the Napoli. Assuming that the muds have a porosity of 80% and that the mud pore waters are saturated with respect to gas hydrates (110 mM CH_4 at 14 °C and 200 bar, calculated after [30]), the methane discharge rates result as $0.2–0.7 \cdot 10^{+6}$ mol yr^{-1} for Milano and $0.5–1.3 \cdot 10^{+6}$ mol yr^{-1} for Napoli. It is reasonable to assume that most of the methane is emitted into the bottom water because the methane-oxidizing microbial consortia have extremely low growth and doubling rates [12] so that mud deposited at the seafloor is not rapidly colonized by these microorganisms. Dissolved methane residing in young mud flows may, hence, escape oxidation to be transported into the overlying bottom water by compaction and diffusion. The limited data currently available suggest that quiescent dewatering and mud expulsion produce similar methane emissions.

6. Conclusions

Large volumes of water are currently discharged into the Black Sea by quiescent dewatering processes at the Dvurechenskii mud volcano (94,000 m^3 yr^{-1}). About $8.9 \cdot 10^{+6}$ mol CH_4 yr^{-1} are transported to the surface with the ascending fluids. However, about 80% of the ascending methane is oxidized by microbial consortia residing in the sulphate-bearing surface sediments of the DMV so that only $1.9 \cdot 10^{+6}$ mol CH_4 yr^{-1} is emitted into the overlying bottom water. Assuming a similar discharge rate for the other 64 SMVs located at the bottom of the Black Sea, the total methane emission via quiescent dewatering at SMVs would contribute less than 0.1% to the total methane release into the Black Sea. Hence, quiescent dewatering through SMVs is not a major source for methane residing in the Black Sea.

The emission data listed in Table 5 indicate that the mean flux of dissolved methane from mud extrusions at the seafloor amounts to $1.9 \cdot 10^{+6}$ mol a^{-1}. However, a very large standard deviation of $2.6 \cdot 10^{+6}$ mol a^{-1} has to be assigned to this value reflecting the large differences between the individual structures. For mud pies, only, the mean emission and the standard deviation result as 3.6±

$2.8 \cdot 10^{+6}$ mol a^{-1} while other SMVs have emission rates of $0.3 \pm 0.3 \cdot 10^{+6}$ mol a^{-1}. Mud pies are, hence, the main methane emitters among SMVs.

Assuming that 5000 SMVs exist [9], the total methane emission into the ocean via fluid flow through SMVs would fall into the order of 10^{+10} mol yr^{-1}. Other pathways of methane transport including gas bubbling, mud extrusion and explosive mud eruptions may add to this number. We postulate, however, that fluid flow is a major pathway for methane release through SMVs located at the continental slope and rise because methane is highly soluble at the low temperatures and high pressures prevailing at the deeper continental margin sites. The fluxes of gaseous methane are, moreover, reduced since gas bubbles are usually transformed into solid gas hydrates at these sites. SMVs located on the continental shelf at shallow water depths may, however, show a similar behaviour as onshore mud volcanoes where methane emissions occur dominantly through the release of free gas. In a previous estimate of the methane release from SMVs, Milkov et al. [9] concluded that $8 \times 10^{+11}$ mol CH_4 a^{-1} are discharged into the ocean via quiescent dewatering and degassing. This large number was obtained by extrapolating onshore measurements to the seafloor. Moreover, the oxidation of methane in surface sediments was neglected. We thus believe that this previous estimate is too high. We do, however, acknowledge that more work needs to be done to better quantify gaseous methane fluxes at SMVs.

The total release of methane from the seabed via cold venting, gas and fluid seepage and gas hydrate destabilization has been estimated as $2–3 \cdot 10^{+12}$ mol yr^{-1} [50]. If this poorly constrained number would hold, fluid flow through SMVs would contribute less than 1% to the total methane emission from sedimentary systems. It is, however, quite likely that methane oxidation in surface sediments has been underestimated, up to now, so that the global methane fluxes into the ocean may be much smaller than currently believed. Moreover, most of the methane is probably released from shallow water deposits on the continental shelf [32] whereas most SMVs are located in deeper waters at the continental slope and rise. Hydrothermal vents at mid-ocean ridges may emit only about $5 \cdot 10^{+9}$ mol CH_4 yr^{-1} into the deep ocean [51]. SMVs may, thus, be an important source for methane residing in deep ocean waters.

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