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Estimates of methane output from mud extrusions at the erosive convergent margin off Costa Rica

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Abstract

Four mud extrusions were investigated along the erosive subduction zone off Costa Rica. Active fluid seepage from these structures is indicated by chemosynthetic communities, authigenic carbonates and methane plumes in the water column. We estimate the methane output from the individual mud extrusions using two independent approaches. The first is based on the amount of CH_4 that becomes anaerobically oxidized in the sediment beneath areas covered by chemosynthetic communities, which ranges from 10^4 to 10^5 mol yr^{-1}. The remaining portion of CH_4, which is released into the ocean, has been estimated to be 10^2–10^4 mol yr^{-1} per mud extrusion. The second approach estimates the amount of CH_4 discharging into the water column based on measurements of the near-bottom methane distribution and current velocities. This approach yields estimates between 10^4–10^5 mol yr^{-1}. The discrepancy of the amount of CH_4 emitted into the bottom water derived from the two approaches hints to methane seepage that cannot be accounted for by faunal growth, e.g. focused fluid emission through channels in sediments and fractures in carbonates. Extrapolated over the 48 mud extrusions discovered off Costa Rica, we estimate a CH_4 output of $20 \cdot 10^6$ mol yr^{-1} from mud extrusions along this 350 km long section of the continental margin. These estimates of methane emissions at an erosional continental margin are considerably lower than those reported from mud extrusion at accretionary and passive margins. Almost half of the continental margins are described as non-accretionary. Assuming that the moderate emission of methane at the mud extrusions off Costa Rica are typical for this kind of setting, then global estimates of methane emissions from submarine mud extrusions, which are based on data of mud extrusions located at accretionary and passive continental margins, appear to be significantly too high.

Keywords: methane plume; chemosynthetic species; mud extrusion; methane output; Costa Rica forearc

1. Introduction

Mud extrusions are abundant on land and offshore (e.g. Kopf, 2002). They form by the expulsion of water, gas, and mud from sedimentary sequences (Judd et al., 2002) and are commonly associated with compressional tectonics at convergent margins (Dimitrov, 2002; Judd et al., 2002; Kopf, 2003; Milkov et al., 2003). Gases discharging from mud extrusions are composed dominantly of methane, which generally exceed 90 vol% of

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the gas phase (Brown, 1990; Dimitrov, 2002; Kopf, 2003). Mud extrusions in which carbon dioxide or nitrogen are the dominant gases are less common and usually associated with geologically recent magmatic processes (Dimitrov, 2002; Milkov et al., 2003).

The CH_4 content of fluids rising in submarine mud volcanoes is influenced by several processes decreasing the amount of CH_4 finally reaching the sediment–water interface. CH_4 that reaches the gas hydrate stability zone can be removed by hydrate formation (Reed et al., 1990). At or near the sediment surface, CH_4 can provide the energy source for seep organisms and lead to carbonate precipitation (Sibuet and Olu, 1998; Suess et al., 1999). Even though the methane flux to the ocean is reduced by these processes, a fraction of CH_4 is injected into the water column. This CH_4 can either be emitted dissolved in fluids or, in case of over-saturation, in form of gas bubbles (Valentine et al., 2001).

Estimates of the amount of methane discharging from submarine mud extrusions worldwide are sparse (Judd et al., 2002). Henry (1996) estimated the amount of methane emitted from two mud diatremes, Atalante and Cyclops, situated in the Barbados trench. Ginsburg (1999) approximated the output of CH_4 from the Håkon Mosby Mud Volcano located on the passive continental Norway–Barents–Svalbard margin. Kopf and Behrmann (2000) estimated the amount of CH_4 discharging from the Milano- and the Napoli-mud volcano in the accretionary system of the Mediterranean Sea. The global output of methane from submarine mud extrusions was estimated to lie in the order of 10^{10}–10^{11} mol yr^{-1} (Kopf, 2003; Milkov et al., 2003). These global methane budgets are highly uncertain, because of the limited information of the number of mud extrusions offshore and the scarcity of data on CH_4 output from these structures.

In order to better constrain these estimates and contribute data from an erosional subduction setting (Ranero and von Huene 2000, Saffer et al., 2000, Silver et al., 2000), we estimated the CH_4-output from four of the 48 mud extrusions discovered offshore Costa Rica (Fig. 1). The diapiric structures of Mound Culebra and Mound 10 (Mörz et al., 2005) are situated on the continental slope northwest of Nicoya Peninsula, where numerous mud extrusions were detected. Mound 12 and Mound 11, which are described as mud volcanoes (Mörz et al., 2005), are located to the southeast of Nicoya Peninsula, where only few mud extrusions have been found (Fig. 1). In contrast to the published estimates above, which are based on heat flow data or mud volume and assumptions of gas content in fluids (Henry et al., 1996; Ginsburg et al., 1999; Kopf and Behrmann, 2000), we derive the methane output from surficial and water column observations above mud extrusions. Two independent approaches are presented. The first is based on areas

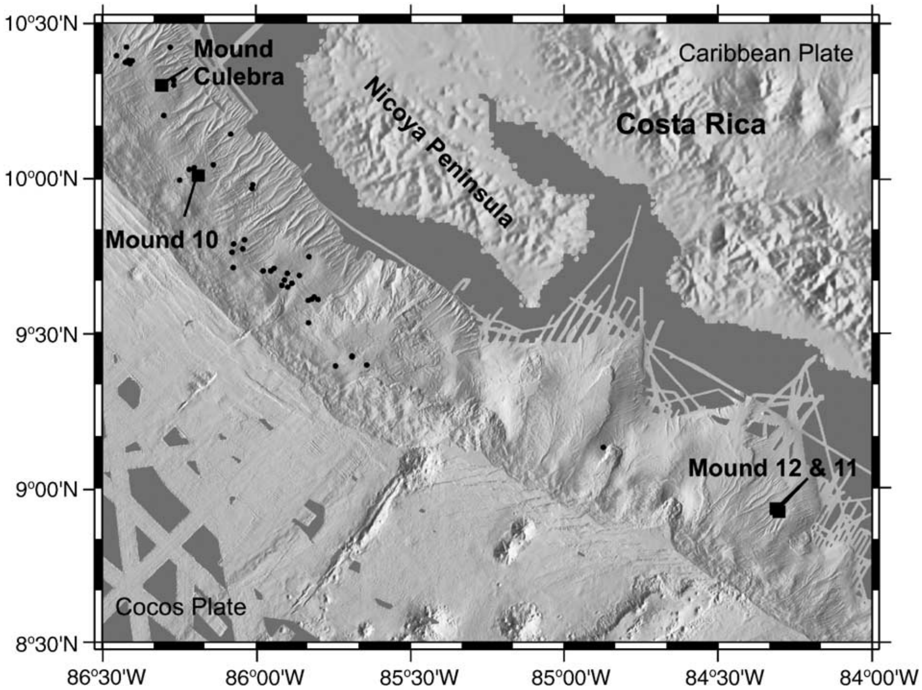

Fig. 1. Bathymetry of the continental margin off Costa Rica and locations of mud extrusions (filled circles).

covered by chemosynthetic communities and typical methane flux rates for the different fauna. The second approach is based on CH_4 concentrations in the water column and bottom current velocities.

2. Methods

2.1. Sampling and analysis

The seafloor was surveyed with ocean floor observation systems (OFOS) during four cruises with the research vessels SONNE and METEOR: SO 144 (Sept.–Nov. 1999), SO 163 (Apr.–May 2002), M 54 (Aug.–Sept. 2002), and SO 173 (Sept. 2003). OFOS is a towed camera sled equipped with video, still cameras, and a CTD unit. Seafloor maps showing the distribution of geological and biological indications of fluid seepage were constructed based on the interpretation of available position and depth data as well as congruence of repeated observations; a method that has successfully been used on many previous occasions (e.g. Wiedicke et al., 2002).

During expedition M 54, water column work was conducted with a standard CTD system (Neil Brown Mark III) equipped with a 24 × 10-L-rosette water samplers as well as with a bottom water sampler (BWS). The BWS consists of five 5-L-water bottles placed at different heights above ground (0.14–1.2 m) in horizontal position within a frame outfitted with two fins to assure positioning in the direction of bottom current flow. Rosette/CTD water samples for determination of CH_4 and O_2 were taken with decreasing depth intervals towards the seafloor (see data points in Figs. 3, 5, 7, 9). For CH_4-analyses aboard a modification of the vacuum degassing method described by Lammers and Suess (1994) was used, modified by Rehder et al. (1999). In addition to the oxygen sensor of the CTD, Winckler titration (Grasshoff et al., 1997) was used for the determination of oxygen.

Current measurements were performed by upward looking ADCPs (Acoustic Doppler Current Profiler; RD Instruments) attached to lander devices during M 54. At Mound Culebra a 300 kHz ADCP was deployed for ~14 days and at Mound 12 and Mound 11 a 1200 kHz ADCP was deployed for 48 h. The data obtained were processed over a time frame of 24 h and at different depth levels.

2.2. CH_4 output calculations

2.2.1. Calculation based on seafloor observation

This approach to estimate the amount of methane emitted from a mud extrusion is based on the assessment of the total area covered by different chemosynthetic communities and methane flux rates presumed to be typical for the different habitats.

To estimate the total area covered by dominant chemosynthetic species (vesicomyid clams, bacterial mats), seafloor observations were used to define a basal plane in which patches of clams or bacterial mats occur. The area observed by the camera sled within this basal plane was estimated by assuming a constant 2-m wide image of the seafloor along the length of the track. The area covered by clams or bacterial mats was estimated by classifying them as circular clusters with diameters of 0.5, 1, or 2 m. This was done by scaling the images with the help of two parallel laser pointers mounted on the sled at 20 cm (RV SONNE) or 50 cm (RV METEOR) distance. The total area covered by clams and bacterial mats was calculated by assuming that the ratio of observed clams/bacterial mats in the area covered by video observation is the same as the ratio of total clams/bacterial mat-covered area to the basal plane. As this first-order approximation is rather crude we allow all parameters to vary by 20% and calculated minimum and maximum values. Regions covered by *Lamellibrachia*-colonies or mytilid bivalves were not considered, because of their partly loose occurrence and spatial distribution, which could hardly be estimated.

To estimate a methane budget for each of the studied mounds, the area estimates of the dominant vent fauna were multiplied by outflow rates of CH_4 that are characteristic of the different habitats. The total methane flux from beneath the seafloor can be divided into two fractions: the amount of methane anaerobically oxidized in sediments and the fraction seeping into the bottom water. Anaerobic oxidation of CH_4 below bacterial mat sites at Hydrate Ridge was determined by radiotracer technique and porewater modeling to be between 1.8 and 51.1 mol m^{-2} yr^{-1} (Boetius et al., 2000; Knittel et al., 2003; Luff and Wallmann, 2003; Treude et al., 2003). Seepage of methane into the overlying bottom water was measured with a benthic barrel at Hydrate Ridge with values of 10.9 to 32.8 mol m^{-2} yr^{-1} (Torres et al., 2002). The geochemical environment at bacterial-mat sites at Mound 12 was constrained by modeling in situ benthic chamber and porewater data (Linke et al., 2005). The methane flux is about 10.3 mol m^{-2} yr^{-1}, of which 5.9 mol m^{-2} yr^{-1} is oxidized in the sediments and 4.4 mol m^{-2} yr^{-1} is escaping into the overlaying bottom water. These values lie at the lower end of the range of values reported. The CH_4 fluxes reported by Linke et al. (2005) are the only data measured in the region offshore Costa Rica. However, to account for the large variability of this type of environment (Tryon and Brown, 2001; Torres et al., 2002), we used the entire range documented in the literature to estimate the amount of CH_4 consumed in sediments as well as the CH_4 output in the bottom water.

The flux estimates for vesicomyid clams are less well-defined; preliminary porewater data of Mound Culebra and Mound 10 draw an inconclusive picture of methane oxidation rates in the vesicomyid habitat with values ranging from 0.05 to 3 mol m^{-2} yr^{-1} (Hensen, pers. comm.). Radiotracer techniques and porewater modeling yield methane oxidation rates in the range of 14.6 to 20.4 mol m^{-2} yr^{-1} at Hydrate Ridge (Knittel et al., 2003; Treude et al., 2003) and 19 mol m^{-2} yr^{-1} at the Aleutian trench (Wallmann et al., 1997). Almost all of the methane is oxidized in the sediments; only zero to <0.2 mol m^{-2} yr^{-1} escaped into the bottom water, as determined by benthic barrel experiments at Hydrate Ridge (Torres et al., 2002). Again, we used the range of values reported to derive the portion of CH_4 anaerobically oxidized in sediments and the CH_4 output into the water column. The estimates for the different mounds are summarized in Table 1.

The use of data from the different geological settings, where direct methane flux measurements at cold seeps have been performed, has been chosen simply because of the lack of enough flux measurements from mud extrusions off Costa Rica, or at least from an erosional margin. We felt that using just the data gathered off Costa Rica, sampled with towed, video guided instruments, would not represent the uncertainty in the methane flux from areas covered by the various benthic communities. So we extended the range of data by adding the measurements from the accretionary systems off Oregon and the Aleutan Trench, and use the minimum and maximum of all data to calculate the output of the individual mounds (see Table 1). The given uncertainty mostly reflects this range in flux measurements and emphasizes the need for a broader data base on benthic fluxes at active cold seep settings.

2.2.2. Calculation based on methane measurements in the water column

In a second approach, the methane output per mud extrusion was calculated using measured CH_4 concentrations in the water column and bottom-near current

Table 1
First-order estimate of the total area occupied by the dominant chemosynthesis-based species and the resulting CH_4 output

Mound	Dominant community	Area occupied by the dominant community (Min–max m^2)	Calculation	CH_4 flux (mol m^{-2} yr^{-1})	CH_4 output (10^3 mol yr^{-1})
Mound Culebra	Vesicomyid clams	6000–20,200	74 m^2 clam fields observed during 4 OFOS profiles (area of OFOS profiles: 10,000 m^2) in total area of 1,500,000 m^2 (SO 163 OFOS 1 and 2, M 54 OFOS 117-1, SO 173 OFOS 50)	AOM flux 0.05– 20.4 Benthic flux 0–0.2	AOM uptake 0.3– 412.1 Benthic output 0–4.0 Total output 0.3–416.1
Mound 10	Vesicomyid clams	600–2100	19 m^2 clam fields observed during 5 OFOS profiles (area of OFOS profiles: 3600 m^2) in total area of 230 000 m^2 (SO 173 OFOS 80)	AOM flux 0.05–20.4 Benthic flux 0–0.2	AOM uptake 0.03–42.8 Benthic output 0–0.4 Total output 003–43.2
Mound 12	Bacterial mats	1500–5000	60 m^2 bacterial mats observed during 3 OFOS profiles (area of OFOS profiles: 2200 m^2) in area of 100,000 m^2 (M 54 OFOS 161)	AOM flux 1.8–51.1 Benthic flux 4.4–32.8	AOM uptake 2.7–255.5 Benthic output 6.6–164 Total output 9.3–419.5
Mound 11	Bacterial mats	500–1700	16 m^2 bacterial mats observed during 4 OFOS profiles (area of OFOS profiles: 580 m^2) in area of 40,000 m^2 (SO 173 OFOS 107)	AOM flux 1.8–51.1 Benthic flux 4.4–32.8	AOM uptake 0.9–86.9 Benthic output 2.2–55.8 Total output 3.1–142.7

The calculation is based on the range of CH_4 fluxes given in literature for the different chemosynthetic habitats (Section 2.2.1). AOM flux/uptake – amount of CH_4 anaerobically oxidized in sediments, Benthic flux/output – amount of CH_4 emitted in bottom water, total output – sum of AOM uptake and benthic output.

velocities. For that purpose the method described in Heeschen et al. (2005) was slightly modified. These authors calculated the methane inventory as the product of CH_4 concentration and a volume of a box defined by two CTD-transects perpendicular to the main current flow. The height of the box is given by the height of the CH_4 plume. As our data lack such a defined base, we designated the base to be the area which is covered by water column measurements, leaving out the hydrocasts that showed no methane anomalies close to the seafloor. At Mound 11 we calculated the output from an area roughly encircling the main vent fields as examined by seafloor observations because of the poor coverage by hydrocasts. CH_4 concentrations were averaged over layers of 10 m in height with the seafloor defining the 0-depth level. Background values of 0.5–2 nmol L^{-1} were subtracted from these averaged values. These vent-derived "excess" CH_4 concentrations were then multiplied by the volumes of the layers and the sum of the amount of methane in all layers yields the inventory of the entire box above the mound. The 'clearing time', i.e. the time it takes to remove all CH_4 from the volume inside the box, was calculated by dividing the length of the box along the current direction by the current velocity. Finally, the methane output is determined as the quotient of inventory and 'clearing time'.

3. Results

3.1. Mound Culebra

Mound Culebra is located at the continental slope of Costa Rica, west of Nicoya Peninsula (Fig. 1). The mound is elongated in southwest-northeast direction, with diameters of 1 to 1.6 km. It rises about 140 m above the surrounding slope at 1650 m water depth. Authigenic carbonates are predominantly exposed on the summit, but also outcrop in the central depression tracing the northwest–southeast trending fault (Fig. 2). Vesicomyid clams are abundant but patchy at the eastern summit, the northwestern flank and, to a minor extent, at the eastern flank. Typically, the clams were observed in 1-m size clusters in soft sediments between the massive carbonates at the summit or between smaller-sized carbonates at the flanks. The clam-covered area at Mound Culebra is estimated to be much larger than the clam or bacterial mat-covered areas of the other mounds (Table 1). Apart from the predominant vesicomyid clams, a few small *Lamellibrachia* colonies were observed.

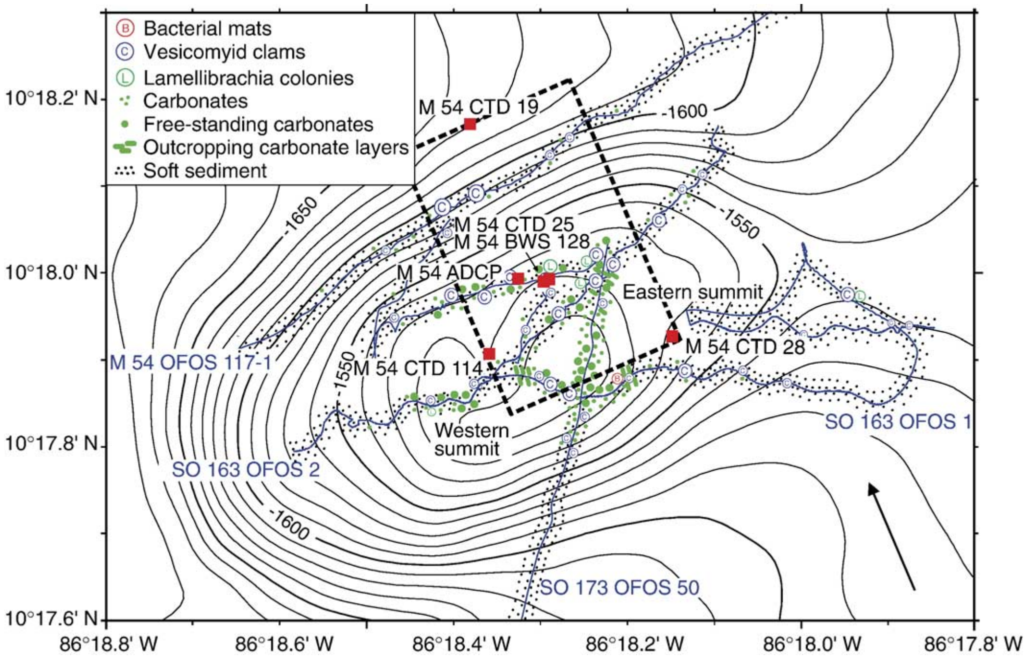

Fig. 2. Seafloor observations and CTD/BWS stations at Mound Culebra. Seafloor surveys were conducted with the camera sled OFOS and TV-guided multicorer (lines). Methane seepage is concentrated at the eastern summit and northwest of it as indicated by the densest occurrence of vesicomyid clam clusters. Currents were recorded by ADCP: the main current direction is indicated by the arrow in the right, lower corner. The rectangle shows the base used for calculation of the benthic output by the water column approach (see Discussion). Contour interval: 10 m.

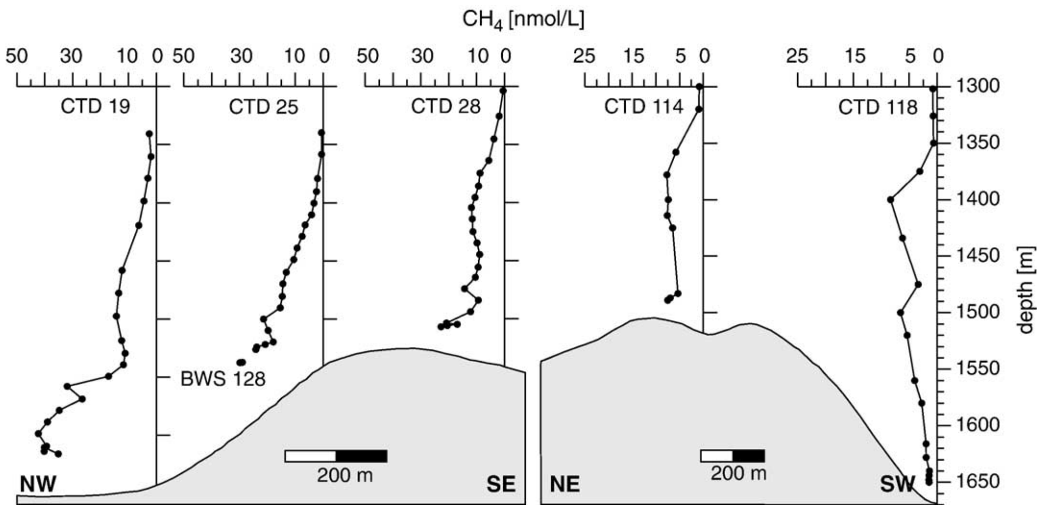

Fig. 3. CH_4 concentrations in the water column at Mound Culebra (for location of CTDs, see Fig. 2). Highest values were observed closest to the seafloor at the top of the mound (M 54 CTD 25, 28, and BWS 128) and at a depth of 1600 m on the northwest flank of the mound (M 54 CTD 19). The methane concentrations are lower at the central depression (M 54 CTD 114) and no bottom-near anomaly has been observed southwest of the mound (M 54 CTD 118, 10° 17.57 N; 86° 18.56 W; position not indicated in Fig. 2).

Increased CH_4 concentrations towards the seafloor were observed at the eastern summit region (M 54 CTD 25, 28, BWS 128) and on the northwestern flank (M 54 CTD 19) verifying proximity to areas of active CH_4 seepage (Fig. 3). Increased CH_4 concentrations at the northwestern flank (M 54 CTD 19) may result, at least in part, from accumulation in the sheltered zone behind the mound where reduced bottom water currents and

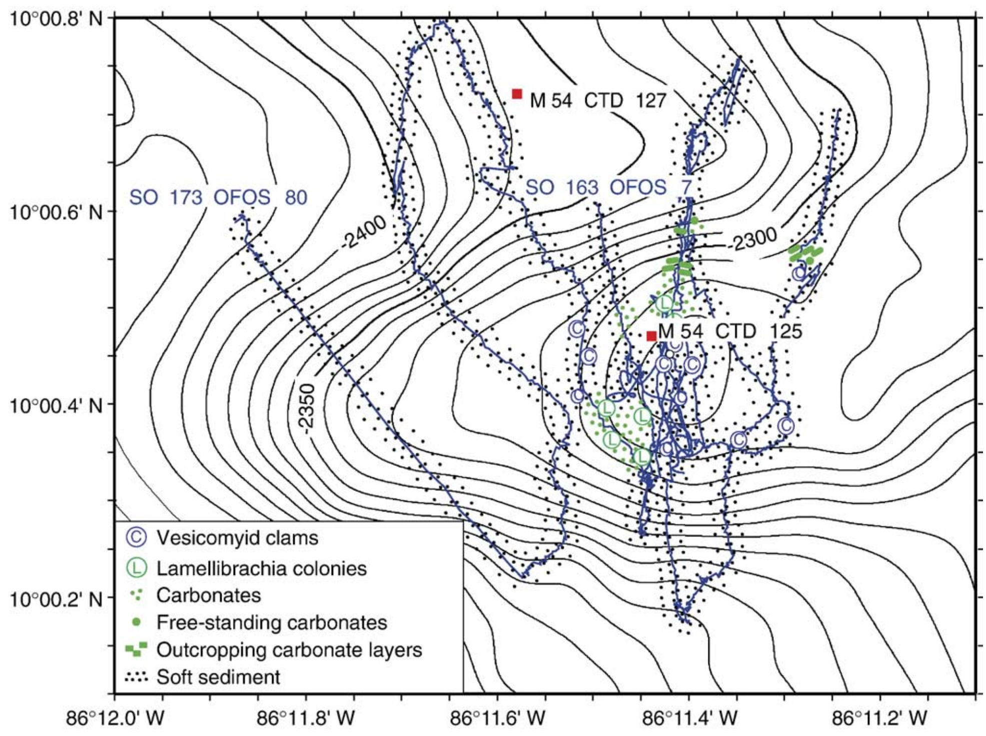

Fig. 4. Seafloor observations and CTD locations at Mound 10. Vesicomyid clams occur in the sediments at the summit. Tubular carbonates were found in association with *Lamellibrachia*-colonies. Sediment layers and authigenic carbonates are exposed at a scarp north of the summit. Contour interval: 10 m.

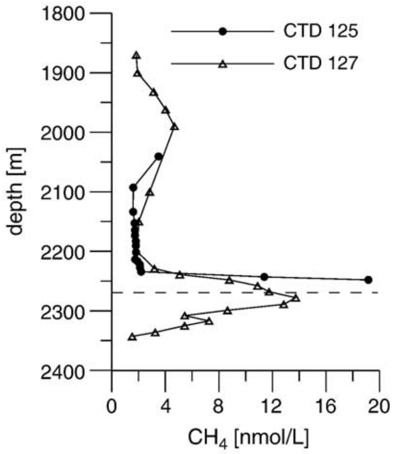

Fig. 5. CH_4 concentration versus depth at Mound 10 (for location, see Fig. 4). Methane is injected into the bottom water at the summit area of the mound (M 54 CTD 125). The dashed line marks the depth at the top of the mud extrusion. Methane is apparently transported with bottom currents to the northwest (Station M 54 CTD 127).

turbulent mixing are expected. The central depression did not appear to be a major source for CH_4; the concentration in the water close to the seafloor is only slightly elevated (M 54 CTD 114).

3.2. Mound 10

Mound 10 is located southwest of Nicoya Peninsula at a water depth of 2400 m. It is an elongated structure with diameters between 0.7 and 1.8 km and an average height of about 80 m. Seafloor observations revealed that authigenic carbonates and chemosynthetic communities occur in the summit area (Fig. 4). Clam clusters and bushes of *Lamellibrachia*-colonies and associated tubular carbonates were observed. Compared to Mound Culebra less carbonates are exposed at Mound 10 and the area of active methane seepage as indicated by vesicomyid clams is considerably smaller (Table 1).

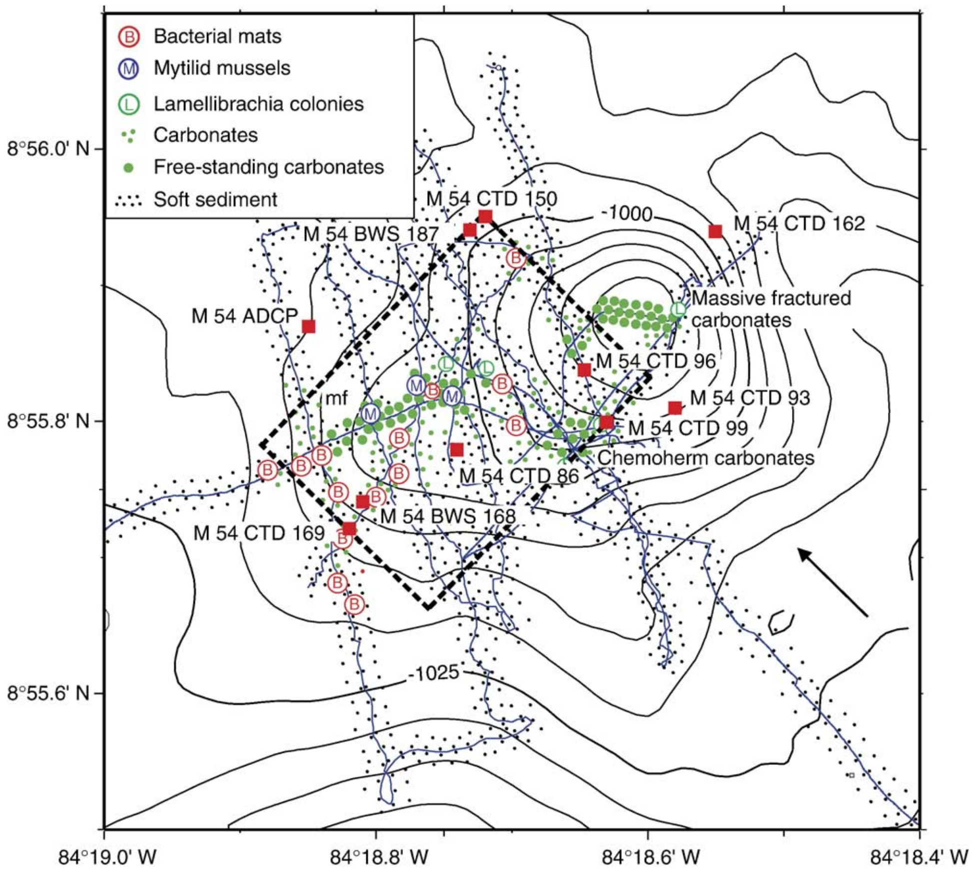

Fig. 6. Seafloor observations and CTD/BWS stations at Mound 12. OFOS-tracks are indicated by thin lines. Massive carbonates occur at the top area. A mélange of pebble-sized carbonates, shells, and sediments is present toward the southwest. Mytilid mussels occur in fractures of massive carbonates. Chemosynthetic communities partly buried by sediments indicate recent mud flows (mf). ADCP marks location of current measurements. The main current direction is indicated by the arrow in the right, lower corner. The rectangle shows the base used for calculation of the benthic output by the water column approach (see Discussion). Contour interval: 5 m.

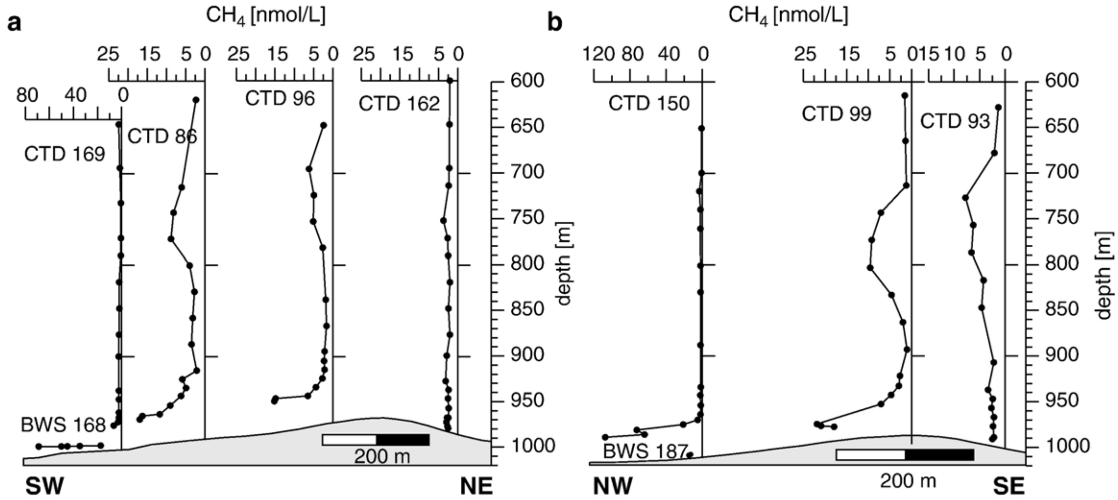

Fig. 7. CH_4 concentrations in the water column above Mound 12 (for location see Fig. 6). Note different scales of individual diagrams. (a) Profile from southwest to northeast and (b) profile from northwest to southeast. Methane venting occurs in the region southwest to northwest of the mound. The highest value of 107 nmol L^{-1} was measured at station M 54 CTD 150. CH_4 is carried to the northwest with bottom water currents.

Venting was confirmed by increased CH_4 concentrations in water samples taken right above the summit area (M 54 CTD 125; Fig. 5). The CH_4 plume spreads from Mound 10 to the northwest. Water samples at station M 54 CTD 127, about 500 m northwest of the summit, show a methane anomaly at the same depth

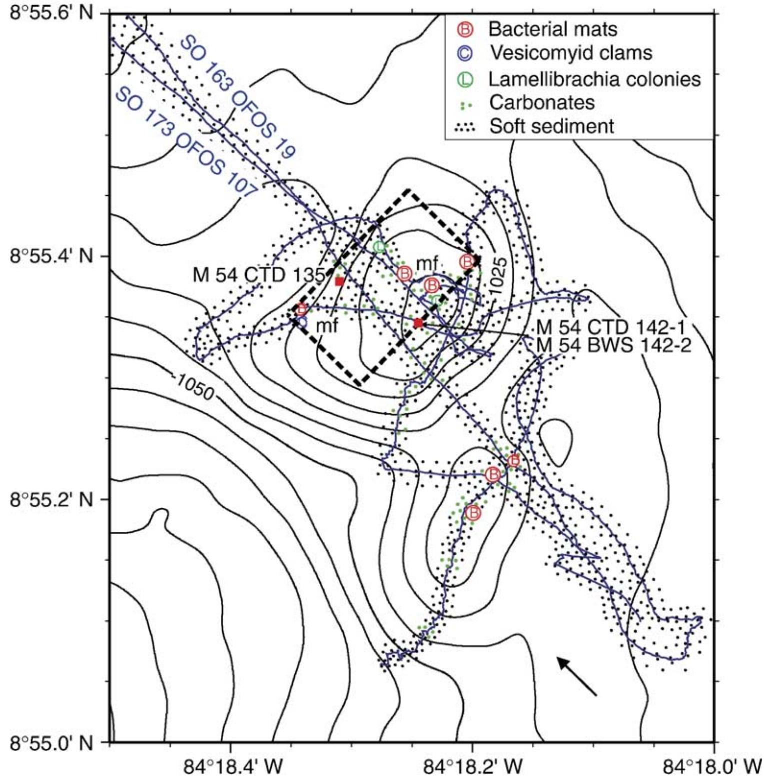

Fig. 8. Seafloor observations and stations at Mound 11. The mound has a complex surface morphology consisting of two elevations where bacterial mats occur. Buried chemosynthetic communities gave evidence of mud flows (mf). The rectangle indicates the area of main venting at the northern summit used for calculating the benthic output by the water column approach. The main current direction is indicated by the arrow in the right, lower corner (Contour interval: 5 m).

range and in a similar density layer (σ_Θ=27.708 at M 54 CTD 125 and σ_Θ=27.711 at M 54 CTD 127) as in the hydrocast above the summit.

3.3. Mound 12

Mound 12 and Mound 11 are located farther to the southeast at the Costa Rican continental margin at water depths around 1000 m (Fig. 1). Mound 12 is only 30 m high and elongated in northeast–southwest direction with diameters of about 1 to 1.6 km. The seafloor observations revealed that authigenic carbonates and chemosynthetic communities occur along a central northeast–southwest trending axis (Fig. 6). The main active venting area is located southwest of Mound 12, where bacterial mats were much more common than mytilid mussels or *Lamellibrachia* colonies. As bacterial mats are the dominant communities, we used their spatial distribution to estimate the active seepage area (Table 1).

Water column investigations illustrate that CH_4 is emitted from vent areas at the southwestern and northwestern flank (Fig. 7). The highest methane concentration of all investigated mud extrusions (107.3 nmol L^{-1}) was measured at station M 54 CTD 150, northwest of the mound. It may originate from the small vent site nearby (Fig. 6) being transported to the northwest by the bottom water. This interpretation is supported by the low CH_4 concentrations in the bottom water (M 54 BWS 187) sampled at this location. Transport to the northwest is further verified by two hydrocasts in the northeast (M 54 CTD 162) and southeast (M 54 CTD 93), which did not show any elevated CH_4 concentrations.

3.4. Mound 11

Mound 11 is located southeast of Mound 12. It is about 20 m high with complex small-scale seafloor structures. It consists of two separate elevations at which bacterial mats were found (Fig. 8). Only two small *Lamellibrachia* colonies and one cluster of vesicomyid clams were observed at the mound; however, the remains of a diverse chemosynthetic community were found in the sediments. Mörz et al. (2005) suggest that a high energy event caused brecciation and chaotic relocation of shells and carbonate pieces, which were subsequently covered by a mud flow. Carbonate talus of pebble to boulder-size was exposed at the summits or on the flanks. In order to estimate the active seepage area, we calculated the bacterial mat-covered area, which is smaller than the area at Mound 12 (Table 1).

The CH_4 concentration was measured above the northern elevation of Mound 11 (Fig. 9). A continuous increase of the CH_4 concentration towards the seafloor indicate that methane is released in dissolved form, as observed at the other mounds. However, the methane concentrations at Mound 11 are distinctly lower than at the other mounds (see Discussion 4.2).

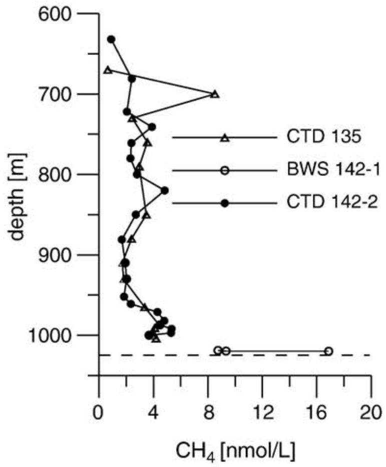

Fig. 9. CH_4 concentrations in the water column above Mound 11. The dashed line marks the depth at the top of the mud extrusion. Water samples contained less methane than samples of the other mounds.

4. Discussion

4.1. Chemosynthetic communities

Differences in the geochemical environment at the mounds cause differences in the composition of the chemosynthetic communities as well as in the types of authigenic carbonates. High methane supply causes anaerobic oxidation of methane (AOM) close to the sediment–seawater interface. Low methane supply leads to AOM deeper in the sediments (Luff and Wallmann, 2003; Han et al., 2004). Thus, the methane supply and the fluid advection rate mainly influence the depth of this zone. We did not find any evidence for the emission of methane as free gas and the methane distribution in the lower water column strongly suggests that methane is mainly transported dissolved in vent fluids. Methane supply is therefore directly coupled to fluid advection rates and methane concentration in the fluid.

The chemosynthesis-based species depend, in general, on hydrogen sulfide rather than methane (Fisher, 1990). Thus, the species indicate the sedimentary depth level where hydrogen sulfide is produced in the course of AOM. Bacterial mats live at or close to the surface of soft sediments and mytilid bivalves were predominantly observed in fractures of carbonates. Both organisms indicate AOM close to the sediment–seawater interface and thus, high fluid flow rates. In contrast, vesicomyid clams live in soft sediments and have access to sulfide that is produced deeper in the sediment at a depth range of centimeters to decimeters, and thus indicate lower flow rates. This simple concept that the variation in flow rates causes vertical shifts in the zone of AOM, and thus sulfide production, is also supported by carbonate formation: high fluid flow rates push AOM up to the sediment–water interface, even into fractures of previously existing carbonates that are subsequently lined by aragonitic cements as documented in Han et al. (2004). Low fluid flow causes the precipitation of carbonates in the sediments. Based on this concept we infer that the fluid flow rate at Mound 12 is high, indicated by the prevalence of bacterial mats, mytilid mussels and aragonite linings. Fluid flow rates at Mound 11 are also high, indicated by the occurrence of bacterial mats, and supported by reported fluid advection rates of 300 cm yr^{-1} derived from modeling of pore water data (Hensen et al., 2004). In contrast, the fluid flow at Mound Culebra and Mound 10 appears to be lower, as indicated by vesicomyid clams, a lack of bacterial mats and carbonates that formed by cementation of sediments (Han et al., 2004).

We briefly discuss the evidence for the concept proposed above that greatly depends on the fact that the observed fauna relies on hydrogen sulfide produced by AOM instead of directly using methane as energy source. The recovered bacterial filaments resembled morphologically *Beggiatoa*, a sulfur-oxidizing organism (Nelson and Jannasch, 1983). Mytilid bivalves have been described with both thiotrophic as well as methanotrophic endosymbionts. The mytilids off Costa Rica probably belong to a new species; genetic studies on the host and endosymbionts are in process (S. Hourdez, pers. comm.). The $\delta^{13}C$ values obtained for two specimens recovered from Mound 12 fall in the range between −30 to −40‰ PDB (U. Struck, pers. comm.) which are typical for specimens that live in symbiosis with sulfur-oxidizing bacteria (Fisher, 1990). Furthermore, the $\delta^{13}C$ values of the seeping methane from that site are below −70‰ PDB (Rehder et al., 2004). A significant contribution of this methane would result in more negative $\delta^{13}C$ values of the mytilid tissue than −30 to −40 ‰ PDB. Thus, we suppose that the mytilids live in symbiosis with thiotrophic endosymbionts. Various different species of vesicomyid clams were discovered off Costa Rica, some of which are new (E. Krylova, pers. comm.). The recovered tubeworms are genetically identical to *Lamellibrachia barhami* (McMullin et al., 2003). The endosymbionts of all vestimentiferan tubeworms and vesicomyid clams are described as thiotrophic (Fisher, 1990). Thus, apparently all chemosynthetic specimens encountered off Costa Rica rely on hydrogen sulfide rather than on methane.

4.2. Methane seeps and methane anomalies in the water column

Methane is currently escaping through all four mounds. The observed enhanced CH_4 concentrations in the bottom water indicate similar source regions as depicted from the distribution of the chemosynthetic communities. The CH_4 concentrations are elevated by up to two orders of magnitude above the regional background of 0.5–2 nmol L^{-1}. Methane is dissolved in the fluids, as shown by the concentration profiles (Figs. 3, 5, 7, 9) and by surveys using acoustic or video-guided instruments, which did not reveal any signs of bubbles emanating from the seafloor.

In general, methane concentrations at ~20 m above the seafloor are similar for all mounds except Mound 11. Here, the lower methane values could be explained by the fact that the CTD and BWS stations were not deployed exactly at the very small area of seepage. Alternatively, the low concentrations could also be related to the relatively small area of venting compared to the other mounds or to effective methane degradation and/or accumulation processes within the near-surface sediment. The latter scenario is based on findings of shallow gas hydrate deposits at Mound 11 (Schmidt et al., 2005).

When methane is emitted into the ocean, it is subject to transport and dilution by ocean currents and to removal by aerobic oxidation. Near-bottom currents strongly influence the distribution of methane in the water column. The plumes mapped at Mound Culebra (Fig. 3) and Mound 12 (Fig. 7) indicate a northwestward flow. Highest methane concentrations were observed on the northwest-flanks of these mounds, pointing to an enrichment in the lee side of the mounds. Nevertheless, part of the enrichment probably originates from vent sites nearby. At Mound Culebra, vesicomyid clam fields were observed on the northwest side of the mud diapir (Fig. 2) and at Mound 12 a small field covered by bacterial mats seems to contribute to the methane anomaly found slightly offset to the site (Fig. 6). The northwestward flow derived from the shape of the methane plume is in agreement with the major current direction directly measured above the mounds by ADCP. The mean velocities were 2.4 ± 1.4 cm s^{-1} at Mound Culebra and 3.2 ± 2 cm s^{-1} at Mound 11 and Mound 12. Therefore, vent methane will be carried over the mound area in direction of the current flow within hours to days.

The time frame of dilution by ocean currents is much shorter than that of methane oxidation. Valentine et al. (2001) studied methane oxidation rates and turnover times by incubation of tritium-labeled methane (^3H–CH_4) in water samples from a gas hydrate bearing area of active seepage in the Eel River Basin, off the coast of northern California. Their results demonstrate that methane is oxidized more rapidly in areas of high methane concentration (20–300 nmol L^{-1}) than in waters of low methane concentration (3–10 nmol L^{-1}). Because of comparable CH_4 concentrations over the mounds we assume similar oxidation rates and turnover times. The data of Valentine et al. (2001) suggest a turnover time of a few years for a concentration of ~20 nmol L^{-1}. In contrast, de Angelis et al. (1993) reported turnover times in the range of weeks to one month for such concentrations in deep-sea hydrothermal plumes of the Juan de Fuca Ridge. They also measured oxidation rates by incubation, but used $^{14}CH_4$ instead of ^3H–CH_4. However, fast mixing with background waters decreases CH_4 concentration and increases turnover time. This suggests that dilution is more significant in lowering CH_4 concentrations than is oxidation. Consistently, Damm and Budeus (2003) examined carbon isotopic signatures in the plume water above the Håkon Mosby mud volcano (Norwegian Sea) and report that the $\delta^{13}C$-depleted methane in the water column is consistent with mixing of ambient sea water and water containing vent methane.

4.3. Methane budgets

We calculated the output of methane from the mounds using: 1) seafloor observations of chemoautotrophic communities and characteristic flux rates for these communities adopted from literature; and 2) by calculating the inventory of methane in excess of the CH_4 background and the flushing time of the water body above the mounds (see Section 2.2). The former approach uses typical CH_4 fluxes (in mol m^{-2} yr^{-1}) for the fraction of methane oxidized in the upper sediment (AOM flux) and for the fraction escaping into the water column (benthic flux) at different vent habitats. Multiplication by the area covered by the dominant benthic community yields the amount of CH_4 consumed by “AOM uptake” as well as the amount of CH_4 discharging into the bottom water (benthic output). The sum of these two yield the total CH_4 output. The second approach directly quantifies the benthic output of the entire structure of the mound as the quotient of excess inventory and flushing time. It neglects the fraction of methane oxidized in the upper sediments. The different estimates of CH_4 fluxes and outputs are summarized in Tables 1 and 2.

4.3.1. Calculation based on seafloor observations

The dominant chemosynthetic species at Mound Culebra and Mound 10 are vesicomyid clams, whereas bacterial mats are dominant at Mound 11 and 12. The areas covered by clams or bacterial mats vary by one order of magnitude between Mound Culebra and Mound 10, and by about a factor of two between Mound 12 and Mound 11 (Table 1). We used the range of these areas and faunal characteristic flux rates to derive estimates of CH_4 output. This approach is conservative, because regions covered by *Lamellibrachia*-colonies or mytilid bivalves were not considered. Also, this approach does not include active seepage that is transient, too slow, or too fast to sustain chemosynthetic communities.

The few available CH_4 flux rates, which are pointed out in Section 2.2.1, indicate that most of the methane is consumed in the sediments, whereby the AOM flux ranges in the same order of magnitude below bacterial mats and vesicomyid clams. Interestingly, the benthic flux differs by at least one order of magnitude; it is higher at bacterial mat sites than at vesicomyid clams sites. Due to this difference, the benthic output from Mound Culebra and Mound 10 appears to be lower than that of Mound 11 and 12, while the total output estimates of CH_4 for Mound Culebra and Mound 12 are similar.

Table 2
Methane inventories, benthic output, and benthic flux derived from methane concentrations in the water column and current measurements

Mound	(Area) km^2	Plume height (m)	(Inventory) (mol)	Current velocity (cm s^{-1})	Clearance time (d)	Benthic CH_4-output (10^3 mol yr^{-1})	Benthic CH_4-flux (mol m^{-2} yr^{-1})
Area covered by water column measurements							
Mound Culebra	0.22	260	410–486	2.4 ± 1.4	0.17–0.66	625 ± 398	1.0–4.7
Mound 12	0.12	80	102–117	3.2 ± 2.0	0.06–0.27	406 ± 270	1.1–5.6
Area covered by vent indicative fauna							
Mound 11	0.04	80	6.9–11.3	3.2 ± 2.0	0.03–0.14	70 ± 53	0.4–3.1

4.3.2. Calculation based on methane measurements in the water column

In this approach, the benthic CH_4 output from the mud extrusions into the water column is directly assessed using water column measurements (see Section 2.2.2). Due to a complete lack of current measurements, we could not address Mound 10 by this method. For the other three mud extrusions, this approach results in benthic output estimates in the order of 10^4 to 10^5 mol yr^{-1} for each mound (Table 2). 10–20% of the uncertainty of each estimated benthic output results from variations of the local background methane concentration (from 0.5 to 2 nmol L^{-1}). More than 50% of the uncertainty of each value is caused solely by the variation of current velocities. The depth levels covered by the ADCP do not cover the full plume height, and we assumed that the velocities stay about the same above the recorded depths range. Besides, long-term variations could not be assessed within this study, because the calculation is based on methane measurements collected over a single month.

A similar benthic output of CH_4 was calculated at Mound Culebra and Mound 12 whereas the benthic output from Mound 11 is considerably lower. Even though the area of Mound Culebra is almost twice as large as the one of Mound 12 and the dominant chemosynthetic communities differ, the benthic fluxes derived from the benthic output estimates indicate a similar venting activity of these two mounds. The low benthic output of Mound 11 is most likely due to the smaller venting area (base of box, Table 2) depicted and the low methane concentrations measured above this mound.

4.3.3. Comparison of methane outputs

4.3.3.1. Comparison of the two approaches. The estimates for the benthic output derived from the water column investigations are up to three orders of magnitude higher than those based on seafloor observations. This discrepancy may be explained by the different parameters of the two approaches. The seafloor observation approach is based on observations over four years and includes only CH_4 emission from areas covered by the dominant chemosynthesis-based species (Table 1). In contrast, the water column approach is based on measurements of CH_4 concentration during Aug.–Sept. 2002. These values may vary over longer time scales. The water column approach includes CH_4 emission over the whole area depicted as actively venting area (base in Figs. 2, 6, 8), i.e. CH_4 emission from areas covered by the dominant vent, covered by other vent communities, and areas where methane seepage is too slow or too vigorous for faunal growths to be established (Table 2). Still, the CH_4 measurements in Aug.–Sept. 2002 show a coherent picture and during this cruise we investigated the chemosynthetic communities as well as CH_4 concentrations in the water column. Thus, the comparison suggests that considerable amounts of CH_4 seep through areas not covered by the dominant community.

The role of the dominant vent fauna on methane seepage can be determined by comparing the benthic fluxes listed in Tables 1 and 2. This eliminates the influence of the partly different base areas used in the two approaches. The benthic fluxes derived from the water column approach should be similar to the faunal characteristic benthic fluxes used for calculation of the benthic output based on the dominant vent fauna, if the faunal covered areas present main sources of methane seepage. The benthic fluxes of Mound 11 and 12 yield values which are below or at the lower end of values reported of bacterial mats in literature (see Section 2.2.1, Table 1). However, to obtain the calculated benthic output of the water column approach a much larger area covered by bacterial mats would be necessary than the one depicted by seafloor observation. This suggest either that the areal coverage of OFOS surveys was not sufficient to do a proper estimate of the fraction of seafloor covered by bacterial mats, or that a large additional amount of CH_4 discharges at sites which are not covered by bacterial mats. The benthic fluxes of Mound Culebra derived from the water column approach are similar to the benthic fluxes of Mound 11 and 12. But in contrast to Mound 11 and 12 only a small patch of a bacterial mat was observed at Mound Culebra and the main chemosynthetic community consists of vesicomyid clams. At clam sites, however, only a minor fraction of methane is seeping into the water column, as pointed out in 2.2.1. We suppose that a large amount of CH_4 enters the bottom water through localized channels. Conduits with diameters of 5–10 mm, which could partly be traced for more than 2 m, were found in sediments obtained by gravity corer at Mound Culebra (Mörz et al., 2005). Vertical conduits were also observed in sediments of Mound 12 and 11 (Mörz et al., 2005). Increased flow rate in such conduits might enable CH_4 to bypass the benthic filter.

The comparison of the two approaches shows that seepage at sites covered by the dominant vent fauna is not sufficient to generate the observed CH_4 plumes in the water column above the investigated mud extrusions. The explanation that large areas covered by chemosynthetic communities have not been discovered and thus, the areal extend has been largely underestimated, appears unlikely. While a larger data base of seafloor observations surely would refine the areal estimate of seep communities, the video-guided investigations shown here are representative and, thus, do not allow an error of an order of magnitude. Hence, the comparison of the two approaches point to the important conclusion that fluid venting not supporting faunal growths, for example rapid fluid flow through localized channels, is a crucial factor of CH_4 discharge into the water column.

4.3.3.2. Comparison with other investigated vent sites. For comparison with the estimated methane outputs of other cold seep locations, we only use the estimates derived from the water column approach, because all cited references estimate the output from the entire structures including all seep phenomena rather than being based on seepage at defined habitats.

Our estimates of methane output are lower than reported estimates from other mud extrusions (Table 3). Two examples from the Barbados accretionary wedge are described as diatremes by Henry et al. (1996). A higher CH_4 output from diatremes than from mud diapirs/volcanoes is very likely in view of a higher fluid content of the material of a diatreme in contrast to mud volcanoes or even mud diapirs (Brown, 1990; Kopf, 2002). Lance et al. (1998) demonstrated a higher fraction of fresh water from hydrate dissociation at these diatremes than at mud volcanoes. Methane seeps mainly through the central active area of a diatreme where warm mud is circulating and chemosynthesis-based species are absent (Henry et al., 1996). Håkon Mosby Mud Volcano off Norway is structured concentrally; a central zone, devoid of fauna and too warm for gas hydrate to form, is surrounded by gas hydrate rich mud covered by bacterial mats (Milkov et al., 2004). The Dvurechenskii mud volcano (DMV) situated in the Black Sea is a round, flat-topped elevation with a central part, where several small round spots indicate active gas or fluid expulsion sites. Such flat structures with active central zones point to a more vigorous flow setting , which could account for higher CH_4-outputs in contrast to the mound-shaped mud extrusions off Costa Rica.

The discrepancy between our estimates and the reported values might also be caused by the different approaches of calculating the annual release of methane. Henry et al. (1996) assumed that half of the fluids escaping from the diatremes at the Barbados margin comes from hydrate destabilization and calculated the resulting methane output. Ginsburg et al. (1999) suggest that the methane concentration in the fluid emitted at the Håkon Mosby mud volcano is close to its solubility and computed the methane output from the total amount of discharged water. Furthermore, Kopf and Behrmann (2000) estimated the annual output of methane at Milano and Napoli mud volcanoes at the Mediterranean Ridge based on their mud volume and published CH_4 emissions of other mud extrusions. These authors calculated the total CH_4 output (AOM uptake + benthic output). Thus, the data are not directly comparable with the benthic outputs derived from methane measurements. Taking into account that about 60% (Linke et al., 2005) to 80% (Wallmann et al., submitted for publication) of the CH_4 output becomes oxidized in the sediments, the discrepancy between the reported annual releases and our estimates

Table 3
Comparison of CH_4 output from mud extrusions and other vent sites (benthic CH_4-output – CH_4 emission into the water column, total CH_4-output – including AOM uptake and benthic output)

Area	Benthic CH_4-output in (mol yr^{-1})	Total CH_4-output	Reference
Mound Culebra off Costa Rica	$6 \cdot 10^5$		This study
Mound 12 off Costa Rica	$4 \cdot 10^5$		This study
Mound 11 off Costa Rica	$7 \cdot 10^4$		This study
Atalante, mud diatreme, Barbados		$2 \cdot 10^8$	Henry et al., 1996
Cyclops, mud diatreme, Barbados		$1 \cdot 10^7$	Henry et al., 1996
Håkon Mosby Mud Volcano, Norwegian Sea		$7 \cdot 10^6$	Ginsburg et al., 1999
Milano, mud volcano, Mediterranean Sea		$6–28 \cdot 10^6$	Kopf and Behrmann, 2000
Napoli, mud volcano, Mediterranean Sea		$12–45 \cdot 10^6$	Kopf and Behrmann, 2000
Dvurechenskii, mud volcano, Black Sea	$2 \cdot 10^6$		Wallmann et al., submitted for publication
Northern summit, Hydrate Ridge off Oregon	$5 \cdot 10^6$		Heeschen et al., 2005
Southern summit, Hydrate Ridge off Oregon	$4 \cdot 10^6$		Heeschen et al., 2005
Santa Barbara Basin/Channel	$1 \cdot 10^9$		Clark et al., 2000
	$2 \cdot 10^9$		Hornafius et al., 1999

is still one to three orders of magnitude. Thus, the mud extrusions off Costa Rica appear to be less active than the mud volcanoes and diatremes at accretionary margins and at passive margins.

The benthic output of the water column approach can be directly compared to estimates from the northern and southern Hydrate Ridge (Heeschen et al., 2005) and the Santa Barbara Basin/Channel (SBBC) (Hornafius et al., 1999; Clark et al., 2000), because these authors used similar approaches. Table 3 shows that the CH_4 output is at least one order of magnitude larger at these sites compared to the Costa Rican mud extrusions, which is already indicated by observations of bubble plumes reported from Hydrate Ridge and from SBBC. The area of SBBC presents still the upper end-member of present day release whereas our values present the lowest CH_4 outputs reported so far.

5. Summary and conclusions

Four mud extrusions, which all show signs of active fluid seepage, were investigated offshore Costa Rica. The methane plumes are locally bound to the extrusions; thus, the CH_4 emitted contributes to the carbon budget in the ocean rather than directly reaching the atmosphere. Estimates of the amount of CH_4 discharging in the water column per mud extrusion range from 10^2 to 10^5 mol yr^{-1}. These estimates are considerably lower than methane discharge assessed for other mud extrusions worldwide, even if we take into account that most references include the portion of CH_4 consumed by anaerobic oxidation in sediments.

If all 48 mud extrusions observed along the Pacific coast of Costa Rica are as active as the four representative examples described here (taking $4 \cdot 10^5$ mol yr^{-1} as the average CH_4-output) and if they would emit methane continuously over time, then $20 \cdot 10^6$ mol yr^{-1} ($310 \cdot 10^6$ g yr^{-1}) methane would enter the ocean along this part of the erosive subduction zone. This estimate only accounts for the mud extrusions excluding emissions from other vent sites, e.g. landslides, fault zones, as well as it accounts for only a small segment of the continental margin. Therefore, it is not surprising that it is a small quantity compared to the global methane discharge from the seafloor, which was estimated to be in the order of $20 \cdot 10^{12}$ g yr^{-1} (Kvenvolden et al., 2001). However, the values reported here are the first estimates of methane emissions from mud extrusions at an erosional continental margin. A common phenomenon of erosional or non-accretionary subduction zone is a limited supply of terrigenious material, usually providing a large contribution to the organic carbon pool available for methane generation (von Huene and Scholl, 1991). More than 50% of the continental margins worldwide are non-accretionary (von Huene and Scholl, 1991; Clift and Vannucchi, 2004). If the different style and moderate emission of methane at the mud extrusions off Costa Rica is typical for this kind of setting, then global estimates of the methane emissions from submarine mud extrusions, so far heavily biased towards accretionary and passive continental margins systems (Kopf, 2003; Milkov et al., 2003), might considerably overestimate the role of mud extrusions on erosional/non-accretionary margins for the marine release of methane.

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