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Hypothesis for increased atmospheric methane input from hydrocarbon seeps on exposed continental shelves during glacial low sea level

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Abstract

Natural marine hydrocarbon seeps on continental margins today represent a small source of methane in the global atmosphere budget, which is dominated by anthropogenic sources and contributions from wetlands in the tropics and northern high latitudes. In glacial times with lowered sea level, exposed seeps must have vented directly to the atmosphere and the portion of methane that was formerly dissolved and oxidized in the ocean contributed to the global atmospheric methane budget. We estimate that during lowered sea level 40–100 $\times 10^{12}$ g/yr of methane were added to the atmosphere from gas seeps on the exposed shelves. This source could account for much of the atmospheric methane during glacial episodes because major wetlands were largely absent prior to the Holocene.

Keywords: Sea-level changes; Global warming; Greenhouse gases

1. World methane budget today

The global atmosphere methane budget is of obvious interest because methane is a potent greenhouse gas, 20 times or more effective in irradiative heating than carbon dioxide (Khalil and Rasmussen, 1995). It is estimated at present that between 535 and 598 Tg/yr (Houghton et al., 2001; IPCC, 2001; Prather et al., 1995) (1 Tg (Teragram) equals 10^{12} g) enters the atmosphere of which 375 Tg are from anthropogenic and 160 Tg from natural sources (Prather et al., 1995; Table 1). The more recent estimates given in the report of the Intergovernmental Panel for Climate Change (IPCC) are a total of ~600 Tg/yr with 60% anthropogenic (~360 Tg/yr) leaving ~240 Tg/yr as the natural contribution (IPCC, 2001). That report does not indicate a preferred partitioning of sources so we use the study of Prather et al. (1995) for subdivisions in Table 1 while also identifying ranges of values. The majority of the methane is biogenic; geologic methane, which is ^{14}C-depleted, makes up about 20% of present sources (Cicerone and Oremland, 1988; Quay et al., 1999). Geologic methane is also distinguished from biogenic methane by more positive values of $\delta\ ^{13}$C (Hunt, 1996). The most significant natural methane sources today are tropical and northern high latitude wetlands providing about 70% or more of the natural flux or at least 115 Tg/yr (Crutzen, 1995; Hein et al., 1997; Prather et al., 1995). Other natural methane sources include continental and marine hydrocarbon seepage (Etiope and Klusman, 2002; Hornafius et al., 1999; Hovland et al., 1993), mud volcanoes (Dimitrov, 2002; Hedberg, 1980; Judd et al., 2002) decay of organic matter in marine and lake sediments (Hovland et al., 1993; Judd and Hovland, 1992), fires, termites, leakage from coal beds, enteric fermentation in animals (Khalil and Rasmussen, 1995; Prather et al., 1995) and geothermal systems (Etiope and Klusman, 2002). Reeburgh (2003) has reviewed some of the difficulties and uncertainties in the estimation and partitioning of source strengths.

Natural geologic methane sources previously have been estimated to contribute from about 10 (Khalil and Rasmussen, 1995) to 45 Tg/yr (Kvenvolden and Rogers, 2004) to the global budget. Kvenvolden et al. (2001) estimated a modern contribution of 10–30 Tg/yr to the atmosphere from marine hydrocarbon gas seeps alone. Because almost half of the world's hydrocarbon basins are located offshore (Hornafius et al., 1999), the global flux

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Table 1
Present day annual global methane budget compared to likely glacial methane budget (with range)

Global methane	Holocene	Glacial
	535 Tg/yr[a] (410–660)	80 Tg/yr[b]
Anthropogenic	375[a] (300–450)	None
Natural	160[a] (110–240)	80[b]
Wetlands	115[a] (55–150)	15[b]
Marine HC seeps	20[c] (18–48)	40[b] (40–100)
Other	25[b]	25[b]

[a] IPCC (2001) and Prather et al. (1995).
[b] This paper.
[c] Hornafius et al. (1999).

should be even higher if seepage rates onshore and offshore are similar. Present estimates of the geologic methane contributions from onshore seeps are estimated at more than 11.5–23.3 Tg/yr (Etiope and Klusman, 2002).

2. Natural marine hydrocarbon seeps

Gas and oil seepages associated with hydrocarbon deposits are found onshore and on continental shelves (Wilson et al., 1974). Present day hydrocarbon seepage from reservoirs beneath the world's continental margins discharge oil and natural gas (including methane) into the ocean and atmosphere. Marine seeps have received increasing interest in part because they indicate the presence of hydrocarbon deposits (Hovland et al., 1993; Hunt, 1996) and because they are sources of regional ocean and air pollution (Hornafius et al., 1999). This observation includes oil slicks, dissolved oil and hydrocarbon gas in the ocean, floating and beach tar balls, and methane and reactive organic gases discharged into the atmosphere.

On the northern continental shelf of the Santa Barbara Channel, California the Coal Oil Point marine seep field discharges at least 100,000 m^3 of gas into the atmosphere and 100 bbl of oil into the ocean per day (Hornafius et al., 1999; Quigley et al., 1999; Fig. 1). The hydrocarbons seep from faulted anticlines in the Neogene Monterey and Sisquoc Formations. These seepage rates were determined from a combination of calibrated sonar surveys (Hornafius et al., 1999; Quigley et al., 1999) and in situ gas and oil capture at the sea surface (Clester et al., 1996a,b; Egland, 2000; Washburn et al., 2001). At the sea surface the gas is between 60 and 80% methane (Clark et al., 2003; Leifer et al., 2000). Therefore, the Coal Oil Point seep field emits daily at least 40 metric tons of methane to the atmosphere. $\delta^{13}C$ values are between −40 and −45‰ indicating that the methane is thermogenic in origin (Boles et al., 2001).

Hovland et al. (1993) and Hornafius et al. (1999) used emissions measured at the Coal Oil Point seep field to estimate the total contribution of marine seeps to the global atmospheric methane budget. The estimates, which range between 18 and 48 Tg/yr (Hornafius et al., 1999), were constructed by assuming that the Coal Oil Point field is one of the larger or largest marine sources of methane in the world. Judd et al. (1997) (Table 2) estimate that the methane discharge from the Coal Oil Point seep is 10 times larger than the next largest known seep in the world. It then was assumed, following Wilson et al. (1974), that marine seeps are log-normally distributed in size, as is the case for world

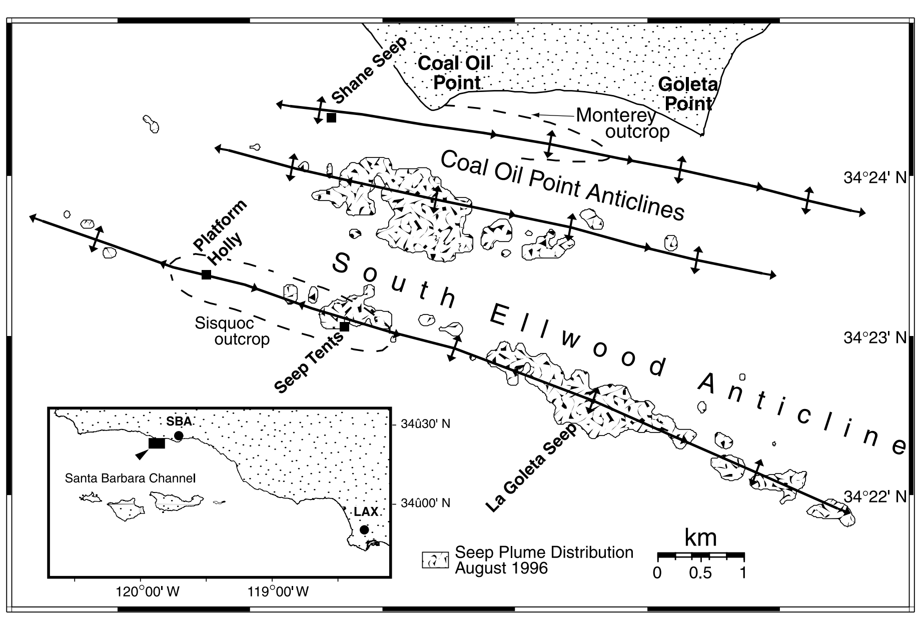

Fig. 1. Location and map of Coal Oil Point marine seep field in southern California on shelf of northern Santa Barbara Channel. Seep bubble plumes shown in shading. These were mapped by sonar methods (Hornafius et al., 1999; Quigley et al., 1999). About 10^5 m^3 of gas is emitted to the atmosphere each day. Major seeps are named including *Shane* and *Seep Tent* (Table 2).

Table 2
Gas compositions (%) at sea bed and sea surface in the Coal Oil Point Seep Field, California

Seep	Depth (m)	CH_4	N_2	O_2
Shane[a]	1	76.7–79.5	12.6–14.4	4.5–6.0
	20	81.9–84.2	1.4–2.5	0.2-0.3
Seep tent[b]	1	62.8	22.8	7.69
	65	87.5	0.79	0.14

Locations: Shane seep, 34°24.370′ N; 119°53.428′ W. Seep tent seep, 34°23.060′ N; 119°53.410′ W.
[a] Clark et al. (2003).
[b] Leifer et al. (2000).

oil fields; these assumptions lead to a global mean flux value by using the Coal Oil Point values as a calibration point. The global mean flux then was multiplied by the area of the continental shelves thought to have a high potential for seepage −1.7 million km^2 (Wilson et al., 1974) to give total global flux estimates.

Oceanographic observations at Coal Oil Point show that up to half the volume of methane vented at the sea floor dissolves in the water column during transport of hydrocarbon gas bubbles 20–70 m to the ocean surface (Clark et al., 2000, Fig. 2a); the remaining half enters the atmosphere. The dissolved methane is advected away from the seeps by currents and dissipates throughout the waters of the Southern California Bight (Cynar and Yayanos, 1992; Ward, 1992). Ultimately this dissolved methane is oxidized by microbes in the ocean or escapes to the atmosphere (Scranton and Brewer, 1978; Valentine et al., 2001). The relative amounts due to these processes are unknown (Valentine et al., 2001), but a significant proportion of the dissolved methane is oxidized to carbon dioxide in the ocean (Hovland et al., 1993; Reeburgh, 2003). Kvenvolden et al. (2001) estimated that between two-fifths and two-thirds of the total methane seepage vented to the seabed dissolves and is oxidized in the ocean and the remainder enters the atmosphere. The degree and rate of oxidation of dissolved methane in near-surface waters (the mixed layer) is not yet fully understood. However, we assume all of the dissolved methane is oxidized so that we can present an end-member case. This is a crucial assumption for our argument below.

3. Low sea level

Because sea level has varied about 100–120 m during the last several glacial stages (e.g. Fairbanks, 1989; Weaver et al., 2003; Yokoyama et al., 2001), most present day marine hydrocarbon seeps on the continental shelves would all have been subaerial as recently as 14 ka. Sea level changes, therefore, probably significantly affected global atmospheric methane budgets (Judd et al., 2002; Luyendyk et al., 2002). About 27 million km^2 of shelf (Gross and Gross, 1996) would have been exposed including regions with hydrocarbon basins such as the Persian Gulf, Sunda shelf, Argentina shelf, Timor Sea and Gulf of Mexico. Ice sheets likely covered high latitude hydrocarbon shelves such as in the North Sea and could have conceivably reduced the volume of seep emissions in these areas (Judd et al., 2002). On the exposed shelves, gas escaped directly to the atmosphere and tar mounds and pits formed at seep vents (Fig. 2b). Furthermore, during low sea level gas seeps on the upper continental slope became shallower, thereby decreasing the portion of methane from these seeps that was oxidized in the water column and increasing the contribution to the atmosphere. Sea level fall also resulted in decreasing hydrostatic pressures over seeps and thereby increased seepage rates. This pressure drop enhancing effect on seepage rates is so pronounced that it can be detected during tidal cycles (Boles et al., 2001; Chanton et al., 1989). Lowered sea level in places also exposed organic rich sediments in estuaries and deltas that rapidly discharged methane as marine regression progressed (e.g. Yim et al., 2002).

As a result of glacial sea level fall methane that was formerly dissolving in the ocean and oxidizing was directly released into the atmosphere adding to the methane that was already escaping to the atmosphere during high sea level. During glacial episodes there was no anthropogenic input of methane and major wetlands ecosystems were very limited or non-existent (Adams et al., 1990; Gajewski et al., 2001; Kennett et al., 2003); therefore, exposed hydrocarbon gas seepages on the continental shelves may have been a major contributor to the global atmosphere methane budget.

4. Discussion

The greenhouse effect of the increased methane input from seeps to the atmosphere would have served as a negative feedback to other factors driving the decrease in global temperatures during glacial episodes (e.g. Paull et al., 1991). Other factors including erosion and desiccation of wetlands, burial of continental and continental shelf seeps by advancing ice sheets, and advance of permafrost in high latitudes could have provided positive feedback (Judd et al., 2002). The increased release of methane from the world's continental shelf could have reduced the extent of global cooling that might otherwise have been greater. Because about half of the methane emitted at the seabed dissolves and oxidizes in the oceans at present, we speculate that during low sea level the amount entering the atmosphere doubled from present estimates of 18–48 Tg/yr (Hornafius et al., 1999, Table 1) to between 40 and 100 Tg/yr. This additional source could in effect replace much of the contribution lost from wetlands that were then very restricted due to an expanded cryosphere, global aridity, and low sea level (Kennett et al., 2003).

Long-term records of methane from ice cores indicate that during glacial times atmospheric mixing ratios were about 50% of pre-industrial interglacial levels (Chappellaz et al., 1990). Assuming similar residence times as today this

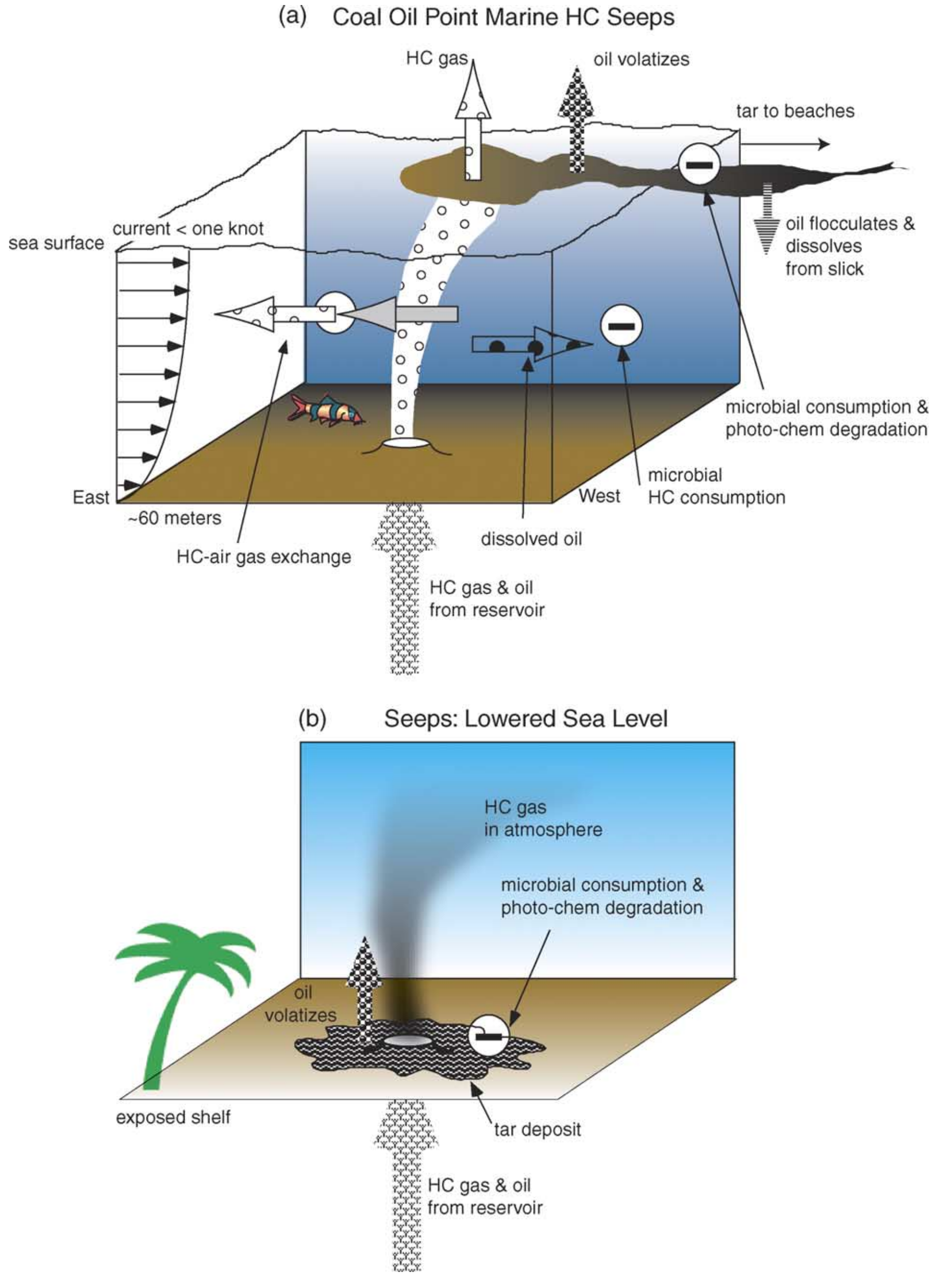

Fig. 2. (a) Model for the marine seeps system at Coal Oil Point California. Open arrows are gas fluxes, shaded arrows are oil fluxes, and negative signs indicate sinks including microbial consumption (oxidation). HC, hydrocarbons. Gas is vented at the sea floor forming a bubble plume. Methane and other higher hydrocarbons diffuse out of the bubbles and into the water effectively dissolving part of the bubble. At the same time dissolved air in the ocean enters the bubble. Methane, dissolved in the ocean, is in turn oxidized by microbial activity. The bubbles that survive upward transport burst at the surface releasing hydrocarbon gas and air into the atmosphere. Oil traveling upward with the plume partly dissolves with the remainder forming a slick at the sea surface. (b) Diagram for a marine seep system that has been exposed due to lowered sea level and changed to a subaerial seep. Methane that dissolved in the ocean when the seep was submarine now enters the atmosphere directly. Vented oil forms tar pits and mounds.

implies a global flux during glacial episodes of half the natural flux today or about 80 Tg/yr. A problem in explaining the methane budget in glacial episodes is that major wetland systems were much reduced then (Kennett et al., 2003). Wetlands today are the main source of natural methane (110–115 Tg/yr; Prather et al., 1995). Continental ice sheets, dryer climate (Adams et al., 1990; Crowley, 1995; Petit-Maire, 1999; Sarnthein and Diester-Haass, 1977), lowered sea level (Fairbanks, 1989) and lowered water tables probably reduced wetland areas in glacial compared to interglacial episodes resulting in less methane contributions from these sources. Other sources are needed to account for much of atmospheric methane during glacial periods. Increased source strength of geological methane was likely. An alternative to increased geologic methane source strength during glacials is a decreased efficiency of methane sinks

(Cicerone and Oremland, 1988; Reeburgh, 2003) prior to Holocene time. At present the most significant methane sink is atmospheric OH (Cicerone and Oremland, 1988; Reeburgh, 2003). Soils also are sinks but much less so (about 2%, Reeburgh, 2003).

Added methane introduced from exposed marine seeps on the continental shelves could resolve the problem of requiring wetlands as a major source of methane during lowered sea level of the Last Glacial Maximum (LGM; ca. 21.5–18.3 ka) and other glacial episodes, in order to account for the concentrations of methane found in glacial ice bubbles.

Significant methane sources during the Last Glacial Maximum and other glacial episodes of low sea level are likely to have been the following: exposed marine gas seeps on the continental shelves and submerged seeps on the upper continental slope, onshore gas seeps and outcrops, methane released from continental shelf sediments (including possibly a transient burst as organic rich sediments were exposed as sea level fell), termites and wild animals, remnant wetlands, lakes, fires, and geothermal systems. Methane released suddenly from the conversion of gas hydrates (Kennett et al., 2003) is another potential source of large magnitude although shelf depths are generally too shallow to maintain a stable reservoir of methane hydrates. The implication of our hypothesis is that in the absence of major wetland sources the methane sources during glacial episodes were largely geologic methane. This methane would be relatively enriched in ^{13}C and depleted in ^{14}C (for the more recent glacial times of the LGM and Younger Dryas—although Cicerone and Oremland (1988) suggested that some ^{14}C depleted methane is now being released from wetlands).

5. Conclusions

The global methane flux during the Last Glacial Maximum and other glacial episodes was possibly around 80 Tg/yr (Table 1). Without major wetlands as a significant methane source (Kennett et al., 2003) other sources are needed to account for that budget. Obvious candidates are either exposed marine seeps or methane hydrate decomposition or both. Exposed marine seeps could have been a major contributor of atmospheric methane accounting for half or even the entire budget, with other sources like those at present being minor components. This hypothesis can be tested by carbon isotope analysis of methane in ice sheets. The discovery of ^{13}C enriched (thermogenic) methane in glacial episode air (e.g. Schaefer et al., 2003) should rule out wetlands as a major source and support our hypothesis that a significant portion of glacial episode methane was from hydrocarbon gas seepage directly into the atmosphere.

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