Natural seabed gas seeps as sources of atmospheric methane

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Abstract Microbial and thermogenic methane migrates towards the seabed where some is utilised during microbially-mediated anaerobic oxidation. Excess methane escapes as gas seeps, which occur in a variety of geological contexts in every sea and ocean, from inter-tidal zones to deep ocean trenches. Some seeps are localised, gentle emanations; others are vigorous covering areas of >1 km^2; the most prolific seeps reported (offshore Georgia) produce ~40 t CH_4 per year. Gas bubbles lose methane to the water as they rise, so deep water seeps are unlikely to contribute to the atmosphere. However, bubbles break the surface above some shallow water seeps. Estimates of the total methane contribution to the atmosphere are poorly constrained, largely because the data set is so small. 20 Tg yr^{-1} is considered a realistic first approximation. This is a significant contribution to the global budget, particularly as methane from seeps is ^{14}C-depleted. A seep measurement programme is urgently required.

Keywords Methane · Gas seeps · Atmosphere

Introduction

Natural oil and gas seeps have been known to exist for millennia, and for decades it has been realised that they may be indicators of petroleum-bearing sedimentary basins (Link 1952; Landes 1973; Wilson and others 1974). Clarke and Cleverly (1991) reported that one oil company (BP) had records of 'about 6,000 petroleum seeps' distributed throughout the world (excluding most of the USA and parts of Western Europe), mostly onshore, almost all of which are of gas, with or without oil. However, it is only relatively recently that gas seeps have been recognised as a potential source of atmospheric methane (literature reviews have shown that methane is the dominant seep gas, except in seeps associated with volcanic or hydrothermal activity), and therefore a contributor to the 'Greenhouse Effect'. Lacroix (1993), and Etiope and Klusman (2002) reviewed estimates of the contributions made to atmospheric methane by geological sources. Several authors have investigated contributions made by natural seabed gas seeps in individual marine areas (Judd and others 1997; Hornafius and others 1999; Dimitrov 2002a; García-Gil 2002) and globally (Hovland and others 1993;Cranston 1994; Judd 2000; Kvenvolden and others 2001); they have suggested global fluxes from the seabed to the atmosphere varying from 0.4 to 48 Tg yr^{-1}. This paper also concentrates on submarine seeps.

The methane escaping from seabed seeps is generally considered to originate from one of two sources: the microbial degradation of organic matter in shallow sediments, or the thermocatalytic breakdown of complex organic molecules as part of the petroleum-generating processes occurring deep within sedimentary basins. Methane of these two origins, microbial (sometimes referred to as 'biogenic') and thermogenic, may be distinguished by their carbon and hydrogen isotope signatures and the relative proportions of methane and the higher hydrocarbon gases (Whiticar 2000). In both cases, the methane is associated with sedimentary environments, ranging in age from geologically Recent, to rocks of Tertiary, Mesozoic, and even Palaeozoic age. It has been shown that there is a considerable range of geological contexts that are suitable for methanogenesis, and that these can be found in every sea and ocean, from coastal environments to the deep ocean trenches (Judd 2003). With the exception of microbial methane that has been (and still is being) generated in recently-deposited sediments, this methane can be assumed to be ^{14}C-depleted, 'fossil' methane.

To understand natural seabed gas seeps it is necessary to recognise each of the processes illustrated in Fig. 1. The complexity of this part of the global carbon cycle makes

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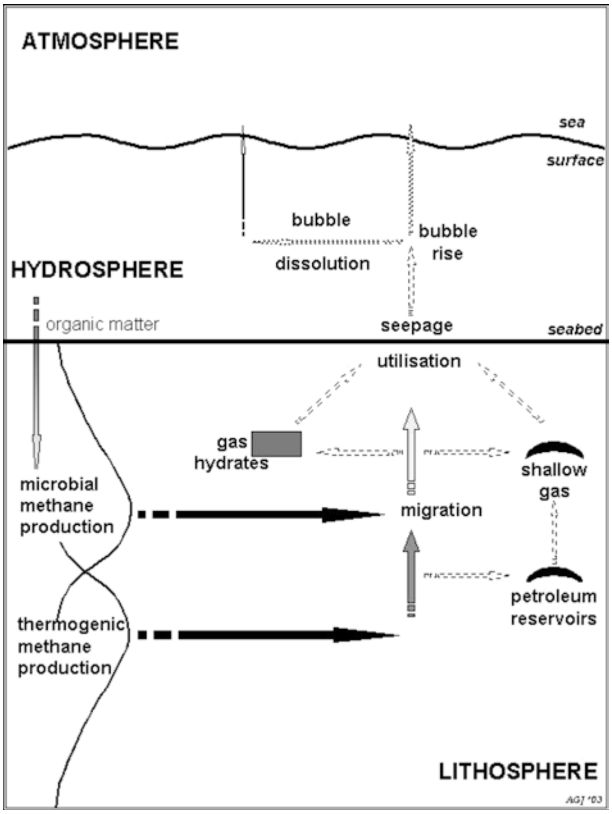

Fig. 1
Principal sources and fates of methane in marine sediments

the task of quantifying the contribution they make to the atmosphere remarkably challenging. Various authors have approached the problem by addressing different individual processes. This paper considers each process before appraising estimates of the flux of methane through the seabed, and the contribution to the atmosphere.

Sedimentary sources of methane

An essential prerequisite for the formation of methane in sediments, whether by microbial or thermogenic processes, is an abundance (at least 0.5%) of organic matter. Microbial methanogenesis generally commences beneath the sulphate-reduction zone, which is normally restricted to within a few metres of the seabed. The responsible organisms, the methanogenic archaea, function in a wide temperature range, the optimum being 35 to 45°C and the maximum being about 55 to 60°C (Rice 1992). Assuming an 'average' geothermal gradient of about 30°C per kilometre, methanogenesis may continue to a depth of about 2 km. The common supposition that microbial methane is formed close to the seabed is not correct. In comparison, thermogenic methane comes from even deeper within the sediments (except in areas with an exceptionally high geothermal gradient), formation continuing to depths of 4 or 5 km, or in some areas, much more. The distribution of methane-producing sediments is therefore constrained by the availability of suitable sediments and the thickness of the sedimentary column. The areal extent of the world's sedimentary basins was estimated by Klemme (1987) to be 99.5×10^6 km^3, and Kvenvolden (2002) suggested conservatively that there is 5,000 Gt (5×10^6 Tg) of carbon locked in fossil fuel reservoirs.

Clayton (1992) estimated that about 10% of the total organic carbon in sediments can be converted to methane in the zone of microbial methanogenesis. Methane production may total about 4.9 m^3 per cubic metre of source sediment for every 1% of total organic carbon. As the porewaters of the sediment would be saturated when only 0.2% of the carbon is converted, the remaining production must be expelled from the source sediments. Similar volumetric calculations are possible for thermogenic sources; however, these are complicated by the need to distinguish between different types of organic matter (kerogens) which may be prone to the generation of oil, condensate, wet gas (i.e. methane plus a significant proportion of the higher hydrocarbon gases) or dry gas (dominantly methane), as well as the amount of organic matter present, and the thermal maturity of the source rocks. Estimates presented by Kubala and others (2003) suggest that the Upper Jurassic Kimmeridge Clay, the main source rock of the central and northern North Sea, has yielded 1,000 billion m^{3}of oil and 583 billion m^3 of gas. However, only 2.7% of this oil and 1% of the gas has been 'discovered' in petroleum reservoirs. Although much of the undiscovered portion lies trapped in structures too small to be of interest to the petroleum industry, a substantial proportion is assumed to have escaped to the surface during the period (<75 million years) since the onset of maturity.

Migration pathways

The sediments and sedimentary rocks in which there is enough organic matter for significant methane generation (whether microbial or thermogenic) are mainly fine grained, and therefore impermeable. Consequently, migration of the buoyant gas or methane-rich porewater tends to be focussed on migration pathways. Kubala and others (2003) mapped the distribution of migration pathways used by petroleum fluids in the central and northern North Sea, however, it is unusual for such detail of a sedimentary basin to be understood. Generally, it is thought that migration pathways include permeable (relatively coarse-grained) carrier beds within sedimentary sequences, faults, etc. As explained by Clarke and Cleverly (1991), seeps tend to occur where these pathways approach the surface (land or seabed). However, migration pathways do not always enable methane and methane-bearing porewater to reach the seabed, as is clear from the existence of gas reservoirs (including those exploited by the petroleum industry), and the shallow gas accumulations that are widespread in most areas of methane generation. Fleischer and others (2001) reviewed the global distribution of shallow gas.

Although the rocks and sediments forming the seals to reservoirs are commonly considered impermeable, over long periods of geological time most prove to be leaky, allowing some gas to escape to higher-level traps, or to the seabed. Some situations lend themselves to migration, for example the up-doming caused by salt diapirism tends to attract buoyant fluids towards the diapirs, and extensional faulting above the diapirs leads these fluids to the seabed. Consequently, there is a strong association between salt diapirs and seeps, for example in the North Sea and in the Gulf of Mexico. Mud diapirs and mud volcanoes provide another major pathway, however, these are discussed by Etiope and Milkov (2004) so they will not be considered in this paper.

In deep water environments upward migration may be inhibited where temperature and pressure conditions are favourable for the formation of gas hydrates. These ice-like compounds, which are stable only under high pressure—low temperature conditions (Kvenvolden 1998), are thought to be present over vast areas of the world's oceans. Soloviev (2002) estimated their extent to be 3.57×10^7 km^2, about 10% of the world ocean. These accumulations sequester enormous volumes of methane. There have been numerous attempts to quantify the amount of methane stored in gas hydrates. Kvenvolden (2002) noted that estimates vary between 500 and 24,000 Gt (5×10^5 to 2.4×10^7 Tg), and suggested a 'consensus' figure of 10,000 Gt (1.0×10^7 Tg). Seabed observations show that active seeps are often present even within the gas hydrate stability zone, for example on Hydrate Ridge, Cascadia Margin (offshore Oregon, USA—Suess and others 1999), in the Gulf of Mexico (Sassen and others 2001), so some methane is able to escape even here.

Methane utilisation at the seabed

Methane generated in, or migrating to the seabed sediments may be utilised by microbes as a source of chemosynthetic energy. The process involves consortia of methanogenic archaea and sulphate-reducing bacteria; the by-products are hydrogen sulphide and bicarbonate (Boetius and others 2000). The bicarbonate results in the precipitation of carbonate cement that binds the seabed sediments to form a concrete-like rock, methane-derived authigenic carbonate (MDAC). The hydrogen sulphide is utilised by sulphide oxidising bacteria such as *Beggiatoa*, a ubiquitous indicator of seeps, and various macrofaunal species that host microbial chemosynthesisers. Therefore, the presence of methane seeps supports localised benthic 'cold seep' communities. These are particularly significant in the deep waters beyond the continental shelves (Sibuet and Olu 1998), but the presence of MDAC, *Beggiatoa*, and specialist macrofauna with microbial chemosynthesising symbionts demonstrate that methane utilisation also occurs in waters less than 300 m deep (Hovland and Judd 1988; Bauer and others 1990). Aharon (1994) and Sibuet and Olu (1998) discussed the global distribution of cold seep communities.

Where the rate of methane production and/or migration exceeds the rate of utilisation, seepage occurs. It has been suggested that the efficiency of methane utilisation at individual seep sites increases over time as the migration pathway is progressively blocked firstly by bacterial mats, and eventually by the formation of MDAC (Hovland 2002).

The distribution of seabed gas seeps

Gas bubbles reflect acoustic energy, so they are 'visible' on seismic systems such as echo sounders, high frequency profilers, and side scan sonars. However, the gas in the swim bladders of fish presents a similar acoustic target, so distinguishing between gas and fish is not easy, and often subjective. It is easier to identify features associated with seeps, including seabed features such as pockmarks and mud volcanoes (Judd and Hovland 1992), than the seeps themselves. Several attempts have been made to map the distribution of seeps and associated features, notably: seeps and pockmarks (Hovland and Judd 1988), shallow gas (Fleischer and others 2001), cold seep communities (Aharon 1994; Sibuet and Olu 1998), mud volcanoes (Milkov 2000; Dimitrov 2002b), and gas hydrates (Kvenvolden 1998). However, these maps, the GIS database of gas seeps and their indicators described by Judd and others (2002a), and (no doubt) the distribution map presented here as Fig. 2, have rapidly been made out of date as the pace of new discoveries increases. To appreciate the true distribution of seabed gas seeps it is necessary to consider the distribution of the environments in which they occur as well as the known (and published) distribution.

Judd (2003) described the range of geological (plate tectonics) and oceanographic contexts suitable for methane formation. Table 1 shows that methane is formed not only in deep sedimentary basins, but also in accretionary prisms and various shallow coastal environments. It is therefore not surprising that methane is a common fluid in marine sediments, nor that seabed gas seeps are widespread, and found in every sea and ocean.

Gas flux rates at seabed seeps

Despite the large number of recorded gas seeps, the number of flux rate measurements is very small, mainly because of the technical difficulties (and costs) involved. Seep flux rates are generally obtained by deploying measuring equipment over an individual vent or bubble stream for a limited period (minutes or hours), and then assuming a) that the measured vent(s) is/are representative of the seep area, and b) that the time period over which measurements were made was representative, and that there are no significant temporal flux variations. The second of these assumptions is particularly suspect as temporal variations are known to occur (Boles and others

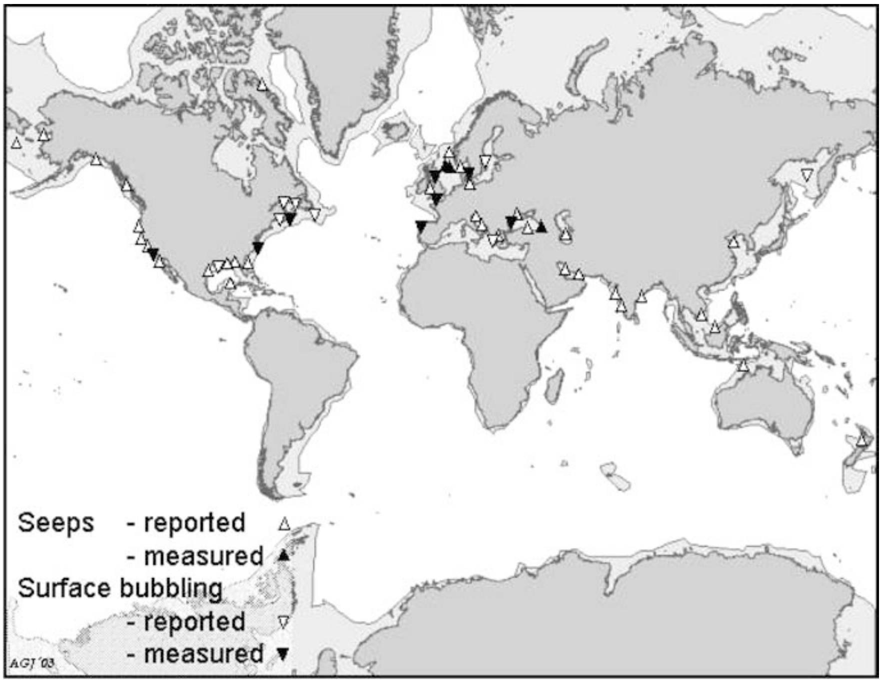

Fig. 2
The distribution of seabed seeps on the continental shelf. Each of the symbols represents an area of reported seepage. There is no implication about the size of the area or the number of seeps. Some may represent small numbers of gentle seeps whilst others represent '*literally thousands*' of vigorous seeps over a wide area. Surface bubbling indicates that gas bubbles have been observed breaking the sea surface. Infilled symbols indicate that flux measurements have been made at the seabed

Table 1
Geological and oceanographic environments in which microbial and thermogenic methane are formed (based on Judd, accepted)

Environment			Examples
Geological (plate tectonics) environments	Convergent plate boundaries		Barbados accretionary wedge
			Cascadia margin (Oregon Subduction zone)
			Japan Subduction zone
			Mediterranean Ridge
	Transform plate boundaries		Gulf of Cadiz, offshore Iberia
			Offshore Monterey, California
	Intra-plate:	Sedimentary basins	Gulf of Mexico
			North Sea
			Southern Caspian Basin
		Deep-sea fans	Congo
			Mississippi
			Niger
			Nile
Oceanographic environments	Coastal:	Deltas	Fraser
			Mississippi
			Yangtze
		Drowned coast lines	Outer Thames Estuary, North Sea
			Norton Sound, Alaska
			West coast of India
		Estuaries and bays	Cape Lookout Bight, North Carolina, USA
			Cardiff Bay, Wales
			Firth of Forth, Scotland
			Penobscott Bay, Maine, USA
		Rias	Chesapeake Bay, Maryland/ Virginia, USA
			Rias Bajas, NW Spain
			Tamar and Plym Rivers, England
	Continental shelves: sedimentary basins		North Sea
			Gulf of Mexico
	Continental slopes and rises: deep-sea fans		Amazon
			Mississippi
			Niger
	Outcropping sedimentary rocks		Monterey Bay Canyon, California, USA
	Deep oceans: contourites		Argentine Basin, Southern Atlantic
			Blake Ridge, offshore Nth & Sth Carolina/ Georgia, USA
	Ocean trenches:		Aleutian Trench
			Japan Trench
			Peru Trench

2001; Judd and others 2002b). The data set from the Seep Tents offshore California, analysed by Boles and others (2001), represents the longest continuous measurements. The Seep Tents were installed in 1982 to gather naturally seeping oil and gas. Production rates have been monitored ever since, and during one 9-month period in 1999/2000, hourly measurements were made. Also, because the tents cover a large area (1,860 m^2), the measurements represent the total flux from numerous seeps with a range of flux rates.

Other data available from publications, summarised in Table 2, are not as representative as the Seep Tent data. Of these, some are presented as flux rates from individual seep vents, and others are given as the estimated total flux over a seepage area. Either way, they show that the emissions from individual seep localities vary from gentle emanations from a small number of individual vents, to vigorous bubbling over a considerable area, such as at Coal Oil Point, California, and offshore Georgia. It is anticipated that deep-water seeps will make no direct contribution to the atmosphere, as explained in the next section; consequently Table 2 includes only data from continental shelves. However, flux rate measurements of methane-charged water have been made in deeper water (e.g. Linke and others 1994; Suess and others 1998; Tryon and others 2001).

Together, the data presented in Table 2 indicate a total methane flux of approximately 77,500 t.yr^{-1}(0.0775 Tg yr^{-1}) at the seabed over an area of approximately 2,500 km^2. Clearly the sites represented by these data are not representative of the continental shelves as a whole. However, by assuming a lognormal distribution (which

Table 2
Published gas seeps flux rate measurements and estimates—seabed (continental shelves only)

Location	Methane flux rate[a] per seep vent g yr^{-1}	Methane flux rate[a] by area g m^{-2}yr^{-1}	Number of individual seeps	Size of seep area m^2	Estimated seabed Flux[b] t yr^{-1}	Water depth m	Source(s)
Anvil Point, Dorset UK	–	–	–	–	68	–	Hinchcliffe 1978
UK block 15/25 North Sea	830–3550	300	–	22,825[c]	6.8	160–175	Flux from Clayton and Dando 1996; area from new data.
Kattegat coast Denmark	900–130,000	350	–	1700	0.595	<3	Dando and others 1994
Kattegat	–	–	[~100 sites]	25×10^9	63.7	–	Dando and others 1994
Tommeliten Norwegian North Sea	–	6400	120	6,500	41.6	65–75	recalculated fromHovland and Judd 1988
Torry Bay, Firth of Forth Scotland	–	520–750	70–100	2400	1.25–1.8	Inter-tidal	Judd and others 2002b
Golden Sands Bulgarian Black Sea	42800–3.2×10^6(mean 641,180)[>*150 measurements over 16 year period*]	–	1200	300,000	770	7–20	Dimitrov 2002a
Golden Sands NE Bulgarian Black Sea		–	200	12,500	128	–	Dimitrov 2002a
Zelenka Bulgarian Black Sea		–	800	330,000	513	5–15	Dimitrov 2002a
Seep Tents, Coal Oil Point, California, USA	–	1.3–3.9×10^6	–	1,860	2,976	67	Boles and others 2001
Cape Lookout Bight North Carolina, USA	–	–	–	1 km^2	690	<10	Martens and Klump 1980
Black Sea 5 sites [disseminated flow]	–	0.014–0.11	0	–	–	36–65	Trotsyuk and Avilov 1988
Offshore Georgia Black Sea	428,000 –1,700,000	405,260	–	100,000	40,526	25–150	Tkeshelashvili and others 1997
Santa Barbara Channel California, USA[d]	–	1,600	>500	3 km^2	34,670–49,530	20–100	Hornafius and others 1999

[a] Flux rates are quoted in various units. For the purpose of comparison, all units have been converted to g yr^{-1} (flux per vent) or g m^{-2} yr (flux per area) assuming a methane density of 0.6785 kg m^3, and STP (Standard Temperature and Pressure)

[b] Calculated as either [flux per area x area] or [flux per seep×number of seeps]

[c] Total area of the bases of 5 individual pockmarks

[d] Mid-water, ~18–28 m water depth

seems to apply to most geological populations), classifying the shelf according to the probability of there being seeps, and extrapolating the data accordingly, a rough global approximation may be made. This approach was taken by Hovland and others (1993) who suggested a seabed flux of 8 to 65 Tg yr^{-1}.

Losses to the water column

Methane concentration profiles recorded above deep-water seeps associated with gas hydrates show that considerable volumes of methane might be released to the water. For example, Suess and others (1999) identified a methane-rich plume hundreds of metres high and several kilometres wide above the Hydrate Ridge area of the Cascadia Margin, offshore Oregon. However, it seems that this methane dispersed and was oxidised within the water column, a conclusion subsequently supported by Grant and Whiticar (2002). In contrast, observations show that bubbles break the sea surface above shallow water seeps such as those in the Santa Barbara Channel, California (Leifer and Clark 2002) and near the Bulgarian coast (Dimitrov 2002a). Locations at which observations of bubbles breaking the sea surface have been reported are shown in Fig. 2.

The proportion of the methane escaping from seabed seeps that passes through the water column to enter the atmosphere is primarily dependent upon the initial bubbles size, the water depth, and the temperature, salinity and methane concentration of the water (Leifer and Patro 2002). Other significant factors include the nature of the surface of the bubbles ('dirty' bubbles with a coating of oil, for example, lose methane more slowly and rise more slowly than 'clean' bubbles) and the presence or absence of upwelling flows of water (water entrained by a plume of rising gas bubbles—if the bubbles are rising through water that is also rising, then the speed of ascent is increased and the rate of methane loss is decreased). Leifer and Patro (2002) and MacDonald and others (2002) provided explanations of these matters. It seems that some methane from shallow water seeps escapes to the atmosphere, whilst all the methane from deep-water seeps is lost to the hydrosphere. This is significant as it implies that only seeps in coastal and continental shelf water depths are relevant to estimates of atmospheric contributions. Essentially, the shallower the water, the greater the atmospheric contribution.

Three possible exceptions are suggested. First, bubbles released by seeps within the gas hydrate stability zone (GHSZ) will become 'armoured' by a coating of gas hydrate which inhibits the loss of methane by solution (Brewer and others 1998; Heeschen and others 2003). This protects the bubbles until they reach the limit of the GHSZ, so methane bubbles have a greater chance of escaping to the atmosphere. This may explain observations of gas bubbling at the sea surface above seeps at water depths of 700 m in the Sea of Okhotsk (Cranston and others 1994). Secondly, bubbles may be coated in oil, which prevents gas solution. For example, Sassen and others (2001) reported oil slicks in the Gulf of Mexico formed when oil-coated bubbles breached the sea surface.

A third circumstance in which more significant proportions of methane may reach the atmosphere is when natural gas 'blow-outs' occur. Some think that such events do not happen as evidence for them is somewhat sparse, and is mainly limited to chance observations of sea surface 'boiling'. However, it is probable that, unlike most pockmarks, certain large pockmarks in the Barents Sea (Solheim and Elverhøi 1985; Long and others 1998) and the North Sea (Judd and others 1994) owe their formation to catastrophic gas escapes analogous to blow-outs during offshore drilling. These events are thought to have occurred as a result of gas hydrate or permafrost melting as seawater warming occurred during the transition from the last glacial period to 'modern' conditions.

In the absence of positive evidence of natural gas blow-outs, it must be assumed that deep-water seeps make no significant direct contribution to the atmosphere.

Contributions to the atmosphere

Methane from seeps may enter the atmosphere either directly, by the escape of bubbles, or indirectly, by diffusion from methane-saturated waters. Dissolving bubbles and methane diffusing through the seabed ('microseeps') both contribute to the methane content of the hydrosphere. There is a considerable literature about fluxes of methane to the atmosphere from ocean waters, however, in most cases it seems that no attempt has been made to investigate the possibility of a link between geological/seabed sources and seawater concentrations. Lambert and Schmidt (1993), who reviewed published measurements of methane concentrations in near-surface ocean waters, remarked that the origin of this methane was '*an open question*'. Their analysis suggested the existence of strong but localised sources of methane, associated with seabed seeps, in coastal waters. Examples of this have been reported: elevated methane concentrations in the waters off Southern California and North West Borneo can be related to seeps (Cyanar and Yayanos 1992; Rehder and Suess 2001, respectively). It seems that this is a potentially fruitful area for future investigation; however, contributions from methane-saturated waters are not considered here.

Estimates of the direct contribution by seeps to the atmosphere from individual areas (the UK continental shelf, offshore Bulgaria and California, and Ría de Vigo, NW Spain; see Table 3) are based on the distribution of geophysical evidence of seeps, limited seabed flux measurements, and suppositions about the survivability of gas bubbles rising through the water. Estimates of emissions from seabed seeps regionally and globally (also shown in Table 3) are also based on extrapolations from these small data sets. An exception is Kvenvolden and others (2001) who adopted a dual approach, one based on the seep flux, the other based on the amount of geological methane

Table 3
Published gas seeps flux rate estimates—sea surface

Region	Area km^2	Flux Tg yr^{-1}	Source(s)
Regional Estimates			
Toney River, Nova Scotia, Canada	–	1.33×10^{-5}	Cranston 1994
Rías Baixas NW Spain	530	0.0005–0.019	Garcià-Gil 2002
Coal Oil Point, California	3	0.035–0.05	Hornafius and others 1999
Bulgarian Black Sea	12,100	0.033–0.151	Dimitrov 2002a
Black Sea continental shelf	131,700	0.356–1.614	Dimitrov 2002a
UK continental shelf	602,000	0.12–3.5	Judd and others 1997
Global estimates			
Continental shelves		1.9	Trotsyuk and Avilov 1988
Oceans and sediments		1.3 to 13	Cranston 1994
Global: natural seabed gas seeps		18–48	Hornafius and others 1999
Global: natural seabed gas seeps		0.4 to 12.2	Judd 2000
Global: natural seabed gas seeps		10–30	Kvenvolden and others 2001

produced and the proportion available to seeps. It is reassuring to see that these two approaches produced comparable results, 30 and 10 Tg yr^{-1} respectively, leading Kvenvolden and others (2001) to accept 20 Tg yr^{-1} as a realistic estimate. This also lies close to the median of the estimates of the other authors quoted in Table 3. Nevertheless, it is fair to comment that the degree of extrapolation in all these estimates does not inspire confidence. Also, it is noted that contributions from seeps on land have not been considered here.

Were a new estimation to be derived for the purposes of this paper, it too would have to rely on this same sparse data set. Rather than do that, it is considered more appropriate to accept 20 Tg yr^{-1} as a first approximation of the contribution of natural seabed gas seeps to atmospheric methane, and to remark that a more extensive measurement programme is required before a reliable estimation can be made. The motivation for a new measurement programme comes from a comparison of this estimate with those of other sources of atmospheric methane identified in the Inter-governmental Panel for Climate Change (IPCC) budgets (Ehhalt and others 2001). Many publications, including those of the IPCC, erroneously attribute all fossil methane entering the atmosphere to the activities of the fossil fuels industries. This is clearly not the case as the majority of methane from seeps is ^{14}C-depleted 'fossil' methane. So it is concluded that the contributions from seeps, and other geological sources such as mud volcanoes (see Etiope and Milkov 2004), should be more carefully constrained.

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