

Effects of climate change on methane emissions from seafloor sediments in the Arctic Ocean: A review

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Abstract

Large quantities of methane are stored in hydrates and permafrost within shallow marine sediments in the Arctic Ocean. These reservoirs are highly sensitive to climate warming, but the fate of methane released from sediments is uncertain. Here, we review the principal physical and biogeochemical processes that regulate methane fluxes across the seabed, the fate of this methane in the water column, and potential for its release to the atmosphere. We find that, at present, fluxes of dissolved methane are significantly moderated by anaerobic and aerobic oxidation of methane. If methane fluxes increase then a greater proportion of methane will be transported by advection or in the gas phase, which reduces the efficiency of the methanotrophic sink. Higher freshwater discharge to Arctic shelf seas may increase stratification and inhibit transfer of methane gas to surface waters, although there is some evidence that increased stratification may lead to warming of sub-pycnocline waters, increasing the potential for hydrate dissociation. Loss of sea-ice is likely to increase wind speeds and sea-air exchange of methane will consequently increase. Studies of the distribution and cycling of methane beneath and within sea ice are limited, but it seems likely that the sea-air methane flux is higher during melting in seasonally ice-covered regions. Our review reveals that increased observations around especially the anaerobic and aerobic oxidation of methane, bubble transport, and the effects of ice cover, are required to fully understand the linkages and feedback pathways between climate warming and release of methane from marine sediments.

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Special Issue: Methane Emissions from Oceans, Wetlands, and Freshwater Habitats: New Perspectives and Feedbacks on Climate. Edited by: Kimberly Wickland and Leila Hamdan.

Introduction

Arctic and sub-Arctic marine sediments are thought to host vast reservoirs of methane stored in methane hydrate (~ 100–9000 Gt C: Kvenvolden 1988; Biastoch et al. 2011; Hunter et al. 2013; Kretschmer et al. 2015) and trapped beneath submerged permafrost either as hydrate, or as free gas (~ 2–1400 Gt C: McGuire et al. 2009; Shakhova et al. 2010) (Table 1). These carbon pools can be highly sensitive to increases in temperature, and they provide the basis for release of methane to the atmosphere where this greenhouse gas contributes to further global warming. As high latitudes of the northern hemisphere are expected to experience a larger temperature increase than other regions due to climate change (IPCC 2013), there is a need to better understand the linkages between environmental variables and the processes that regulate methane emissions from Arctic marine sediments into the atmosphere (e.g., Biastoch et al. 2011; Ferré et al. 2012; Steinle et al. 2015).

Environmental change in the Arctic Ocean

The Arctic Ocean is an intercontinental sea surrounded by the land masses of Alaska/U.S.A., Canada, Greenland, Norway, Iceland, and Siberia/Russia (Fig. 1). It represents about 1% of the global ocean volume but receives about 10% of global runoff (Lammers et al. 2001). It has a central

Table 1. Estimates of the methane inventory of Arctic marine sediments. The methane inventory for the atmosphere, and the inventory of organic carbon in northern high latitude terrestrial permafrost (that has the potential for release as CH₄ and CO₂), are also shown for comparison.

Reservoir	Inventory (Gt CH ₄)	Reference
<i>Marine sediments</i>		
Methane hydrate	30–9000*	Kvenvolden (1988), McGuire et al. (2009), Biastoch et al. (2011), Hunter et al. (2013), Kretschmer et al. (2015)
Submerged permafrost	2–1400 [†]	McGuire et al. (2009), Shakhova et al. (2010)
<i>Terrestrial</i>		
Permafrost carbon	1330–1580 [‡]	Schuur et al. (2015)
<i>Atmospheric burden</i>		
2011	4.95 ± 0.01	Ciais et al. (2013)

*Estimates of the quantity of methane stored in gas hydrate are strongly dependent on hydrate saturation. The consensus converges on values of a few hundred Gt.

[†]These values are highly uncertain. McGuire et al. (2009) give a figure of 2–65 Gt for the entire Arctic; Shakhova et al. (2010) report that ~ 1400 Gt alone is stored on the East Siberian Arctic shelf; ~ 540 Gt as hydrate and ~ 360 Gt as free gas trapped beneath the permafrost.

[‡]Gt C.

deep basin and is characterized by extensive shallow shelf areas including the Barents Sea, Kara Sea, Laptev Sea, East Siberian Sea, Chukchi Sea, and Beaufort Sea. Monitoring of Arctic Ocean waters has revealed that deeper waters of Atlantic origin have expanded in volume since 1993 (Carmack et al. 1995), although circulation models indicate that this phenomenon could have started as early as 1979 (Maslowski et al. 2000). These deep Atlantic waters are carried into the Arctic Ocean via the West Spitsbergen Current, continuing into the European and Makarov basins where they contribute to a temperature increase which may be up to 1°C above the pre-1999 mean (Walczowski and Piechura 2006), and shoaling of Atlantic water by 75–90 m (Polyakov et al. 2010). Over the same period, the temperature of Pacific waters flowing into the Arctic Ocean through the Bering Strait has increased by ~ 0.5°C (Woodgate et al. 2006), although bottom water temperatures along the Russian slope remain almost unchanged (Biastoch et al. 2011).

Parts of the Arctic Ocean off Canada and Greenland are ice-covered throughout the year, but the rest is ice free in the summer months. Sea-ice coverage has decreased in recent decades, especially in the summer, becoming both younger and thinner (Maslanik et al. 2007). Sea-ice extent reached a record low (since satellite measurements began) in September 2012 (<http://nsidc.org/>; Fig. 2), such that ~ 45% of the Eurasian Basin north of 78 °N was ice-free.

Both a simple extrapolation and numerical modelling suggest that the Arctic may be seasonally ice-free by 2050, or possibly earlier (Stroeve et al. 2008; Wang and Overland 2009), although this is far from certain (Serreze 2011). A seasonally ice-free ocean would influence Arctic ecology and climate, enhancing available solar irradiance, increasing mixing, and radically reducing the albedo of the Arctic Ocean during the boreal summer. Sea-ice decline seems to be related at least in part to increasing greenhouse gas concentrations as this is the only known climate forcing that has strengthened in recent decades (IPCC 2013), although black soot may also play a role (Jacobsen 2004). Further decline in sea-ice coverage can be reasonably expected as long as Arctic warming continues (Stroeve et al. 2011).

Methane in Arctic marine sediments

Methane is produced in marine sediments either by cracking of complex organic molecules at high temperatures and great depths, or by microbial transformation of organic or inorganic carbon at shallower depths (Reeburgh 2007; Rother 2010). At relatively low temperature (< 10°C) and moderate pressure (> 3–5 MPa, which corresponds to combined water and sediment depths of 300–500 m) conditions found on the Arctic continental slope and beyond, methane and water combine to form methane hydrate, an ice-like substance consisting of a methane molecule encaged by water molecules forming a solid (Sloan and Koh 2007; Fig. 3). Methane occurs as free gas below the depth of the

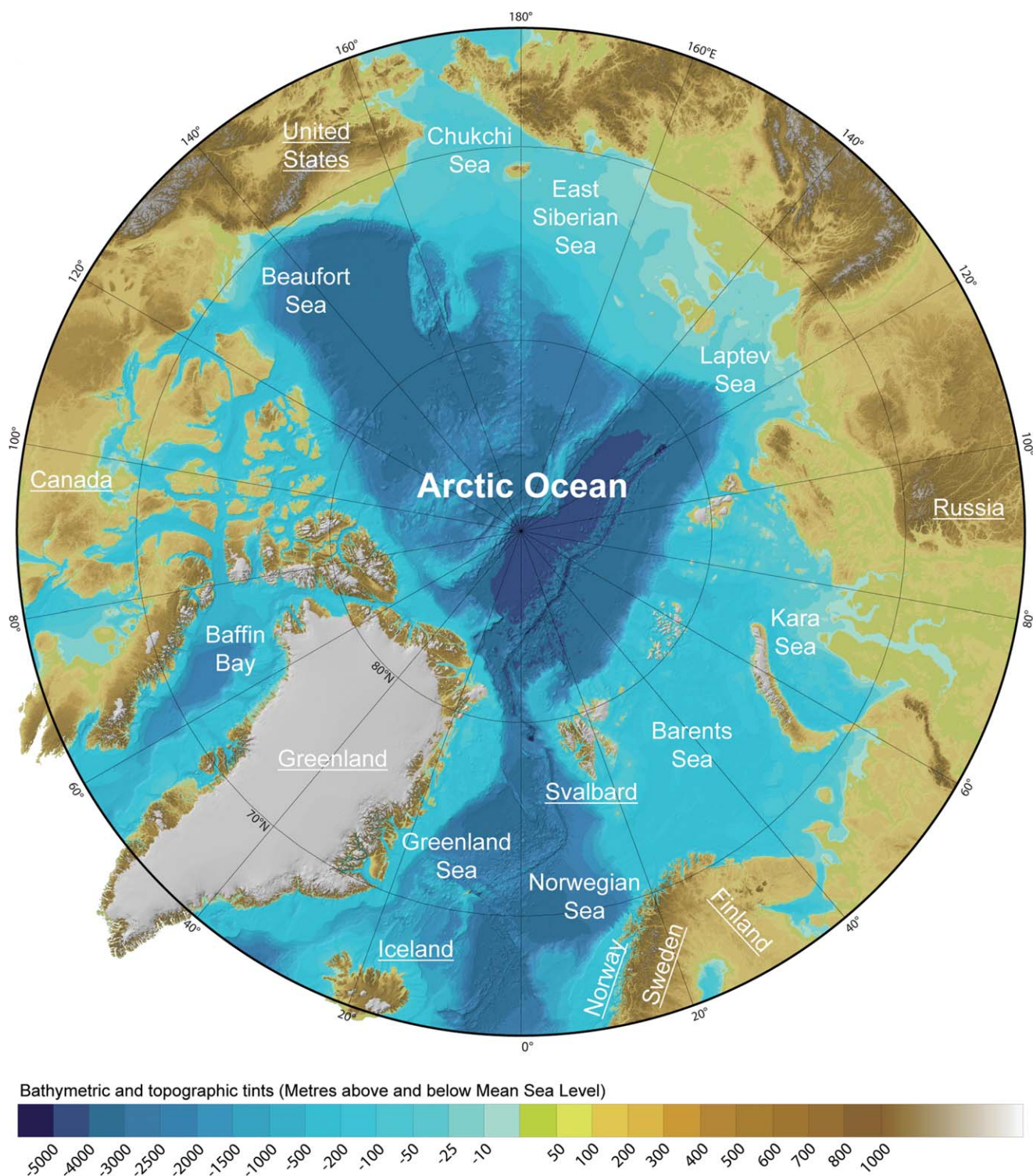


Fig. 1. Bathymetric map of the Arctic Ocean, showing shallow coastal seas. Adapted from Jakobsson et al. (2012).

hydrate stability zone, and may be transferred directly into the overlying water column through faults and fractures in the sediments (e.g., Berndt 2005; Sarkar et al. 2012; Smith et al. 2014).

In 2008, more than 250 plumes of methane bubbles were discovered issuing from the seafloor offshore western Svalbard, close to the depth at which the hydrate stability zone outcrops at the seafloor (~ 400 m; Westbrook et al. 2009).

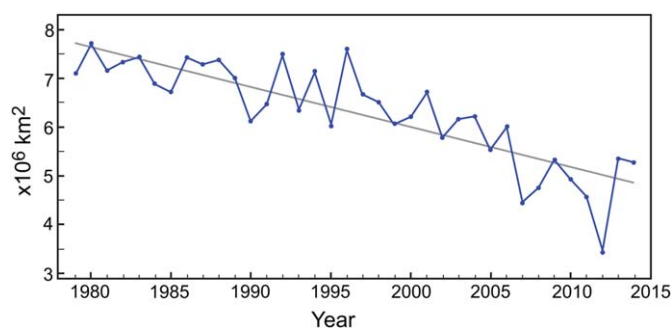


Fig. 2. September sea-ice minimum in the Arctic 1979–2014. Data courtesy of the Alfred Wegener Institut and Universität Bremen (<http://meerisportal.de>).

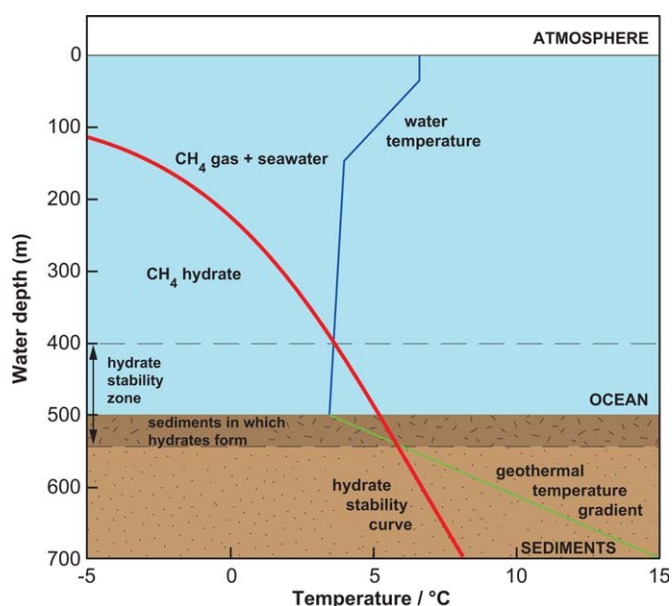


Fig. 3. Schematic diagram of the occurrence and distribution of hydrate in the Arctic Ocean. The intersection of the water column and geothermal gradient with the hydrate stability curve controls the depth interval in which hydrate can form if pore water is saturated with methane.

The methane emissions have been attributed, at least in part, to hydrate dissociation as a result of seasonal fluctuations in bottom water temperatures (Berndt et al. 2014), and warming of bottom waters in this area over the last ~ 30 yr (Westbrook et al. 2009; Thatcher et al. 2013). In this connection, observations of methane-rich gas bubbles venting from the seafloor focused on pingo-like features on the Beaufort Sea shelf have also been attributed to gas hydrate decomposition driven by inundation of relatively warm water (Paull et al. 2007). Models of hydrate behaviour based on predictions of ocean warming offshore western Svalbard indicate that the seafloor methane flux from the continental slope and shelf region is likely to increase in future years (Marín-Moreno et al. 2013; Kretschmer et al. 2015). However, at the

current time, direct methane emissions from the ocean offshore western Svalbard account for $< 10\%$ of the atmospheric input to this region (Fisher et al. 2011; see also Gentz et al. 2014).

Extensive shallow-water areas of the Arctic continental shelf are underlain by permafrost (Rachold et al. 2007), which formed under terrestrial conditions and was subsequently submerged by post-glacial rise in sea level. Methane can be trapped within this permafrost, as well as below its base. In the Beaufort Sea, seismic data indicate that submerged permafrost is confined to relatively shallow water depths (< 20 m), within 30 km of the shoreline (Brothers et al. 2012). While methane concentrations in seafloor sediments in the Beaufort Sea are relatively high (Coffin et al. 2013; Treude et al. 2014), there is no evidence for bubble seepage from the seafloor, and there are no systematic changes in methane concentrations close to the seafloor between nearshore sediments underlain by permafrost, and those lacking such permafrost (Pohlman et al. 2012). By contrast, partial thawing of permafrost on the shallow (average depth ~ 45 m) East Siberian Arctic Shelf is considered to be responsible for very high dissolved methane concentrations in the water column (> 500 nM) and elevated methane concentrations in the atmosphere, by 5–10% up to 1800 m in height above the sea surface (Shakhova et al. 2014). Other authors have shown that, in the Laptev Sea, methane released from thawing permafrost is efficiently oxidised in the overlying unfrozen sediments, such that methane concentrations in the water column were close to normal background levels (Overduin et al. 2015).

Scope of this review

The work outlined above provides evidence for ongoing and possibly increasing release of methane stored within seafloor sediments in the Arctic Ocean, which may be linked to changing environmental conditions. The processes that regulate methane fluxes across the seabed, the fate of this methane in the water column, and its flux to the atmosphere, are however poorly understood. Moreover, these processes are not currently considered at all in global climate and Earth system models. With this in mind, this review sets out to identify the principal physical and biogeochemical processes that regulate methane distributions in Arctic seafloor sediments, its fate if transferred into the water column, and the controls on subsequent release of methane to the atmosphere. The possible effects of future climate warming on all of these processes are also discussed.

Processes affecting methane distributions in Arctic marine sediments

Transport processes through the sediment

In the porous sediment matrix, methane dissolved in pore waters is transported by diffusion and advection, and as gas by buoyancy in form of individual bubbles or a continuous

gas phase. Diffusive transport is driven by the methane concentration gradient in the aqueous phase according to Fick's first law of diffusion (Fick 1855), following a tortuous path around the sediment grains, which is usually expressed as a function of sediment porosity (e.g., Bear 1972; Boudreau 1996; Tomonaga et al. 2015). Pore water advection and gas migration are driven by pressure gradients and are typically described by Darcy's equation (Darcy 1856; Bear 1972). Hence, they are affected by sediment permeability and fluid/gas viscosity.

In passive marine margin settings (i.e., margins that are unaffected by tectonic processes), diffusion and burial of pore water (due to sediment accumulation) are the governing transport mechanisms. In these settings, methane is usually completely consumed within the sediment by anaerobic oxidation of methane (AOM) (Reeburgh 2007; Knittel and Boetius 2009; see below).

In active marine margin environments, external (tectonic) pressure forces, together with high sedimentation rates and compaction, induce upward fluid flow that can exceed the (downward) burial velocity resulting in fluid expulsion from the sediment into the overlying water column at velocities of several millimetres to 1–2 m per year. However, high fluid velocities are locally confined to focused fluid flow pathways which are expressed as pockmarks, mud volcanoes, or carbonate pavements. In the Arctic Ocean, methane produced at depth in marine sediments has been observed venting from pockmarks offshore Western Svalbard (Fig. 4), as well as on the Vestnesa Ridge (e.g., Smith et al. 2014), from the Haakon Mosby mud volcano in the Barents Sea (e.g., Felden et al. 2010; Pape et al. 2011), and in Disko Bay, east Greenland (Nielsen et al. 2014).

If sedimentary methane fluxes are high, for example at the landward limit of the gas hydrate stability zone (Fig. 3), or at sub-seafloor faults that intersect deeper gas-rich layers, methane solubility in the local pore waters may be exceeded. In these circumstances, free gas is formed which migrates through the sediments and is released into the overlying water column as methane bubbles (Fig. 4). In contrast to diffusion and fluid flow, which are quite well understood (e.g., de Beer et al. 2006), our knowledge about gas migration in the subsurface in the marine environment is limited and accurate mechanistic models for gas migration by ebullition are only slowly being developed (Boudreau et al. 2005).

The upper part of the sediment sequence on large parts of the Arctic shelf consists of glacial sediments (glacial diamictites) that are extremely poorly sorted and have low porosity ($\sim 30\%$), due to smaller grains filling pore spaces between larger grains, and very low intergranular permeability ($\sim 10^{-17} \text{ m}^2$) (Hubbard and Maltman 2000). This impedes vertical migration of methane dissolved in fluid. In permafrost horizons, sediment permeability is principally controlled by freezing of pore waters, which provides a perfect seal for upward migrating fluids and gases. Subsequent thaw-

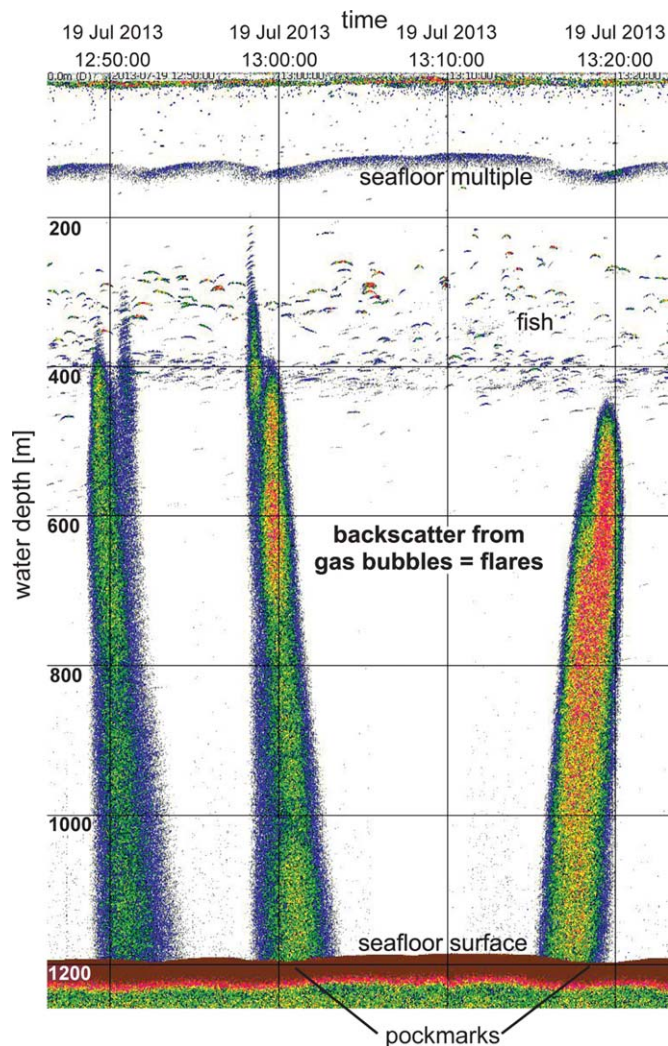


Fig. 4. Hydroacoustic image of gas bubble plumes rising from the seafloor in ~ 1880 m water depth within the gas hydrate stability zone offshore western Svalbard. Note the depressions, or pockmarks, in the seafloor (shown in dark brown) immediately below the plumes (see Smith et al. 2014). Note that the ship turned through 180° at $\sim 13:10$; all flares are tilted to the northeast as that is the direction of the prevailing current.

ing of this ice barrier as a result of warming will open up pathways for fluid and gas seepage again. Gas hydrates also form a barrier to fluid and gas seepage, but the seal is usually incomplete (Naudts et al. 2006). In the same context, permafrost and gas hydrate thus provide increased geomechanical strength to the sediment matrix.

If hydrate dissociates, for example as a result of warming, the gas produced will increase pressure in sediment of low permeability, creating cracks or even causing the sediment matrix to collapse abruptly, leading to slumping and collapse structures (e.g., pockmarks; Fig. 4) (e.g., Vanneste et al. 2007). The presence of cracks increases the effective permeability of glacial sediments by around four orders of

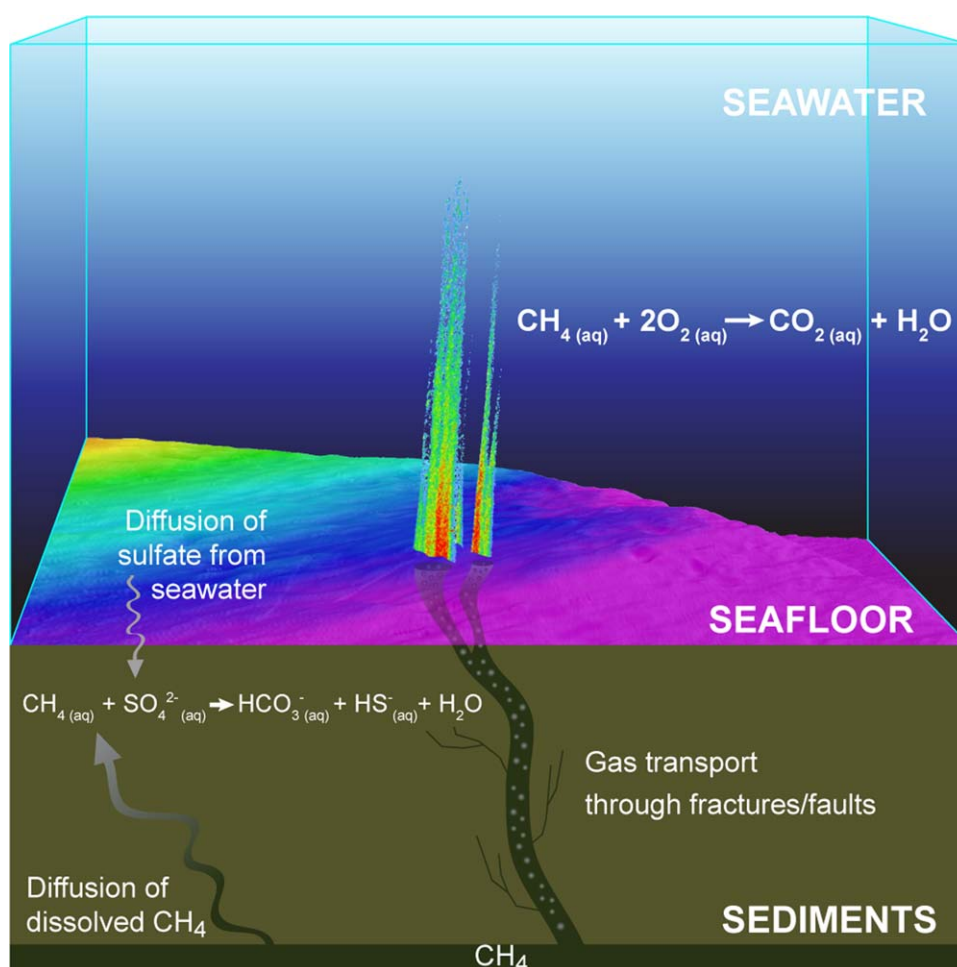


Fig. 5. Methane consumption by (i) anaerobic oxidation of methane, and (ii) aerobic methane oxidation. Note that methane gas can bypass microbially mediated oxidation reactions because microbes can only access dissolved methane.

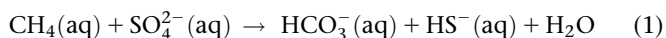
magnitude, to $\sim 10^{-13} \text{ m}^2$ (Thatcher et al. 2013), increasing the likelihood of gas flow at the seabed.

The colder water column in the Arctic Ocean allows methane to accumulate as hydrate in sediments in shallower water depths than is possible in most other parts of the world's oceans (Fig. 3), and it is this hydrate that climate warming will reach soonest and most strongly (e.g., Hunter et al. 2013). A number of recent modelling studies have assessed the potential for seafloor methane release in the Arctic Ocean as a result of hydrate dissociation based on observed and predicted warming scenarios (e.g., Reagan and Moridis 2009; Biastoch et al. 2011; Reagan et al. 2011; Thatcher et al. 2013). Although the process of dissociation is endothermic (i.e., it requires heat), and the increase in pressure caused by released gas and the salinity decrease caused by released water both increase the stability of hydrate, most of the modelling studies agree that bottom water warming over the past 30 yr (e.g., Walczowski and Piechura 2006; Westbrook et al. 2009) is already likely to have resulted in

increased methane fluxes across the seabed as a result of hydrate dissociation, and that these fluxes are expected to increase if warming were to accelerate in the future.

The microbial methane filter in Arctic marine sediments

After reduction by photochemical processes in the troposphere, microbial consumption is the largest sink of methane on our planet (Hinrichs and Boetius 2002; Reeburgh 2007). Pioneering work in the 1970s and 1980s (e.g., Martens and Berner 1974; Zehnder and Brock 1980) showed that a significant fraction of the methane that is produced in seafloor sediments is retained in the anoxic part of the sediment column, apparently oxidised with sulphate as the terminal electron acceptor by a process known as "anaerobic oxidation of methane" (AOM; see reviews by Reeburgh 2007; Knittel and Boetius 2009 and references therein):



As a result, upward migrating methane and downward diffusing sulfate (originating from seawater) are consumed in a distinct sediment horizon, the so-called sulfate-methane transition zone (SMTZ) (Fig. 5). The yield of Gibbs free energy from AOM is however very small ($\Delta G^{\circ} = -17 \text{ kJ mol}^{-1}$), and AOM-mediating microorganisms have only been identified relatively recently. To date, three clades of anaerobic methane oxidisers (ANME-1, -2, -3) belonging to the euryarchaeota have been shown to mediate AOM. ANMEs often form aggregates with sulfate-reducing bacteria (SRB) of the genus *Desulfococcus/Desulfosarcina* (ANME-1, -2) or *Desulfobulbus* (ANME-3) (Hinrichs et al. 1999; Boetius et al. 2000; Niemann et al. 2006; see detailed review by Knittel and Boetius 2009). However, the role of SRB in the AOM process is unclear.

In addition to sulfate-dependent AOM, recent studies have provided evidence for novel modes of AOM coupled to the reduction of oxidised metal species (Fe(III), Mn(IV)) (Beal et al. 2009; Sivan et al. 2011) and nitrite (NO_2^{-}) (Ettwig et al. 2010). However, the environmental significance of these pathways, particularly in marine environments, is yet to be determined.

In oxygen-replete surface sediments and the ocean water column, methane is oxidised aerobically with oxygen as the terminal electron acceptor (Fig. 5) (Hanson and Hanson 1996; Murrell 2010):



The yield of Gibbs free energy during aerobic methane oxidation (MOx) is relatively high ($\Delta G^{\circ} = -820 \text{ kJ mol}^{-1}$) compared with AOM. Nevertheless, MOx is of lesser importance in shallow marine sediments as the penetration depth of oxygen into sediments is very limited. Consequently, methane is typically consumed in the SMTZ via AOM, so significant concentrations of oxygen and methane do not coexist in most marine sediments. However, MOx becomes more important if methane bypasses the AOM filter and migrates into the oxic water column (see below).

The ecology of AOM communities is not well understood, particularly for high-latitude environments, so predicting the effects and feedback mechanisms of rising temperatures in the Arctic and higher than present-day methane fluxes due to hydrate dissociation and degradation of submerged permafrost remains, to a large extent, speculative. Nevertheless, based on our knowledge of methane cycling at cold seeps, the following factors are likely important in controlling methane fluxes across the seabed:

1. *Thermodynamic constraints.* AOM communities are typically found in a narrow sediment horizon within the SMTZ (Knittel and Boetius 2009). As the sulfate flux is dominated by diffusion, an increase in the methane flux

(which can be advective, see above) will ultimately lead to an upward shift in the depth of the thermodynamic and kinetic optimum for AOM (Niemann and Boetius 2010).

2. *Microbial activity and growth.* To some degree, the AOM communities may counterbalance an increase in methane flux by increasing their metabolic activity (Nauhaus et al. 2002). The maximum velocity (v_{max}) of the AOM enzymatic machinery is high (and the limit is not yet known: Nauhaus et al. 2002; Deusner et al. 2010), so it is reasonable to assume that v_{max} is probably not the limiting factor for efficient methane consumption, even under future high methane flux regimes. However, large changes in the methane flux will ultimately relocate the optimal depth for AOM (i.e., the SMTZ), as described above. Thus, for efficient methane consumption, a new population of AOM communities must grow at the depth of the new SMTZ. The doubling time of ANME-2/DSS consortia is ~ 7 months (Nauhaus et al. 2007), so the genesis of an effective AOM microbial filter (typically consisting of $> 10^{10}$ cells cm^{-3} : Lösekann et al. 2007; Knittel and Boetius 2009) in sediments with only small ($< 10^5$ cells cm^{-3}) AOM communities would be on the order of decades. Permeable sediments with fast exchange between sediment pore waters and the water column, i.e., fast supply of sulfate as well as removal of sulfide, could promote growth of AOM organisms (Wilfert et al. 2015), but they would also facilitate transfer of methane from sediments to the water column.
3. *Mode and magnitude of methane transport.* As discussed previously, methane is transported within sediments either in the dissolved phase (by diffusion or advection) or as free gas (ebullition of bubbles), which strongly controls the efficiency of the microbial methane filter. While the AOM communities may counterbalance increased transport of dissolved methane, they typically consume only a fraction of the advective methane flux (Treude et al. 2003; de Beer et al. 2006; Niemann et al. 2006). This is because free gas is inaccessible to microbes, which depend on a diffusive transmembrane gas transport. Thus while higher fluxes of methane will lead to higher concentrations of dissolved methane in pore waters, which likely increases rates of AOM (Treude et al. 2003), it increases the likelihood for transport of methane in the gas phase, which will bypass the sedimentary AOM filter. Changing methane flux regimes may also lead to shifts in the AOM community structure but, as yet, evidence for clear preferences of distinct AOM communities to specific habitats and flux regimes is limited (Knittel et al. 2005).
4. *Temperature.* In accordance with the van-'t-Hoff rule, increasing temperatures will stimulate AOM activity (e.g., Iversen and Blackburn 1981), thus acting as a negative feedback to temperature induced increases in methane flux in a warming Arctic. However, field (Iversen and Blackburn 1981) as well as laboratory studies (Nauhaus

et al. 2005) indicate Q_{10} -values (i.e., the change of metabolic activity as a result of a 10°C increase in temperature) of 2–5. Thus, with respect to possible increases in bottom water temperatures of 1–2°C (Biastoch et al. 2011), it is questionable if the increase in metabolic activity will be sufficient to counteract the higher methane flux (Shakhova et al. 2010). Furthermore, the dissociation of gas hydrates consumes energy and therefore lowers the temperature in the ambient sediments (Selim and Sloan 1989), which could lead to the opposite effect, i.e., a decrease in AOM activity. Changing temperatures may also lead to compositional changes in the microbial community. Temperature preferences of AOM communities are largely unknown but circumstantial evidence suggests that ANME-3 is best adapted to the ice-cold temperatures of the Arctic region (Niemann et al. 2009).

5. *Elevated methane-derived biomass.* Higher methane fluxes will lead to an expansion of present day cold seeps or, possibly, the formation of new systems. Thus, the amount of methane-derived biomass and the development of hard substrates (methane derived carbonates; Berndt et al. 2014) will increase as well. It therefore appears likely that organisms consuming methane-derived biomass as well as those utilising hard substrates will have an advantage in a future Arctic Ocean (Niemann et al. 2005, 2013). Nevertheless, owing to an enormous influx of organic carbon from ice algae that is to be expected as the ice caps melt (Boetius et al. 2013), the significance of increased biomass due to higher sub-seafloor methane fluxes needs to be tested. Moreover, bioirrigation by chemosynthetic organisms could strongly enhance methane consumption by increasing the influx of electron acceptors from seawater into the organic-rich sediments (Cordes et al. 2005; Niemann et al. 2006).

Processes affecting methane distributions in the Arctic Ocean water column

The three principal mechanisms that transfer methane from sediment to the overlying water column are: (1) release of dissolved methane either by diffusion or fostered by advective fluid flow, (2) the release of gas bubbles, and (3) rise of consolidated methane hydrates, which may have a density lower than that of seawater, and thus become buoyant when detached from the sediment matrix. Dissolved methane may be oxidised in the water column under oxic conditions (Eq. 2).

Methane release from the seabed

Where the methane flux is sufficiently high, methane escapes the seabed as bubbles that rise singly or as a plume. The fate of a bubble released at the seafloor is critically dependent on bubble size or radius, r . Small bubbles dissolve close to the seafloor, while large bubbles can transport meth-

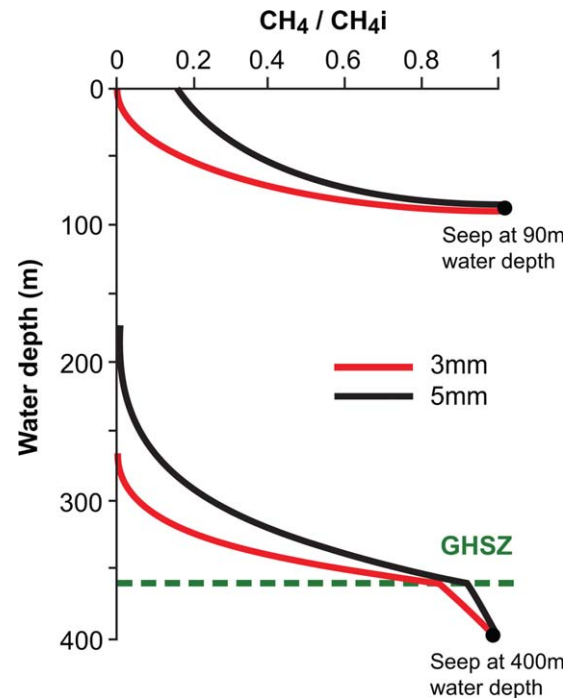


Fig. 6. Proportion of methane remaining in a gas bubble relative to the initial (i) methane concentration in a bubble released at the seabed, for bubbles with initial radii of 3 mm and 5 mm, released at 90 m and 400 m water depth. The green dashed line shows the upper limit of the gas hydrate stability zone (GHSZ) on the Arctic continental slope.

ane across hundreds of meters (Leifer and MacDonald 2003). For example, for a singly rising bubble of radius $r = 5$ mm, $\sim 15\%$ of its methane reaches the atmosphere from 90 m water depth, while a bubble with $r = 3$ mm, released at the same water depth, will dissolve within 8 m of the sea surface (Fig. 6; Leifer and Patro 2002). In the Arctic region, even gas bubbles with a relatively large radius (i.e., ~ 5 mm) will dissolve completely within ~ 200 m of the seafloor (Fig. 6), which means that methane is unlikely to be emitted directly into the atmosphere at water depths $> \sim 200$ m. Methane bubbles released at water depths within the gas hydrate stability zone will be encased by a hydrate skin, which restricts bubble dissolution (Rehder et al. 2009). However, once the bubble rises above the gas hydrate stability zone, the hydrate skin will rapidly dissociate and the rate of methane loss from the bubble increases significantly (Fig. 6).

Bubble dissolution leads to approximately exponentially decreasing methane concentrations with increasing distance above the seafloor (Leifer et al. 2006), and the composition of the gas remaining in the rising bubble can considerably differ from the seabed composition. Due to the higher partial pressure of gases dissolved in seawater (N_2 , O_2 , Ar) and the different gas transfer rates across the bubble interface, in particular for nitrogen, a bubble containing only methane at the seafloor can potentially reach the surface containing

mostly nitrogen and oxygen (Leifer and Patro 2002; McGinnis et al. 2006; Schneider von Deimling et al. 2011).

Methane from floating hydrates may be readily transported to the atmosphere (Brewer et al. 2002), if the lower limit of the gas hydrate stability field is relatively close to the mixed layer depth (e.g., the Arctic), as dissolution within the gas hydrate stability field is relatively slow (Rehder et al. 2009) and decomposition occurs mainly after crossing the hydrate stability boundary (Fig. 6). Decomposition leads to the formation of free gas, which subsequently dissolves and may be subject to oxidation or sea-air exchange (see below). The transport of methane by floating hydrates has been discussed in the framework of slope failures (Paull et al. 2003), with prominent examples in the Arctic Ocean (e.g., Kvenvolden 1999).

Dissolved methane that reaches the winter wave mixed layer by any of the processes discussed above will be transported to the sea surface by wave mixing on time scales that are usually shorter than the time scale for microbial degradation (see below), and will eventually be partly expelled into the atmosphere. By contrast, bubble-mediated transport contributes directly to atmospheric budgets. Winter storms deepen the pycnocline (Rudels et al. 1991), and allow deeper water to be entrained into the surface mixed layer, as can local cross-pycnocline transport mechanisms, such as upwelling (Rehder et al. 2002). However, transport across the pycnocline is a rather slow process (e.g., Jakobs et al. 2014; Leifer et al. 2015; Schneider von Deimling et al. 2015).

Most of the Arctic Ocean is permanently stratified with warmer, but more saline water from the Atlantic and Pacific underlying a surface layer that is colder and fresher derived from river runoff and ice melting (Yang et al. 2002). In the Arctic, freezing and melting have a major control on stratification, rather than thermal seasonal effects as elsewhere, leading to a pycnocline at 50–250 m (Rudels et al. 1991). The pycnocline presents a significant barrier for transport to the sea surface. Thus, methane below the pycnocline will mainly be transported laterally by currents, until storms deepen the mixed layer—potentially to the seabed in areas of shallow water. In the Barents Sea mixing can extend to deeper than 200 m (Rudels et al. 1991), and the Arctic is home to the largest shallow sea of the world's oceans, the East Siberian Arctic Sea (Semiletov et al. 2000), where frequent storms effectively vent the water column (Shakhova et al. 2014). The presence of polar lows, small intense short-lived cyclonic vortices that resemble tropical hurricanes (Emanuel 1989), drives mixing deep through processes like Langmuir circulation (Smith 1998). Thus, for dissolved methane above the winter mixed layer but below the pycnocline, lateral transport and sinking, such as that which occurs on outflow shelves (Carmack and Wassmann 2006), could lead to submergence to depths where the primary fate is microbial oxidation. However, lateral transport also can lead to orographic upwelling or shoaling and more rapid

transport to the atmosphere, particularly along inflow shelves (Carmack and Wassmann 2006).

As Arctic sea-ice cover decreases, and sea surface temperature increases, evaporation will increase and precipitation is predicted to increase by >50% before the end of the 21st century (Bintanja and Selten 2014). Between 1964 and 2000, river discharge to the Arctic Ocean increased by 5.6 km³ yr⁻¹, mostly due to a large increase from the Eurasian rivers (McClelland et al. 2006). Modelling studies indicate that increased river runoff will strengthen stratification (e.g., Capotondi et al. 2012), producing a fresher and shallower surface mixed layer that may hinder delivery of methane from the seafloor to the sea surface. However, a recent study has suggested that increased stratification could increase the temperature of sub-pycnocline waters, at least on timescales of hundreds of years (Nummelin et al. 2015). This could, in turn, increase the potential for hydrate dissociation. By contrast, decline in the summer extent of sea-ice (Fig. 2) enhances the strength and size of Arctic storms (e.g., Long and Perrie 2012), and promotes vertical mixing between surface and deep waters (Pickart et al. 2013; Zhang et al. 2013). The relative strengths of these processes is likely to show significant regional variability; for example, areas affected by Atlantic inflow including the Greenland Sea and outer shelves of the Barents, Kara, and Laptev seas, will experience greater vertical mixing (Popova et al. 2014). It is clear that future predictions of methane distributions in the water column are strongly reliant on reliable projections of freshwater fluxes and rates of sea-ice retreat, both of which are currently a major source of uncertainty in ocean circulation models.

The microbial methane sink in the water column

Organisms involved in MOx are found within several subdivisions of Proteobacteria and have been observed in a variety of terrestrial, limnic and marine environments (Hanson and Hanson 1996; Treude et al. 2005; Niemann et al. 2006; Blumenberg et al. 2007; Lösekann et al. 2007; Elvert and Niemann 2008; Steinle et al. 2015). Two biochemical pathways involved in MOx exist, the so-called RuMP and Serine pathways, which are utilised by Type I and Type II aerobic methanotrophs, respectively (Hanson and Hanson 1996; Murrell 2010 and references therein). A third MOx type, Type X, utilises both pathways.

The Arctic Ocean and shelf seas are generally well-oxidized so methane that escapes the sub-seafloor AOM filter and enters the water column is liable to be oxidized by MOx (Eq. 2). Studies conducted in very different marine settings report water column methane turnover times of the order of weeks to >1000 yr (Fig. 7). Much shorter turnover times with rate constants of up to 15% d⁻¹ have been reported for hydrothermal plumes on the Juan de Fuca Ridge (Kadko et al. 1990; de Angelis et al. 1993). Methane turnover in methane-rich water bodies, at cold vent sites, and above gas-bearing sediments, apparently takes place on time scales of

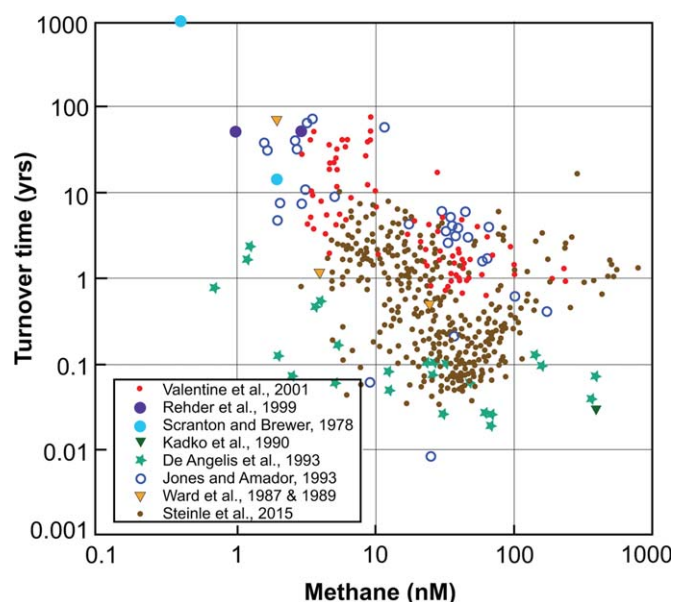


Fig. 7. Compilation of methane turnover time vs. ambient methane concentration, for various marine environments. Note logarithmical scale. Data from Ward et al. (1987, 1989), Kadko et al. (1990), de Angelis et al. (1993), Jones and Amador (1993), and Steinle et al. (2015) were determined using either ^{14}C or ^3H labelling techniques, while the studies by Scranton and Brewer (1978) and Rehder et al. (1999) were determined using tracer/tracer relations. Data from Kadko et al. (1990) and de Angelis et al. (1993) are for hydrothermal systems. Figure modified from Nauw et al. (2015).

weeks to a few years (Valentine et al. 2010; Mau et al. 2013; Steinle et al. 2015). Distinctly longer lifetimes have been reported for methane-poor seawater, from several 10s to 50 yr in cold newly formed deep waters in the North Atlantic and the Weddell Sea (Rehder et al. 1999; Heeschen et al. 2003), to several 100s of years in oceanic deep waters with subnanomolar concentrations of methane (Scranton and Brewer 1978). In general, there is an inverse relationship between methane availability and turnover time (Fig. 7).

Nevertheless, the effectiveness of the microbial MOx filter is not well constrained, particularly for Arctic environments where it may be dependent on variables in addition to substrate availability (Reeburgh 2007; Steinle et al. 2015), so we can only speculate as to how the MOx filter will operate in a future Arctic Ocean. Ocean currents have recently been identified as a globally important control for water column MOx activity above methane point sources (Steinle et al. 2015). If currents are strong, the water mass residence time is comparatively short which hampers the development of MOx communities. Conversely, seeding of MOx bacteria directly from the sediment into the water column through rising methane bubbles could counteract this effect (Schmale et al. 2015). Benthic MOx bacteria have been found in association with gas bubbles rising from sediments, but their survival/growth rate and methane consumption efficiency in the water column is unclear.

Given that modelling work predicts that the aerobic methane oxidation rate is a key control on emission of methane to the atmosphere in shallow Arctic shelf seas (Wåhlström and Meier 2014), further work on water column methane oxidation is consequently of paramount importance for our understanding of methane release from the Arctic Ocean. Furthermore, to the best of our knowledge, there have been no investigations on the effect of ice cover on methane oxidation in marine environments. It is reasonable to assume that methane from bubbles trapped beneath ice will slowly disperse, which may attract MOx communities (Rudd et al. 1976; Rudd and Hamilton 1978) and, in support of this, active methane oxidation has been reported beneath the Greenland ice sheet (Dieser et al. 2014). By contrast, changes in the extent and/or duration of ice coverage of the Arctic Ocean mean that it is possible that methanotrophic bacteria will have less time to consume methane so the methane flux to the atmosphere will increase. Although there appears to be a direct relationship between sea-ice decline and increasing methane emissions in the Arctic, the contribution of oceanic methane sources is, as yet, unclear (Parmentier et al. 2013).

Methane exchange across the sea-air interface

Diffusive transport across the sea surface for a sparingly soluble gas like methane can be described as gas transfer across a resistive aqueous phase boundary layer driven by a concentration gradient (e.g., Liss 1973). Waves and shear stress increase turbulence and reduce the thickness of the boundary layer, leading to higher exchange rates. With the onset of wave breaking, bubbles significantly enhance gas exchange (Carmack and Wassmann 2006). For practical reasons, wind speed is usually the only non-gas specific variable used to quantify the gas transfer rate (e.g., Wanninkhof et al. 2009), although fetch dependency is well known (Liss and Merlivat 1986) and important in polynyas and areas of mixed open water and ice. Large field experiments suggest gas exchange rates increase quadratically (Wanninkhof 1992), cubically (Wanninkhof and McGillis 1999), or between these two (Nightingale et al. 2000), as a function of wind speed. A recent review on advances and the state of the art of the parameterization of gas transfer velocities is given in Wanninkhof et al. (2009). Recent observations in the Arctic Ocean indicate that fast winds during storms considerably enhance methane emission at the sea surface (Shakhova et al. 2014), although the integrated amount of methane released during these events and also all year long remain heavily debated (Berchet et al. 2014).

Reductions in sea-ice coverage in the Arctic Ocean mean that larger waves are likely and swells will be more common (Thomson and Rogers 2014), as well as greater input of water vapour into the atmosphere. Larger swells carry more energy and are more effective both in breaking up sea-ice and vertically mixing surface waters. Both of these effects will

increase sea-air gas exchange in a future seasonally ice-free Arctic Ocean.

Most circulation models predict stronger winds and storm tracks migrating closer to the pole as Arctic climate warms (IPCC 2013), which would increase sea-air exchange. However, some studies suggest that the number of polar lows (small short-lived intense cyclonic vortices that resemble tropical hurricanes; Emanuel 1989) may decline in a warming world (Zahn and von Storch 2010), and zonal circulation appears to have weakened (reducing wind speeds) during recent winters (Francis et al. 2009). All of this points to the conclusion that the effects of climate change on Arctic wind speeds (and consequently sea-air gas flux) remain rather poorly constrained.

Effect of ice cover on sea-air gas exchange

The formation of sea-ice, in particular in winter, gives potential for major restrictions and alterations to the sea-air flux of methane. Even during the onset of ice formation, ice crystals dampen wave formation at the surface and restrict free air-sea exchange (e.g., Loose et al. 2014). Winter sea ice will almost completely suppress air-sea exchange, and a closed sea ice cover will also trap bubbles reaching the surface. In this connection, a number of studies report high methane concentrations under ice, both in the oceans and in lakes. On the East Siberian Arctic shelf, dissolved methane concentrations beneath the sea ice are 5–10 times higher in winter, than they are in summer (Shakhova et al. 2010), and in the Canadian Arctic, methane over-saturation has been found under multi-year sea-ice (Kitidis et al. 2010). It has been suggested that accumulation of methane under ice could enhance the annual sea-air flux due to release of this methane after melting in seasonally ice-covered regions (Lammers et al. 1995). In support of this, a more recent study has shown that sea-ice reduces methane emissions in the Arctic and continuous melting of sea-ice in the Arctic Ocean will drastically increase methane emissions to the atmosphere (He et al. 2013). Concentrations of atmospheric methane have been shown to increase over open leads and regions with fractional sea-ice cover (Kort et al. 2012), providing further evidence that sea ice acts as a barrier to transfer of methane to the atmosphere. Finally, it has been demonstrated that methane release from the River Neva plume is delayed in winter in the seasonally ice-covered Gulf of Finland (Schneider et al. 2014).

Summary and outlook

Atmospheric methane concentrations have undergone significant changes in the past, and it is widely accepted that these have occurred in conjunction with shifts in global climate (e.g., Dickens 2003; DeConto et al. 2012). Critically, it seems likely that Arctic methane emissions may have played a major role both in modern methane emissions (Dlugokencky et al. 2009) and in past global climatic change (Nisbet and Chappellaz 2009).

Our synthesis of recent data indicates that the fate of methane in sub-seafloor Arctic Ocean reservoirs in a warming world is far from certain. Within the sediments, methane may be entirely consumed by AOM if methane fluxes are low. If methane fluxes increase, for example due to hydrate dissociation, AOM communities may increase their metabolic activity, but at the same time increased transport of methane as free gas will reduce the efficiency of the AOM filter. Gas hydrates and permafrost serve as a barrier to fluid and gas migration toward the seafloor but, if they melt, pressure will increase in low permeability sediments creating cracks and fractures, which increase the likelihood of seabed gas flow. Methane bubbles that enter the water column may be rapidly transported to the sea surface if the bubbles are large and water depth is shallow. However, if the bubbles are small, or the seabed is deep, and if the water column is strongly stratified, they will dissolve within a few tens of meters above the seafloor and some fraction of the methane may be oxidised to CO₂ by aerobic methanotrophs. If seawater warms, the rate of bubble dissolution may decrease but, on the other hand, increased river discharge to the Arctic Ocean is predicted to increase stratification, inhibiting gas transport into the winter wave mixed surface layer. Stronger winds will increase sea-air methane exchange, but the number of polar lows, which can strip the water column of methane into the atmosphere, may decrease.

The effects of reduced sea-ice cover on methane emissions are especially poorly constrained. Studies of the distribution and cycling of methane beneath sea-ice are almost absent from the literature, and there have been no investigations on the effect of ice cover of methane oxidation in marine environments. Improving our state of knowledge is vital as Arctic sea-ice coverage continues to decrease.

Enhanced methane concentrations in the water column offshore western Svalbard, on the East Siberian Arctic Shelf, and possibly in the Beaufort Sea, are likely related, at least in part, to melting of gas hydrates and submerged permafrost. However, a critical question centres on the timing of the response of these sub-seafloor methane reservoirs to Arctic environmental change. Numerical modelling of the seafloor offshore western Svalbard predicts that the delay between the onset of warming and emission of gas at the seafloor due to hydrate dissociation may be less than 30 yr (e.g., Thatcher et al. 2013), whereas dating of authigenic carbonates suggests that methane seepage in this area has been ongoing for at least 3000 yr (Berndt et al. 2014). Moreover, a recent study (Dmitrenko et al. 2011) suggests that degradation of subsea permafrost is primarily related to warming initiated by permafrost submergence about 8000 yr ago, rather than recent Arctic warming. As abrupt release of methane increases the likelihood of its release to the atmosphere, a better understanding of the response of hydrate and submerged permafrost to increased temperatures, and especially the identification of any non-linearity, is critical.

With the exception of CO₂, the biogeochemical transformations and physical processes that affect the distributions of climatically active gases in the oceans are poorly represented in Earth system models. Moreover, the role of sea bed processes currently is not considered at all. This review reveals that there are numerous linkages and feedback pathways between climate warming and release of methane from marine sediments, and there is clearly a requirement to develop process-based models for methane. Increased observations, especially for rates of anaerobic and aerobic oxidation of methane, bubble transport, and the effects of ice cover, are needed to support these models. Closer collaboration between the observation and modelling communities, so that the models have the ability to interface with observations, that appropriate datasets are specified, and that they are then created in a suitable format, is vital to this end.

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Acknowledgments

All authors gratefully acknowledge support from the European Cooperation in Science and Technology (COST) Action ES0902. Additional support was provided by: The UK Natural Environment Research Council (NE/D005728/2) and Department of Energy, Environment and Climate Change (RHJ); European Space Agency (ESA) Support to Science Element (STSE) OceanFlux Greenhouse Gases Evolution project (4000112091/14/I-LG) and National Science Center, Poland (NCN) Growing of Arctic Ecosystem (GAME) project (DEC-2012/04/A/NZ8/00661) (JP); the European Union Seventh Framework Programme (FP7/2007-2013) under the MIDAS project, grant agreement # 603418 (MH & LV); the Research Council of Norway through its Centres of Excellence funding scheme grant # 223259 (JG, HN).

Submitted 1 September 2015

Revised 10 February 2016

Accepted 17 March 2016

Associate editor: Leila Hamdan