

Shallow-ocean methane leakage and degassing to the atmosphere: triggered by offshore oil-gas and methane hydrate explorations

Yong Zhang^{1*} and Wei-Dong Zhai²

¹ Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, China, ² Department of Marine Chemistry, National Marine Environmental Monitoring Center, Dalian, China

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*Correspondence:

Yong Zhang,
Key Laboratory of Coastal Zone
Environmental Processes and
Ecological Remediation, Yantai
Institute of Coastal Zone Research,
Chinese Academy of Sciences, 17,
Chunhui Road, Laishan District, Yantai
264003, China
yzhang@yic.ac.cn

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Both offshore oil-gas exploration and marine methane hydrate recovery can trigger massive CH₄ release from seafloor. During upward transportation of CH₄ plume through water column, CH₄ is subjected to dissolution and microbial consumption despite the protection of hydrate and oil coating on bubbles surface. The ultimate CH₄ degassing to the atmosphere appears to be water-depth dependent. In shallow oceans with water depth less than 100 m, the natural or human-induced leakages or both lead to significant sea-to-air CH₄ degassing from 3.00 to 1.36 × 10⁵ μmol m⁻² d⁻¹. To quantify the human-perturbation induced CH₄ degassing, the combination of top-down modeling and bottom-up calculations is essential due to spatial and temporal variability of diffusion and ebullition at water-air interface.

Keywords: methane, seafloor leakage, offshore oil-gas exploration, hydrate, coastal process

Introduction

Methane (CH₄) is an infrared-active trace gas that plays an important role in Earth's climate system (Lelieveld et al., 1998). Despite its low mole fraction in the atmosphere (1.803 ppm in 2011), CH₄ is the second largest contributor (17%, after carbon dioxide) to the total radiative forcing caused by the well-mixed greenhouse gases (IPCC, 2013). The continuous increase of atmospheric CH₄ in the past decades implies an imbalance between CH₄ sources and sinks and prompts urgent questions about the causes (Cicerone and Oremland, 1988; Kirschke et al., 2013; Nisbet et al., 2014).

Although earlier researchers suggest that natural emissions of CH₄ from oceans may only contribute 1% to the global atmospheric methane budget (Bange et al., 1994; Judd et al., 2002; U.S. EPA, 2012), recently the oceanic CH₄ release has received increasing attention under the context of global warming induced Arctic changes (e.g., Whiteman et al., 2013). So far, understanding the maintaining mechanism and variability of the sea-to-air flux of CH₄ remains a huge challenge since most potential source areas of CH₄ are still insufficiently sampled in global oceans (Achterberg, 2014). It is worth noting that marine sediments serve as the global largest reservoir of CH₄ (Kvenvolden, 2002; Milkov, 2004). If a substantial amount of CH₄ were released from seafloor, the atmospheric CH₄ concentration would rise dramatically.

As strong anthropogenic perturbations, offshore oil-gas explorations and marine methane hydrate explorations may play an important role in triggering the CH₄ release from seafloor. The well sites, processing plants, storage tanks, transmission compressor stations, and distribution systems may act as "super-emitter" CH₄ sources, which have been considered to be a cause for larger CH₄ emissions from North American natural gas systems than official estimates (Brandt et al., 2014).

Nowadays preventing CH₄ release from vented and flared natural gas has received considerable attention (e.g., Elvidge et al., 2009; U.S. GAO, 2010), while the CH₄ degassing associated with episodic CH₄ leakage from seafloor is also identified (e.g., Du et al., 2014; Zhang et al., 2014). This mini review summarized recent progresses regarding the CH₄ leakage from seafloor caused by offshore oil-gas and marine methane hydrate explorations and its degassing to the atmosphere.

Offshore Oil-Gas Exploration and CH₄ Leakage

To meet energy demands in both developed and emerging economies, the offshore oil and gas exploration has received international attentions in recent decades. In 2012, the offshore discovery accounted for 90% of world newly increased reserves (Zhao et al., 2014). The newly discovered oil-gas reservoirs concentrated in the coastal shallow waters (**Figure 1**). In addition to offshore boom in the Gulf of Mexico, substantial exploration and development has taken place along coasts of Brazil and the Africa. Interests in the oil-gas exploration in the more challenging Arctic area are also increasing.

Oil and gas can enter the marine environment by natural seepage and/or by leaks and spills caused by human activities (extraction, transportation, etc.). The natural crude-oil seeps scatter in global coastal seas and the amount of global seepage is estimated to be 600,000 tons per year (Kvenvolden and Cooper, 2003). Natural gas seepage has been considered to be the cause of strong subsurface CH₄ anomaly in the Davis Strait, North Atlantic Ocean (Punshon et al., 2014).

Compared to natural seepage, marine oil and gas extraction can cause disastrous oil spills and leakages accompanied by massive CH₄ injections into the overlying water column. Some “landmark” accidents include Ekofish B blowout in the North

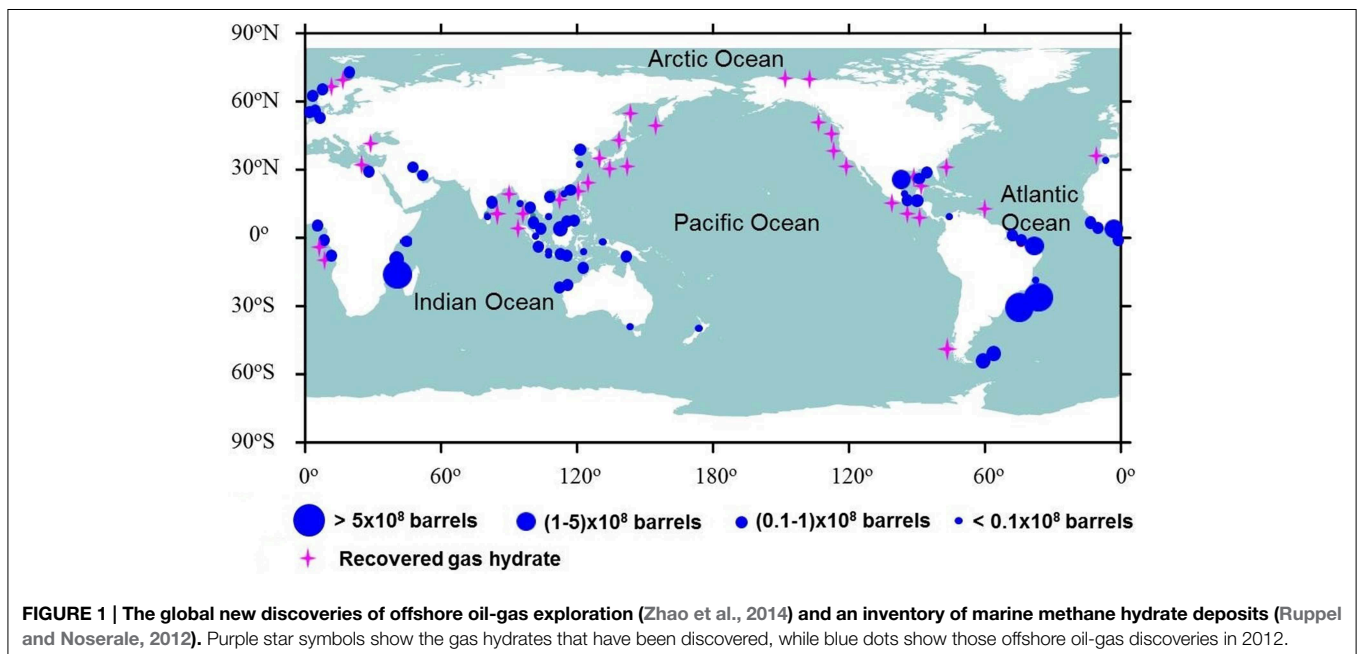
Sea in 1977, Ixtoc I blowout in the Gulf of Mexico in 1979, Adriatic IV blowout in the Mediterranean Sea in 2004, Montara blowout in the Timor Sea in 2009, and Macondo blowout in the Gulf of Mexico in 2010 (Christou and Konstantinidou, 2012). Additionally, CH₄ leakage may occur at any subsea facility, such as the pipeline, the flange, the valve and the weld (Vrålstad et al., 2011). CH₄ emissions from oil and gas systems (including coastal and offshore) were estimated to be 23% of total global anthropogenic emissions in 2010 and they are expected to grow 26% from 2010 to 2030 (U. S. EPA, 2012).

Undoubtedly, reducing CH₄ emission from oil and gas systems has environmental and economic benefits, especially in the Arctic. This issue has been seriously considered by some national governments and non-governmental organizations (e.g., the Global Methane Initiative, <https://www.globalmethane.org/>).

Marine Methane Hydrate Exploration and Potential CH₄ Leakage

Huge quantities of CH₄ are stored in continental margins in the form of methane hydrates under a delicate balance of low temperature (around 0°C) and high hydrostatic pressure (a few MPa) (Sloan and Koh, 2008). Methane hydrate (also called gas hydrate) is an ice-like crystalline form of water and low-molecular-weight gas (mainly CH₄) with a nominal composition of (CH₄)₄(H₂O)₂₃. One cubic meter of fully saturated methane hydrate solid contains ~164 m³ of CH₄ gas at the standard temperature and pressure (Kvenvolden, 1993).

The methane hydrate has been found on nearly all major continental shelves (**Figure 1**). Its reserves are estimated to be 3000–4000 times today’s atmospheric CH₄ reservoir (MacDonald, 1990; Blunier, 2000) or twice the existing reserves of all fossil fuels including coal, oil and natural gas (Kvenvolden, 1993, 2002).



Interest in methane hydrate has been growing rapidly since global resources of conventional oil and gas are on the decline and methane hydrate has emerged as a potential resource to make up the expected shortfall of conventional oil and gas (Kvenvolden, 1993; Makogon et al., 2007; Makogon, 2010). The Gas Hydrate Joint Industry Project in the Gulf of Mexico has confirmed the occurrence of methane hydrates below the seafloor of Gulf of Mexico (Boswell et al., 2012). In early 2012, the U.S. and Japan completed a successful field trial of methane hydrate production technologies in the North Slope of Alaska (<http://energy.gov/>). In March 2013, Japan's Methane Hydrate R&D Program conducted an experimental operation and succeeded to produce a steady CH₄ flow southeast of the Atsumi peninsula, Japan (<http://www.jogmec.go.jp/>). Other earlier global drilling efforts and production test studies were summarized by Ruppel (2011). However, so far no large-scale commercial CH₄ production from methane hydrate deposits has been reported due to scientific and technical challenges and economic viability.

Methane hydrate may serve as an important factor affecting global climate change because they are unstable and subject to dissociation due to slight temperature or pressure change, causing catastrophic seafloor failure and massive (gigaton scale) CH₄ release into overlying ocean-atmosphere system (Kennett et al., 2000; Paull et al., 2003). The release of large volumes of CH₄ to the atmosphere could in theory aggravate climate warming and trigger more methane hydrates to destabilize, creating a positive feedback loop. The positive interaction between climate and methane hydrate has been considered to be a cause in triggering the Palaeogene hyperthermal events, an abrupt period of global warming (4–8°C temperature rise) between 57 and 50 million years ago (Dickens et al., 1995; Kaiho et al., 1996; Gu et al., 2011) and the Late Quaternary (400,000–10,000 years ago) climate change (Kennett et al., 2003).

Without anthropogenic perturbation, most of the world's methane hydrate deposits should remain stable for the next few thousand years (Ruppel and Noserale, 2012). However, marine methane hydrate dissociation in response to ocean warming has been reported in many coastal seas, including the offshore Costa Rica (Crutchley et al., 2014), the offshore southwestern Japan (Bangs et al., 2010), the south Kara Sea shelf (Portnov et al., 2013), the northern U.S. Atlantic margin (Skarke et al., 2014), the offshore Svalbard (Westbrook et al., 2009; Marín-Moreno et al., 2013; Berndt et al., 2014) and sub-sea permafrost-associated methane hydrates in the east Siberian Arctic shelf (Shakhova et al., 2010). U.S. EPA (2012) suggested that the increase of CH₄ leakage from methane hydrate due to ocean warming may have overcome the barrier of water column and resulted in a significant atmospheric CH₄ load. How to evaluate the risks of the future commercial exploitation induced submarine geohazards and the consequently massive CH₄ release remains an open question.

Behavior of Seafloor-Released CH₄

The seafloor-released CH₄ will migrate upward through the water column either as dissolved CH₄ or as bubble CH₄. The rising CH₄ plume in the water column tends to get weak since some

CH₄ are subject to dissolution and microbially-mediated aerobic and anaerobic oxidation (Greinert et al., 2006; Reeburgh, 2007; Römer et al., 2012). The remaining fraction can reach atmosphere through diffusion or ebullition, which is determined by water depth, stratification, and microbiological processes within the water column (Schmale et al., 2005; Mau et al., 2007). Clarifying the behavior of CH₄ in the water column is critical to constrain the hazard potential of offshore drilling activities.

For CH₄ bubbles emanated from seafloor, the upward migration and dissolution of CH₄ is highly dependent on hydrate or oil coverage on bubbles surface. Both field and lab experiments have demonstrated that CH₄ bubbles are likely to be coated by methane hydrate within the local methane hydrate stable field (MHSF), which can significantly decrease but does not halt CH₄ dissolution (Rehder et al., 2002, 2009; Warzinski et al., 2014). The bubbles usually dissolve rapidly at the upper boundary of the local MHSF, which is jointly determined by water temperature, salinity, and gas composition (Römer et al., 2014). When CH₄ spills are accompanied by oil, oil coating around rising bubbles also impedes dissolution, thereby enhancing the likelihood of CH₄ release to the atmosphere (De Beukelaer et al., 2003; Leifer and MacDonald, 2003; Körber et al., 2014).

In deep waters, the scenario is outlined by the Deepwater Horizon oil spill event. From 20 April to 15 July 2010, 9.14×10^9 to 1.25×10^{10} moles of CH₄ were injected into deep waters (~1500 m) of Gulf of Mexico (Kessler et al., 2011). However, only a few (less than 0.01%) of the seafloor-released CH₄ escaped into atmosphere (Yvon-Lewis et al., 2011). The CH₄ plume was trapped below 800 m depth with CH₄ concentrations roughly 20–50 times as high as background levels and the microbial CH₄ oxidation rate quantified to be 10 nmol d⁻¹ (the median value) therein (Valentine et al., 2010). The trapped CH₄ was consumed by methanotrophic bacteria within ~120 days from the onset of release, resulting in significant oxygen anomaly in deep waters (Valentine et al., 2010; Kessler et al., 2011). By comparing the amounts of CH₄ microbial consumed and degassed to the atmosphere, Kessler et al. (2011) suggested that methanotrophic bacterial communities act as a dynamic biofilter that respond quickly and efficiently to the seafloor CH₄ leakage.

In the waters with depth around the upper boundary of local MHSZ, no oil-gas spill event has been reported so the scenario can only be described by some simulated experiments. A gas blowout experiment was conducted in the Norwegian Sea in 2000, during which $\sim 4 \times 10^5$ mole of CH₄ was discharged into the water column of 844 m depth. Since no methane hydrates shell was formed around gas bubbles, the gas dissolved quickly in the water column and no gas bubble was observed at sea surface (Johansen et al., 2003). Schmale et al. (2011) assumed a massive short-term injection of CH₄ release (1.1×10^{10} mole) at depth of 700 m in the Black Sea. They modeled that CH₄ was effectively buffered by microbial consumption and hammered by water column stratification. The simulated CH₄ release in depth resulted in only a 2–3% increase in the sea-to-air flux.

The shallow-ocean CH₄ leakage presents a quite different scenario. By studying oil spills in the Bohai Sea (China) with water depth less than 30 m, Zhang et al. (2014) revealed that the seafloor-released CH₄ can break through the summer

stratification, increasing sea surface CH₄ concentration by up to 4.7 times and enhancing local CH₄ outgassing by up to 14.6 times. However, the function of methanotrophs in this shallow sea is still unknown.

According to McGinnis et al. (2006), most marine sources of the atmospheric CH₄ are located in shallow oceans with water depth less than 100 m. This is coincident with the surface-water CH₄ distribution in the Black Sea, where elevated CH₄ concentrations were only observed above seeps areas with depth <100 m and no significant imprint was observed above high-intensity seeps with water column deeper than 150 m (Schmale et al., 2005). Summarizing sea-to-air CH₄ fluxes from marine environments affected by oil-gas exploration and methane hydrate dissociation (Table 1), we can also find that shallow areas (depth of leakage < 100 m) present intensive CH₄ fluxes of 3.00–1.36 × 10⁵ μmol m⁻² d⁻¹, whereas deeper areas show weaker values of –3.65–800 μmol m⁻² d⁻¹. It is worthy of noting that Solomon et al. (2009) observed that intensive CH₄ bubble plumes ascend from depth 550–600 m to sea surface in the Gulf of Mexico, leading to intensive degassing (up to 10⁴ μmol m⁻² d⁻¹). So water depth may not serve as the only threshold of the CH₄ degassing.

Quantifying CH₄ Degassing

Leakage of CH₄ from seafloor triggered by offshore explorations may contribute directly to atmospheric CH₄ budgets and possibly accelerate global warming (Jiang et al., 2006; Biastoch et al., 2011).

However, so far the global or regional sea-to-air CH₄ fluxes are poorly constrained, leading to uncertainties in carbon cycle and climate models.

The approaches to quantify CH₄ degassing generally fall into two categories: “bottom-up” calculations and “top-down” modeling (also known as inverse modeling). The bottom-up estimation of the CH₄ leakage rate is based on summing up emissions from different types of known sources (Olivier, 2002). CH₄ can enter the atmosphere by diffusion of dissolved CH₄ across the water-air interface or by direct migration of bubbles (if still contains CH₄). As for diffusion, the sea-air flux is estimated using a stagnant laminar layer model proposed by Liss and Slater (1974). Its reliability lies not only on gas transfer velocity and hydrodynamic conditions (Wanninkhof et al., 2009; Johnson et al., 2011), but also on the spatial resolution of sample collections. The surface CH₄ emission hot spots (i.e., areas of high flux) need to be covered (Du et al., 2014; Zhang et al., 2014). Compared to diffusion, ebullition of CH₄-containing bubbles, especially a small fraction of the largest bubbles, may release larger amounts of CH₄ and exhibits much greater spatiotemporal variation (Greinert and Nützel, 2004; McGinnis et al., 2014; Xiao et al., 2014; DelSontro et al., 2015). Floating chamber method has been widely used for direct measurement of both diffusive and ebullitions fluxes at water-air interface, but mostly in lakes and estuaries. Its utilization at sea is greatly challenged due to insufficient temporal and spatial coverage. At extreme shallow coastal waters (<5 m), a submerged chamber device has been developed for *in-situ* and on-line measurement of CH₄ flux

TABLE 1 | Sea-to-air CH₄ fluxes from marine environments affected by oil-gas exploration and methane hydrate dissociation.

Method	Location	Depth of leakage (m)	Flux (μmol m ⁻² d ⁻¹)	References
DIFFUSIVE NET FLUXES				
Bottom-up calculation	Plume area during the Deepwater Horizon oil spill	1500	0.024 ^a	Yvon-Lewis et al., 2011
	Seeps area in the northern Gulf of Mexico	550–1250	–3.65–75.0 ^a	Hu et al., 2012
	Seeps area in the northern Gulf of Mexico	550–600	61.9–10,500 ^b	Solomon et al., 2009
	North Sea	<700	–0.38–6.7 ^c	Bange et al., 1994
	Baltic Sea	<460	0.006–800 ^c	Bange et al., 1994
	Sea of Okhotsk	~200	0.36–88 ^b	Yoshida et al., 2004
	Seep area in Black Sea	>200	40.6–49.2 ^b	Schmale et al., 2005
	Seep area in Black Sea	~90	200 ^b	Schmale et al., 2005
	Coal Oil Point	<70	195 ^b	Mau et al., 2007
	East Siberian Arctic Shelf	~45	299–982 ^b	Shakhova et al., 2010
	Hotspots in the Bohai Sea	<30	3.00–18.71 ^a	Zhang et al., 2014
EBULLITION FLUXES				
Top-down modeling	East Siberian Arctic Shelf	~45	369–1781 ^d	Shakhova et al., 2010
	Arctic lakes (Small individual bubbles)	<25	1563 ± 750 ^e	Walter et al., 2008
	Arctic lakes (open-hole hotspots)	<25	(1.36 ± 0.75) × 10 ^{5e}	Walter et al., 2008
Offshore platforms in the Southeast Asia	Not mentioned	0.16 ^f	Nara et al., 2014	

^aFluxes were calculated using the gas transfer velocity parameterization of Sweeney et al. (2007).

^bFluxes were calculated using the gas transfer velocity parameterization of Wanninkhof (1992).

^cFluxes were calculated using the gas transfer velocity parameterization of Liss and Merlivat (1986).

^dMeasured indirectly, i.e., total flux minus diffusive flux.

^eSynthetic aperture radar imagery combined with field investigation.

^fIncludes but not limited to diffusive flux and ebullition emission.

from seafloor (Di et al., 2014). In the Arctic regions, synthetic aperture radar imagery has been used to locate point-source CH₄ ebullition from ice-covered lakes (Walter et al., 2008). Some numerical models have also been developed to quantify direct bubble transport of CH₄ (Leifer and Patro, 2002; McGinnis et al., 2006; Yamamoto et al., 2009). Yet more efforts are needed to better quantify CH₄ ebullition flux to the atmosphere on the spot, especially at ice-free seas.

Top-down modeling is based on atmospheric CH₄ measurements, atmospheric models, and statistical tools to invert concentration fields into parameters that provide the estimation of CH₄ emissions and sinks (Olivier, 2002). The remote-sensing-based top-down approach has been used to quantify CH₄ emission fluxes from the North American inland natural gas sites (Kort et al., 2014; Schneising et al., 2014). So far only a few similar investigations are designed to constrain CH₄ emissions from offshore oil-gas production. For example, Nara et al. (2014) have estimated CH₄ emission rates from offshore oil and gas platforms in the Southeast Asia based on their observed atmospheric CH₄ peaks and a mass balance approach. Similar atmospheric CH₄ peaks were also revealed at two regional atmospheric background monitoring sites adjacent to the Bohai Sea shortly after an oil-spill accident in June–August 2011 (Zhang et al., 2014). The field-data-based top-down approach is worth to be seriously applied.

Satellite observations are able to monitor gas emissions down to the point-source scale (Velazco et al., 2011). Airborne imaging spectrometry has the potential to provide high resolution mapping of marine CH₄ emissions from point sources (Thorpe et al., 2013). So time-resolved satellite observation supplemented by aircraft and ground-based measurements may provide a feasible method to quantify the large scale CH₄ emission from offshore oil-gas exploration areas.

According to the limited literature data that have already been summarized in **Table 1**, ebullition fluxes generally show

much higher values than diffusive ones and both of them show great spatial variation. However, so far ebullition measurements are seldom conducted at sea, probably due to their episodic occurrence and lack of method, especially at ice-free seas. Inverse modeling observations are even fewer. Therefore, the current investigations from a few scattered sites are quite insufficient to obtain a global estimation of the CH₄ emission triggered by offshore oil-gas and methane hydrate explorations.

Summary

Massive CH₄ leakage from seafloor can be triggered by both offshore oil-gas explorations and marine methane hydrate recovery. Both field investigations and model results showed that CH₄ leakage from seafloor, especially from shallow seafloor with depth less than 100 m, may have affected the atmospheric CH₄ budget. The shallow-ocean CH₄ degassing should be considered in the policy-making on the greenhouse gas mitigation and pollution abatement. While the potential consequence of possible massive CH₄ release due to commercial methane hydrate exploration in the near future is still unknown and should be fully considered.

To quantify the oceanic CH₄ degassing regionally or globally, the combination of “bottom-up” calculation and “top-down” modeling is recommended. However, field monitoring approaches still need to be developed to evaluate CH₄ ebullition fluxes at sea.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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