

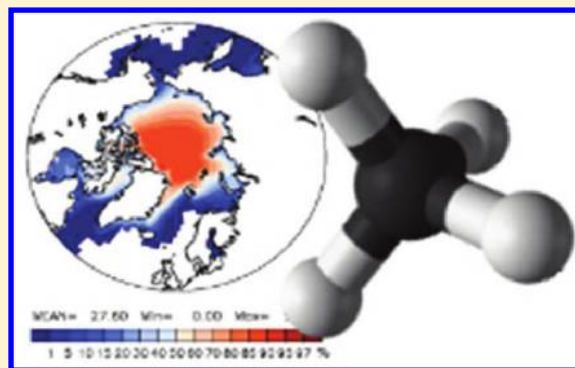
Review of Methane Mitigation Technologies with Application to Rapid Release of Methane from the Arctic

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S Supporting Information

ABSTRACT: Methane is the most important greenhouse gas after carbon dioxide, with particular influence on near-term climate change. It poses increasing risk in the future from both direct anthropogenic sources and potential rapid release from the Arctic. A range of mitigation (emissions control) technologies have been developed for anthropogenic sources that can be developed for further application, including to Arctic sources. Significant gaps in understanding remain of the mechanisms, magnitude, and likelihood of rapid methane release from the Arctic. Methane may be released by several pathways, including lakes, wetlands, and oceans, and may be either uniform over large areas or concentrated in patches. Across Arctic sources, bubbles originating in the sediment are the most important mechanism for methane to reach the atmosphere. Most known technologies operate on confined gas streams of 0.1% methane or more, and may be applicable to limited Arctic sources where methane is concentrated in pockets. However, some mitigation strategies developed for rice paddies and agricultural soils are promising for Arctic wetlands and thawing permafrost. Other mitigation strategies specific to the Arctic have been proposed but have yet to be studied. Overall, we identify four avenues of research and development that can serve the dual purposes of addressing current methane sources and potential Arctic sources: (1) methane release detection and quantification, (2) mitigation units for small and remote methane streams, (3) mitigation methods for dilute (<1000 ppm) methane streams, and (4) understanding methanotroph and methanogen ecology.



■ INTRODUCTION

Methane is the most important greenhouse gas (GHG) after carbon dioxide (CO₂). It contributes 14% of current GHG emissions by the most common measure, and 30% of current net climate forcing.^{1,2} Although emissions of methane are much smaller than those of CO₂ by mass, methane is far more potent a GHG, even as it is shorter-lived in the atmosphere. Averaged over the (most common) 100-year time scale, methane is 25 times more potent than CO₂ per unit mass. Over a 20-year time scale, which is relevant to the near-term threat of crossing a climate tipping point, methane is 72 times more potent.² Recent research suggests that methane is more potent still when accounting for its indirect effect on aerosol formation.³

In addition to the warming effect of current forcing and emissions, methane plays a role in climatic feedback mechanisms that can exacerbate warming and even lead to abrupt, catastrophic climate change in the future. This risk is primarily associated with the rapid release of carbon stores in the Arctic due to warming, leading to higher atmospheric methane levels, especially in the Arctic. Warming due to higher Arctic concentrations, in turn, leads to additional methane releases in a positive feedback cycle.^{4–7}

A major release of Arctic methane would have a devastating impact on the global climate and air quality,⁸ and evidence

indicates it has played a role in past warming events in the paleoclimate record.^{7,9–11} Although the major cause remains disputed, Arctic methane is proposed as a driver of the Paleocene–Eocene Thermal Maximum, when global temperatures rose by about 6 °C, triggering mass extinctions. Contributing to the risk, the climatic response to methane release is superlinear: additional emissions deplete the abundance of the OH· radical in the atmosphere, the primary methane sink, and thereby increase the lifetime of atmospheric methane. Additionally, atmospheric feedbacks with ozone, water vapor, and clouds add to the forcing from methane emissions.^{12,13}

If the beginnings of a rapid methane release are detected, it would very likely be desirable to stage a large-scale technological intervention to contain Arctic methane and avoid triggering the feedback loop. Such an intervention would not replace general efforts to reduce GHG emissions and mitigate climate change, but could be considered an emergency counter-measure to avoid the worst outcomes.

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Climate-feedback risks aside, reducing methane emissions has been identified as a low cost, near-term approach to climate change mitigation.^{14–17} Moreover, in light of continuing failure to address global CO₂ emissions,¹⁸ recent analyses recommend a strategy of aggressive reductions in “short-lived climate forcers,” i.e., methane and black carbon, as an alternative approach to limit warming in the next few decades. Reductions in short-lived forcers open an emissions path for CO₂ that can still avoid dangerous levels of warming, and have substantial cobenefits for human health and crop yields.^{19,20}

Mitigation options have been explored or deployed for the major current sources of methane: livestock, oil and natural gas systems, landfills, coal mines, animal and human waste, and rice paddies. Development of these mitigation technologies has generally been specific to the type of source, with limited application across types. In some cases, technologies that have been developed for other purposes may be applicable to methane mitigation.

This paper first describes the current sources of methane emissions. We then review the mitigation technologies and strategies available, with particular attention to common themes across sources. Where possible, we group the mitigation technologies according to the following categories of sources: (1) confined sources, where the gas is physically contained or in a managed flow, (2) area sources, where the gas is emitted relatively uniformly over an area of land, (3) aqueous sources, where the gas is created within or must pass through a water column, and (4) unconfined sources, where the gas is at a locally elevated concentration but open to the atmosphere. We then briefly review potential sources of rapid methane release in the Arctic. In light of known technologies and sources of methane emissions, we assess the options for future development of mitigation technologies for Arctic sources and for methane generally. We conclude with recommended directions for further work.

■ CURRENT SOURCES OF METHANE EMISSIONS

About two-thirds of current methane emissions are anthropogenic, with the other third coming primarily from natural wetlands.²² Figure 1 shows the sources of anthropogenic methane estimated for the year 2010. The emissions data in Figure 1 are based on the most recent source for global methane emissions estimates,²¹ however several alternative data sets are available.^{23–25} The line between anthropogenic and

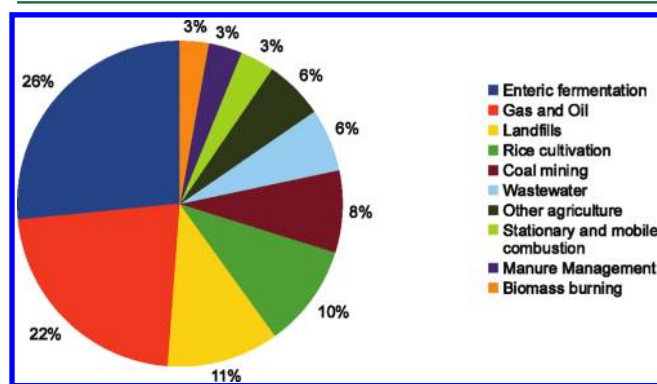


Figure 1. Global anthropogenic methane emissions by source in 2010. Total emissions = 340 Tg (Mt) CH₄. Data from EPA.²¹ The data are projected, with 2005 being the most recent year for which retrospective data are reported.

natural emissions is fuzzy, with human perturbations such as land-use change and climate change influencing emissions from natural systems, but here we use the term to refer only to direct emissions from human activities. Although many such activities contribute to methane emissions, they all essentially operate by one of three mechanisms:

1. Creation of conditions for methanogenesis. This leads to emissions from enteric fermentation, rice cultivation, landfills, manure, wastewater treatment, and agricultural soils (listed under “Other agriculture” in Figure 1).
2. Extraction and release of fossil methane. This includes leaks and venting during extraction and distribution of oil and natural gas, and from coal mining.
3. Release of products of incomplete combustion. This includes emissions from stationary and mobile combustion of fossil fuel, biomass burning, and several sources included under “Other agriculture”: prescribed burning of savannas, burning of forests for clearing, and field burning of agricultural wastes.

Methanogenesis is the conversion of organic material to methane under anaerobic conditions by methanogenic archaea. The process accounts for about 60% of anthropogenic emissions. “Enteric fermentation”, the largest single source of emissions, refers to methanogenesis in the guts of ruminant livestock (cattle, goats, sheep). A number of strategies have been explored to reduce the emissions, not least because the methanogens are parasitic on the livestock by taking useful energy from their feed, though no definitive solution has yet been found.^{26,27} Collections of organic wastes (landfills, manure ponds, wastewater treatment systems) also emit methane through methanogenesis. Some mitigation methods are mature and widely applied in the developed world (especially for landfills, discussed further in the next section) but the sources remain significant globally. In rice cultivation, soils are usually inundated with water, producing methane in the same way as natural wetlands. Other agricultural soils are sometimes a source and sometimes a sink for methane, and on balance are a minor contributor.

Fossil methane is the primary constituent of natural gas and is coextracted, to varying degrees, from oil and coal formations.²¹ Leakage and venting of this gas contributes roughly 30% of anthropogenic emissions. Natural gas systems, in turn, contribute the majority of that share.^{21,28}

The leakage of methane from natural gas systems has received attention lately, driven by the recent and projected massive growth in natural gas extraction from shale formations, or “shale gas”.²⁹ Shale gas extraction tends to be leakier than conventional gas extraction. Based, in part, on a recent upward revision of estimated leakage rates by the U.S. EPA³⁰ and by a recent higher estimate for the warming impact of methane,³ Howarth et al.³¹ reached the provocative conclusion that shale gas can be more harmful to the climate than coal over its life cycle. Wigley³² reaches the same conclusion, though largely by a different route, that is, by accounting for the cooling effect of aerosols associated with coal combustion that do not accompany natural gas combustion. The large magnitude of methane leaks from natural gas production has been disputed in other studies,^{33–35} with Jiang et al., for example, finding that the life-cycle GHG impact of producing electricity from shale gas is 20–50% lower than that from coal.³³ The differences in findings stem primarily from different treatment of (1) the methane leakage rate, (2) the relative greenhouse impacts of

methane versus CO₂, (3) the differential efficiency of coal versus natural gas power plants (neglected by Howarth et al.), and (4) the cooling effect of aerosols (included only by Wigley). All studies agree, however, that the leakage of methane from natural gas and especially shale gas extraction is significant and should be controlled. A number of techniques and technologies are available to reduce leakage, but in the absence of regulatory drivers, many are not in wide use.³¹

In contrast to methane emissions from oil and gas operations, which largely come from equipment leaks, system upsets, and process units, coal mine methane is emitted more directly from the mine itself. About half of coal mine methane is emitted in ventilation air from active underground mines, with significant shares also coming from surface mines, abandoned mines, and pre- and postoperation drainage gas from underground mines.³⁶ Mines are ventilated to keep methane concentrations in the mine below ignition levels, which, by definition, creates a large-volume stream of methane too dilute to treat with conventional flaring. Although only a small fraction of ventilation air methane (VAM) is currently mitigated, it has, more than any other source, motivated development of a range of mitigation technologies for dilute methane streams. Drainage gas is more commonly mitigated because the higher methane concentration allows a wider range of productive uses.

Incomplete combustion is the final mechanism for methane emissions, contributing 9% of anthropogenic emission. It includes biomass burning at small scales for cooking and heating (primarily in the developing world) and for agricultural applications, such as field-burning of residues and clearing of savanna and forests for cultivation. The nonagricultural sources, which contribute at least a third of emissions by this mechanism, can be controlled by well-known methods such as the use of more efficient cookstoves or switching to different fuels.

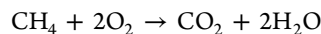
■ REVIEW OF MITIGATION STRATEGIES

Technologies to mitigate anthropogenic methane emissions have been developed for a variety of the sources described above. It is also possible, in principle, to reduce emissions from natural sources, but this would most likely take the form of wetland drainage, which has major drawbacks in terms of ecological consequences and increased CO₂ emissions.³⁷ We reviewed the literature on mitigation for the largest sources of current methane emissions as well as literature on methane catalysis and methane generation and destruction in biotic systems. Nearly all of the mitigation literature focuses on a particular source, and indeed, many mitigation strategies are unique to a type of source. For example, landfill emissions can be reduced by composting organic wastes and diverting paper for recycling;³⁸ enteric fermentation can be reduced by reducing meat consumption; VAM emissions can be reduced by increasing preoperation drainage and utilizing the drainage gas; and natural gas leaks and venting can be reduced by updating and tuning equipment. In this paper, however, we focus on common themes across methane sources and leave the strategies with unique applications to the literature on specific sources.

Across sources, when methane is present in gas phase (in a mixture with air or other gases), the goal of mitigation is usually to oxidize the methane to CO₂. Although CO₂ is also a GHG, its warming effect is much weaker. At least 89% of the greenhouse impact of methane is eliminated by converting it to

CO₂ (methane is considered 25 times more potent on a mass basis, but only 9 times more potent on a molar basis on a 100-year time scale). One could, in principle, also capture the resulting CO₂ and sequester it for additional climate benefit, but this would generally not make sense as long as other, more concentrated CO₂ streams (like power plants) were available.

The complete oxidation of methane follows the reaction



which is strongly exothermic, having $\Delta H_{\text{rxn}} = -891$ kJ/mol. However, the reaction has a substantial activation energy. The first deprotonation, the limiting step, requires 430 kJ/mol.^{39,40} The reaction is spontaneous at 1000 °C,⁴¹ but the required temperature can be lowered by use of a catalyst. Such catalysts have been developed for oxidation of VAM that can lower the activation temperature to 300–400 °C.⁴² Much of the recent work has focused on partial oxidation of methane to species appropriate for liquid fuels, such as alcohols.^{43,44} The catalysts are generally composed of transition or platinum group elements supported on oxides, and may be enhanced by ultraviolet (UV) radiation. These have been shown to work at temperatures as low as 50 °C.⁴⁰ For producing liquid fuels, the difficult aspect of the problem is how to carry out incomplete oxidation,⁴⁵ suggesting that developing a catalyst for complete oxidation would be an easy modification.

In biotic systems, methane is generated from organic matter by methanogenic archaea and is metabolized to oxidation products by methanotrophic bacteria and archaea. The net emissions from a system are determined by the balance between these two processes. Mitigation strategies generally involve containing and treating the methane generated (e.g., the cap over a landfill or manure pond), limiting overall biological activity (e.g., by keeping a landfill dry), or manipulating the balance between the two microbial processes (e.g., by aeration and turnover in a composting facility).

The dominant process is determined primarily by the redox potential of the substrate (aerobic vs anaerobic environment), but also depends on a number of other factors. Electron-accepting species (Fe³⁺, Mn⁴⁺, SO₄²⁻, NO₃⁻) compete with methanogens for hydrogen and carbon substrates. Thus, for example, gypsum (CaSO₄·2H₂O) addition was found to reduce methane emissions in soils even in anaerobic conditions.⁴⁶ Nutrient availability also plays a role, e.g. potassium and phosphorus addition was found to favor methanotrophs in agricultural soils.⁴⁶ Biocides were found to reduce methanogenic activity in soil studies and in the guts of cattle, but generally have a temporary effect.^{27,47,48}

Confined Sources. Methane from confined sources, where the gas is physically contained, can be managed with industrial process units. Methane can be ignited in air at a concentration of 5% or more, in which case flaring is the simplest and least capital-intensive mitigation strategy. However, a number of technologies have been developed to generate energy and/or oxidize methane from more-dilute streams.

Table 1 shows a summary of methane mitigation options. The concentration of methane in a given stream chiefly determines the options available to mitigate it. However, availability of the stream, variability of concentration, and total flow also place constraints on the options available. For comparison, Table 2 shows typical concentrations for some methane sources.

Very reliable, high-purity streams can be used as chemical feedstocks, with methanol and carbon black production among

Table 1. Summary of Mitigation Options for Confined Sources^a

technology	min concn.	notes and references
methanol production	89%	need 95% availability ⁴⁹
carbon black production	84%	49
purification by N ₂ , O ₂ removal	40%	releases waste methane ⁴⁹
spark ignition/internal combustion engine	40%	widely used for landfill gas, demonstrated for coal mine methane ⁵⁰
gas or steam turbine	30%	used for landfill gas ^{49,50}
fluidized bubbling bed combustion	6%	as modeled, demonstrated at 8% ⁵¹
homogeneous charge gas engine	5%	49
open flare	5%	spark point of methane ⁵²
lean-burn gas turbine	1.6%	53
catalytic lean-burn gas turbine	1%	49, 53, 54
catalytic monolith reactor	0.4%	49
concentrator (activated C)	0.4%	prototype ⁴¹
thermal flow reversal reactor	0.2%	36
catalytic flow reversal reactor	0.1%	36
bioreactors	2 ppm	in principle; 300 ppm tested in prototype ⁵⁵
combustion air in coal plant		no limited concn. but limited capacity ⁴⁹
combustion air in gas turbine		need modified design to avoid leaks ⁴⁹
combustion air with waste coal production		depends on cocombustion of waste coal ^{36,49}

^aMin concn. is the minimum sustained methane volume fraction required for operation, and ppm is parts per million.

Table 2. Methane Concentrations for Some Major Sources of Methane Emissions

source	CH ₄ volume fraction	reference
free air (current)	1.8 ppm	56
Arctic air	2–8 ppm	57
urban air	2–10 ppm (Moscow 2003–2005)	58
cattle feedlot, open	2–10 ppm (case study)	59
swine feeding or dairy milking ventilation air	10–300 ppm	55,60
enclosed manure storage headspace	140–28,000 ppm (2.8%)	55
U.S. landfill, at surface	<500 ppm by regulation	61
coal mine ventilation air	0.1–1% typical, <1% by regulation	62
anaerobic digester gas	35–65%	63
landfill drainage gas	40–60% at peak production	63
coal postmining drainage gas	30–95%	49,52
coal premining drainage gas	60–95%	49,52
natural gas, at wellhead	75–99%, typical	64

the highest-volume uses. High-purity streams can also be sold into the natural gas distribution grid. Above about 40% concentration, the stream can be economically purified and then sold into the grid by methods used for conventional natural gas purification. In the concentration range 30–60%, a variety of technologies are applied to coal mine drainage gas, landfill gas, and gas from anaerobic digesters.

Landfill gas utilization is a relatively mature application, with hundreds of facilities operating in the U.S.⁵⁰ Internal combustion engines are used at the majority of the facilities, but gas turbines, steam turbines, and direct utilization of the gas in various industrial processes are also common.⁵⁰ In the U.S., landfill gas utilization for energy is economic compared to flaring in many cases, and would be economic at many more landfills with a minor subsidy.⁶⁵

As discussed previously, VAM from coal mines is a significant source (6% of total U.S. methane emissions).²⁸ By regulation, the ventilation system must keep concentrations below 1%, leading to a large-volume, dilute methane stream. A number of technologies have been developed to treat ventilation air methane (VAM), with commercial units able to handle methane concentrations as low as 0.1% (1000 ppm).^{36,49} The technologies include very lean-burning turbines, which use compression to lower the concentration of methane required for ignition, and catalytic turbines, which employ a catalyst to lower the required temperature of ignition. Both of these generally require some enrichment of the gas stream to operate on VAM. This can be achieved by mixing in some of the premining drainage gas.⁴⁹

Thermal flow reversal reactors (currently the most common VAM solution), catalytic flow reversal reactors, and catalytic monolith reactors can operate on lower concentrations but have less potential to generate energy as a side benefit. They all employ heat exchange to bring the VAM to the autoignition temperature of methane and use the heat of reaction to compensate for thermal losses through the outlet air. The minimum sustainable methane concentration (shown in Table 1) is the thermal break-even point, at which the heat of combustion makes up for losses. The latter two technologies employ catalysts to lower the required temperature, in turn reducing the methane concentration required for thermal break-even. Some thermal inertia in these systems allows temporary fluctuations below the break-even point. When the inlet concentration is significantly above the break-even point, the excess heat can be used for energy.

VAM is the most dilute methane stream for which there is active development of mitigation technologies. It is a very new market, with only a handful of commercial units in place.⁶⁶ Unlike landfill gas, which can generate revenue from energy production, there is no incentive to mitigate VAM in the absence of a carbon market or other regulatory driver. However, in the context of a carbon market the strategy is very cost-effective; the estimated payback period for thermal flow-reversal reactors is 3–6 years at a relatively modest carbon price of \$10/ton-CO₂-equivalent.⁶⁷

A tempting strategy for dilute methane streams is to concentrate the methane using a regenerable sorbent, analogous to CO₂ capture systems, making it available for a higher-value use. Unlike CO₂, however, methane does not react to form a soluble ion in solution. It is only soluble to several ppm by mass in common solvents.⁶⁸ Solid sorbents work better, with activated carbon among the best, adsorbing 300 ppm by mass for 1% methane gas at atmospheric pressure.⁶⁹ Environmental C & C, Inc., in partnership with the U.S. EPA, demonstrated a concentrating system using activated carbon in a dual fluidized-bed configuration. The test was deemed technically successful but the company concluded a better sorbent would be needed for the process to be cost-effective.⁴¹

Bioreactors are used to treat ppm and ppb (parts per billion) concentrations of volatile organic compounds and have been

demonstrated in a range of laboratory- and field-scale experiments for methane mitigation from landfill gas⁷⁰ and gas from manure storage.⁵⁵ They employ a population of methanotrophs on a porous, solid substrate, such as sand, perlite, or woodchips, usually mixed with compost. Because methanotrophs that metabolize methane at atmospheric concentrations (2 ppm) are common, a bioreactor could theoretically treat very low concentrations, however higher concentrations have been tested in practice as most systems are intended for landfill gas. In the review by Scheutz et al., tested concentrations ranged from 0.07% to 100% methane.⁷⁰ Melse and van der Werf measured substantial methane oxidation at inlet concentrations down to 300 ppm in a system designed for gas from manure storage and ventilation from swine and dairy houses.⁵⁵

Very dilute methane streams can also be used as air in combustion processes, such as fossil-fueled power plants. Some complications arise since fluctuations in the methane concentration can interfere with the plant operation. Also, gas turbines are not amenable unless reconfigured, since typically some of the inlet air is used for cooling and vented rather than combusted, which would release unburned methane. Overall, the main drawback is simply the limited capacity of combustion processes likely to be near a given methane source.

Although speculative, another approach is to use UV-activated titania (TiO_2) catalysts to oxidize methane. In the presence of UV light, water vapor, and O_2 , TiO_2 catalysts generate OH, and HO_2 radicals.^{71,72} Koziel et al.⁷¹ propose a system for oxidizing volatile organic compounds in the exhaust of confined swine feedlots using UV-activated TiO_2 . The system is designed to control odor and pathogen emissions; methane reduction was not measured, but the system should, in principle, also reduce methane.⁶⁰

Area Sources. Area sources emit methane somewhat evenly over a large area. Landfills are the most prominent example and are associated with a well-developed suite of mitigation technologies. Some agricultural soils (those with net positive methane emissions) are area sources. Manure ponds, wetlands, and rice paddies, although they are also aqueous sources (discussed further below), are useful to consider as area sources. Three general strategies have been developed to mitigate area sources: suppressing methanogenesis, caps, and biocovers.

Means of suppressing methanogenesis vary by source. For landfills, the strategy is to minimize water intrusion.⁷³ For agricultural soils, periodic drainage, aeration, and manipulation of nutrient additions have been shown to be effective.^{27,46} For manure collected under feeding houses, cooling has also yielded a moderate reduction in emissions.^{26,27}

Caps are the typical method for controlling landfill emissions. The landfill is covered with an impermeable layer—a plastic sheet or layer of clay—and an array of wells and pipes is installed which collects the trapped gas and directs it to treatment. The collected methane is then a confined source, subject to the mitigation technologies described in the previous section. Manure ponds, similarly, can be covered with an impermeable sheet and the gas can be collected. An alternative approach is to collect the manure in an enclosed reactor, an “anaerobic digester”, and promote methanogenesis through control of temperature, moisture, and mixing. This produces a confined stream of methane for utilization. The technique is applicable to many organic materials, and is common for treating sludge from wastewater treatment.^{74,75}

Biocovers are the third approach to mitigating area sources. We use the term in a general sense, to refer to any permeable, biologically active layer which hosts methanotrophs to oxidize the methane passing through. Biocovers have been developed and studied extensively for application to landfills, where they can be used before a cap is installed, in conjunction with a cap and collection system, after the collection system has ceased operation, or, in some circumstances, in place of a cap. While a landfill is still being actively filled, “bio-tarps”—synthetic geotextiles that host methanotrophs—have been proposed as a daily cover.^{76,77} In a laboratory study, biotarps absorbed 4–7.4 g $\text{CH}_4/(\text{m}^2\cdot\text{d})$, although this is much less than measured fluxes at uncovered landfills (e.g., 400 g $\text{CH}_4/(\text{m}^2\cdot\text{d})$)⁷⁸ and did not yield a detectable reduction in field tests.⁷⁷

For intermediate and permanent installations, a layer of soil is the simplest biocover. In a review of studies of cover soils for landfills, Chanton et al. found that 10–89% (mean 36%) of methane escaping from the underlying landfill is oxidized in the cover, amounting to a mean of 72 g $\text{CH}_4/(\text{m}^2\cdot\text{d})$.⁷⁹ Engineered biocovers work similarly, but make use of specially selected substrates to maximize methane oxidation. Scheutz et al.⁷⁰ review studies of simulated engineered biocovers. Steady-state oxidation rates up to 583 g $\text{CH}_4/(\text{m}^2\cdot\text{d})$ and 100% of inlet methane were achieved (mean of 47 reported values = 106 g $\text{CH}_4/(\text{m}^2\cdot\text{d})$, 66% of inlet). A handful of field demonstrations has yielded mixed success, indicating that biocovers must be tailored to the location. Huber-Hummer et al.⁷⁶ identify the most important features in a biocover generally as follows: 0.5–1 m depth, high porosity (especially in the bottom layer, to allow good distribution of gas as it rises), good drainage (to allow steady supply of oxygen and avoid anaerobic zones), and minimal fresh organic carbon (otherwise the pore structure compresses as the fresh organic carbon degrades).

Aqueous Sources. The vast majority of natural emissions are from aqueous sources, primarily from wetlands. As in most natural waters, methane is both produced and consumed in the sediments and water column, but the carbon-rich, shallow conditions in wetlands favor net methane production to a much greater degree than in oceans, lakes, or other water bodies.²² Rice paddies are the most important aqueous, anthropogenic source of methane. They mimic natural wetlands in terms of creating a shallow, nutrient- and carbon-rich environment favorable to methanogenesis. Manure ponds, another important anthropogenic source, are similarly rich in organic carbon, nutrients, and largely anoxic.

Mitigation measures for manure ponds include caps, as discussed in the previous section, or diverting the manure to avoid forming a storage pond in the first place. Mitigation strategies for rice fields, on the other hand, consist of manipulating the redox environment and the availability of organic carbon and nutrients to suppress methanogenesis. For example, periodic drainage of the field, which introduces oxygen and keeps the methanotroph population from taking hold, is widely effective.^{27,46,80,81} Shallow, as opposed to deep, flooding also reduces emissions.^{46,80} The use of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) instead of urea ($(\text{NH}_2)_2\text{CO}$) as a fertilizer reduces emissions as does applying gypsum with urea instead of urea alone.⁸⁰ The use of organic fertilizers with a lower C:N ratio, such as chicken manure and composted rice straw (as opposed to fresh rice straw), reduces emissions.⁸⁰ Similarly, the addition of organic carbon in the off-rice, dry season reduces emissions compared with addition to a wet field.²⁷ These latter

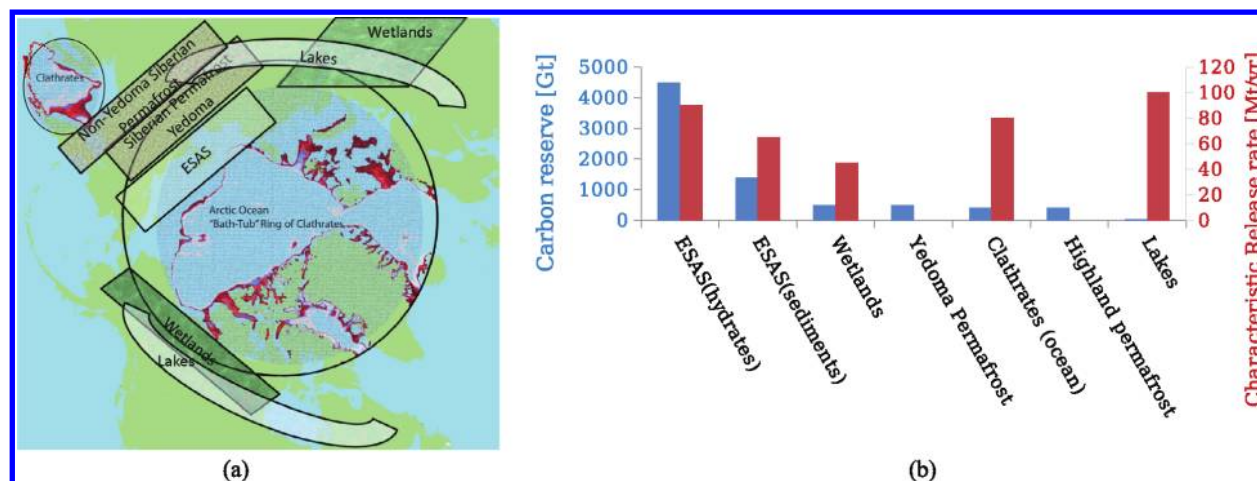


Figure 2. Major potential sources of Arctic methane. (a) Map (looking down from above the North Pole) showing general locations of sources in the Arctic. Red areas indicate clathrate deposits susceptible to melting.⁵¹ (b) Chart showing estimates of carbon stock and characteristic release rate for each source. Characteristic release rate is the high end of estimates of expected release (where multiple estimates are available) but does not include surprise rapid releases, which are not expected but cannot be ruled out. A table of values used in (b) with references is provided in SI.

two strategies reduce the availability of organic carbon in submerged conditions.

Unconfined Sources. We consider anything open to the atmosphere and not captured in the above three categories as an unconfined source. Methane from any source, once released to the air, is unconfined, although it may be present at locally elevated concentrations. In general, mitigation strategies for unconfined sources are speculative, with the exception that some types of land are known to oxidize methane from the air. Boreal forests, temperate forests, and temperate pastures are estimated to be the strongest sinks, with mean fluxes of -65 ± 28 , -44 ± 24 , and $-55 \pm 38 \mu\text{g CH}_4/(\text{m}^2 \cdot \text{hr})$, respectively.⁴⁶

In principle, one could balance unconfined methane sources by land management policies that increase natural sinks, much the way afforestation is suggested as a means to offset CO₂ emissions.¹ However, note that the fluxes for even the best natural sinks are quite small compared with, e.g., the global mean wetland emissions of $3400 \mu\text{g CH}_4/(\text{m}^2 \cdot \text{hr})$.⁴⁶ Accordingly, all land combined oxidizes about 10% of atmospheric methane (the remainder reacting with OH· and other oxidants in the atmosphere).⁵⁶ Only a substantial change in the global balance of land types could noticeably influence atmospheric concentrations.

Another approach to unconfined sources is to ingest air into a treatment system. Such an approach has been proposed to capture CO₂ from the atmosphere as a means of climate mitigation.^{82,83} Although methane is about 200 times more dilute in the atmosphere, the energy released when oxidizing it to CO₂ is much larger than the theoretical minimum energy required to concentrate it. For this reason, Boucher and Folberth³⁹ found promise in atmospheric methane capture and discussed several chemical approaches for further investigation. However, they did not consider the necessary scale of meaningful atmospheric methane capture. Because the chemical lifetime of atmospheric methane is about 10 years, any strategy which significantly reduces atmospheric methane concentrations would have to contact on the order of 1/10 of the atmosphere each year to compete with natural sinks. Such a scale is not feasible with industrial process units of the type proposed for CO₂ capture. In principle, it might be feasible with catalytic aerosols, but a suitable material is not currently known.

A calculation for each case is provided in Supporting Information (SI). Although locating a capture system in a region with higher concentrations would make the task easier, methane concentrations in urban and Arctic air are only modestly elevated (see Table 2). Therefore, efforts should be focused on concentrated sources of methane, near the point of generation or release.

It may be possible to oxidize methane in situ using a catalyst since the reaction is thermodynamically favorable. A catalytic material could be deployed as airborne particles, floated on water surfaces, or anchored to solid surfaces near methane sources. The challenge would be to find a gas-phase catalyst effective at ambient temperature and scalable to large quantities. UV-activated TiO₂ (as discussed above) is a promising route. Generating forms of TiO₂ that efficiently use sunlight is an active area of research.^{72,84}

Biotic systems, of course, do oxidize methane in ambient conditions but using an aqueous-phase mechanism. The key hydroxylation of methane is achieved by the enzyme methane monooxygenase (MMO). This reaction allows microbes to use methane both as a source of carbon and energy.^{85,86} Very recently, the identity of the metal cofactor for one of the types of MMO has been reported.⁸⁷ Research is ongoing into understanding the active site of this enzyme which would allow the building of synthetic mimics for uses including engineered oxidation of methane for environmental applications.⁸⁸ A reactor based on MMO or a cultivated population of methanotrophs could be used to oxidize unconfined sources of methane. However, it would have to operate in a water body, liquid film, or moist solid substrate (as in soil particles). Such a scheme can be considered an open bioreactor. The challenge would be to achieve sufficient air exchange to oxidize a significant fraction of the available methane.

Finally, high-energy lasers can be used to dissociate methane in the gas phase. If the concentration of methane is high enough to sustain combustion, then a laser can be used as a remote ignition source.⁸⁹ Such concentrations are likely to be rare for unconfined sources. At lower concentrations, a laser would need to deliver enough energy to break the first C–H bond (435 kJ per mol of CH₄ destroyed), which is prohibitive,

not to mention that lasers of this intensity also dissociate O₂ and N₂.⁹⁰

■ POTENTIAL SOURCES OF RAPID METHANE RELEASE

There are many natural sources of methane globally, including tropical and northern high-latitude wetlands,⁹² ocean surface waters,⁹³ marine hydrocarbon seeps,⁹⁴ undersea mud-volcanoes,⁹⁵ and other geothermal sources. In this paper, however, we focus on the Arctic sources of methane, which are more vulnerable to a changing climate. Recent reviews^{4–6} on methane emissions highlight the potential role of Arctic releases in warming scenarios. The Arctic is home to massive stores of carbon (see Figure 2) buried particularly in sediments below the sea and in wetlands and permafrost soils. These pools of carbon developed over millennia and are held in place by the unique climatic and geographic features of the region, primarily permafrost layers (soils frozen year-round) and low ocean temperatures. Current and projected warming in the Arctic is more extreme than other parts of the globe, potentially destabilizing large quantities of stored methane and organic matter. Below we describe eight carbon pools that may contribute substantially to atmospheric methane. They are distinguished by geography and pathway of release. Some methane release has been documented for most of these sources. The question is not whether but how much and how quickly methane will be released due to warming, and whether it will be enough to trigger a runaway feedback loop.

The carbon in the sources below essentially takes three forms: methane gas trapped in pockets below the surface or sea bed, methane trapped in ice crystals (known as clathrates or methane hydrates), and organic matter that can turn to methane through methanogenesis. In analogy with the mitigation strategies reviewed in the previous section, we group the sources into aqueous sources and area sources.

Aqueous Sources. Methane from aqueous sources generally originates at the bottom of the water column. It can reach the atmosphere by one of two mechanisms: (1) diffusion through the water column and then across the air–water interface, or ebullition (bubbling) that reaches the surface. Ebullition is the dominant mechanism in Northern lakes, contributing 96% of estimated emissions.⁹⁶ In the ocean over the East Siberian Arctic shelf (described below), ebullition contributes 60% of current methane emissions⁹⁷ and in Arctic wetlands, it contributes 18–50%.⁵

Methane bubbles can range in size from a fraction of a millimeter to several centimeters in equivalent diameter^{98–100} and have been observed originating from ocean depths up to 2500 m.^{99,100} Bubbles can occur individually or in plumes, torches, or curtains.^{97,98,100,102–104} The largest bubbles generally come from discrete releases, known as blowouts or eruptions. Bubbles several meters in size were observed in one such event.⁹⁹

As a bubble rises, some or all of the methane may dissolve into the water column before it reaches the surface. The amount of methane that dissolves depends on the bubble diameter, depth of release, and methane concentration in the surrounding water. Using a rigorous single-bubble model validated against field measurements, McGinnis et al.⁹⁸ conclude that only bubbles released from depths less than 100 m can transfer significant methane to the atmosphere except in cases of “catastrophic” bubble release. Accordingly, much of the methane released to the water column does not

reach the surface. For example, in a study of a large seep field off the coast of California, Mau et al.¹⁰⁵ find that only about 1% of the methane released at the sea floor reaches the atmosphere. The remainder dissolves in the water column and is oxidized by methanotrophs.

The activity of methanotrophs is controlled by the availability of nutrients and oxidants. In fresh waters, the primary oxidant is O₂,¹⁰⁶ whereas in the oceans, it is sulfate (SO₄²⁻), following the overall reaction⁸⁶



While most of the methane released into the oceans is oxidized by this or another mechanism, the work of methanotrophs can be overwhelmed locally. Shallow ocean waters in areas of active methane venting, such as the East Siberian Arctic Shelf (ESAS), are supersaturated in methane,⁹⁷ inhibiting rising bubbles from dissolving. In waters with increased methane venting, we would expect higher methane concentrations in the water column if natural oxidation rates fail to keep up with the larger input. In turn, bubbles would reach the surface more frequently. Higher methane concentrations at the water surface also lead to a larger diffusive flux to the atmosphere.

Below we describe the four carbon pools most at risk to release large quantities of methane to the water column and hence to the atmosphere. They are characterized by large stocks of carbon that are susceptible to release due to shallow conditions or, in the case of deeper ocean clathrates, in the event of rapid destabilization.

Ocean Clathrates (>300 m Depth). Subseabed methane is primarily produced by microbial and thermogenic processes. At sufficiently low temperature and high pressure, it can form methane hydrates (or clathrates), solid crystalline compounds in which gas (mostly methane) molecules are lodged within the lattices of water crystals.^{91,107,108} Hydrate deposits are widespread in the marine sediments on the continental margins and in permafrost regions, trapping a vast quantity of methane.¹⁰⁹ Estimates of the global stock of methane hydrates in the ocean range from 500–3000 Gt C at the low end^{110,111} up to 74 400 Gt C.¹¹² The arctic region alone is estimated to have a large clathrate reservoir of about 400 Gt C.¹¹³

The regions of the ocean floor and sediments of sufficient depth and sufficiently low temperature to support the formation of hydrates are known as the Gas Hydrate Stability Zone (GHSZ). As the ocean warms, the GHSZ migrates, leaving some hydrates to dissociate and release methane. Recent field investigations have observed substantial methane gas plumes emanating from the seafloor along the Arctic ocean margin at depths of 150–400 m, at and above the present upper limit of the GHSZ.¹¹⁴ In a simulation of the Arctic Ocean with expected warming, Reagan et al.⁹¹ estimate the amount of susceptible methane clathrates over the entire Arctic basin is in the range of 1.6–8 Gt CH₄ over the next century, with an additional 4.3–22 Gt CH₄ over the subsequent two centuries without any further temperature change.

If released slowly, most methane from these deeper ocean clathrates is not expected to reach the atmosphere. However, if released in a blowout-type event, such as observed by Leifer et al.,⁹⁹ the plumes can reach the surface, depending on the depth and the size of the blowout. The risk of widespread, rapid release from deep clathrates is generally considered low, but cannot be ruled out.⁷

Clathrates on the East Siberian Arctic Shelf (ESAS). The Siberian shelves and continental slope include the near shore

areas of East Siberian Sea and Laptev Sea between 132–179 °E and 69–74.5 °N covering an area of about 3 million km². The region is a large store of methane hydrates, as well as free gas in pockets below permafrost and in sediment pore space; release of 0.1% of the estimated 6000 Gt CH₄ of stored hydrates could double atmospheric methane.¹¹⁵ Most deposits are in much shallower waters than the hydrates discussed above, with 70% of shelf area less than 40 m in depth.¹¹⁵ The hydrates are generally capped by permafrost sediments that, until recently, were thought to trap the gas even in a warming climate, but field measurements indicate that the permafrost cap is imperfect and older methane from below the permafrost is reaching the atmosphere.^{57,97}

Growth in emissions from the ESAS could occur gradually, as the result of smooth diffusion through sediments, or rapidly, as a result of a blowout or series of blowouts.¹¹⁶ Nicolsky and Shakhova¹¹⁷ propose open taliks (thawed zones connecting the sediments above and below the permafrost layer) as a mechanism for methane release that explains current observations. Biastoch et al.¹¹⁸ use an ocean/sea ice model to predict that 25% of ESAS hydrates can be destabilized in warming scenarios. They find it unlikely that enough methane can be released to trigger a warming feedback this century, but that a feedback on longer time scales can lead to warming of up to 0.8 °C. Their model also predicts substantial ocean acidification this century. They calculate an upper-limit release rate of 162 Tg CH₄/yr. Shakhova et al.¹¹⁹ estimate a release rate of 90 Tg CH₄/yr.

Sediments on the East Siberian Arctic Shelf. Immense amounts of organic matter drain from the Arctic rivers into the ESAS (the Arctic Ocean receives 10% of global river runoff into 1.5% of global ocean volume).^{57,120} In addition, much of the shallow Siberian Arctic shelf becomes exposed in lower-sea-level, glacial eras, forming permafrost layers of these carbon-rich sediments. Methane generated through methanogenesis becomes trapped below the permafrost layers and incorporated into the permafrost as hydrates. This permafrost layer is now preserved below ocean water and below an unfrozen sediment layer in the ESAS. An estimated 1400 Gt C is stored in the ESAS sediments as organic carbon, methane hydrates, and free gas.¹¹⁵

As ocean bottom waters warm, some of the subsea permafrost may thaw, triggering methanogenesis from old organic carbon and releasing associated hydrates.¹¹⁵ This is the same permafrost formation as discussed in the previous section, but here we are concerned with methane released from the sediment itself rather than the sediment acting (or failing) as a cap on the larger store of hydrates beneath. In the present case, we would expect to see methane released to the water column somewhat evenly over a large area of thawing permafrost. In the previous case, we would expect patchy releases, associated with localized weakness in the permafrost layer (such as through taliks).

Elevated methane concentrations and methane plumes have been observed extensively in the ESAS.^{57,97,115,121} Methane emissions from sediment thaw are hard to disentangle from methane emissions from leakage through the cap, which is also driven by thawing in the case of the formation of taliks. However, the evidence seems to indicate that methane release from below the permafrost through breaks in the layer is currently the dominant mechanism in the ESAS.⁵⁷

Arctic Lakes. Glacial, alluvial flood plain, peatland, and thermokarst lakes are common in the Arctic and all types

release methane to varying degrees. Thermokarst (thaw) lakes are of particular concern because they convert carbon stored in permafrost to methane, and appear to have increased emissions in response to recent warming.^{96,122}

Lakes are the dominant mechanism of thermal erosion in permafrost areas. Lake surfaces are darker than surrounding ice, absorbing more sunlight and conducting heat to the underlying and surrounding permafrost by convection. Thawing of permafrost along lake margins releases labile organic matter into the anaerobic lake sediments, where it fuels methanogenesis.

In measurements of North Siberian thermokarst lakes, a small share of methane (5%) escapes by diffusion through the water column and to the air, but the rest reaches the atmosphere by ebullition in localized plumes.⁹⁶ The plumes are concentrated along a particular edge of the lake where permafrost is actively eroding. In winter, gas is sometimes trapped by ice cover, but some “hotspots” of methane bubble quickly enough that ice never freezes over them, leaving a year-round vent.

Isotope measurements confirm that thermokarst lakes are primarily emitting old, Pleistocene-era carbon, supporting the hypothesis that they play a role in climate feedbacks. This and other evidence implicates Arctic lakes in the elevated atmospheric methane associated with past warming events, including the Pleistocene–Holocene transition.¹²³

Area Sources. Wetlands. Wetlands (including peatlands) are widespread in the permafrost regions of the Arctic, especially in the lowlands of West Siberia, where they comprise 50–80% of the land (0.6–1 million km²), forming the worlds largest wetland area.^{5,124} They are a significant carbon stock, with estimates in the range 50–70 Gt C for Arctic peat.^{5,124} The peat is composed mainly of marshland vegetation: trees, grasses, and fungi, as well as other types of organic remains.

Methane is produced in much the same way as in other wetlands and rice paddies. Methanogenesis occurs in the inundated “active” (seasonally thawed) layer, above the permafrost and below the water table. Much of it is then oxidized as it migrates up through the aerobic zone by diffusion through the water, ebullition, or through the roots of plants.

Arctic wetlands are currently a net source of methane¹²⁵ and recent isotopic measurements indicate they are the largest source of elevated methane in Arctic air.¹²⁶ Rising temperatures will increase the depth of the thawed layer, making available a deeper store of organic carbon which can contribute emissions. Adding concern, methane from Arctic peatlands has been associated with past warming events.¹²⁷

In a model of Russian permafrost wetlands under several warming scenarios, Anisimov⁵ estimates the annual net flux of methane will increase by a modest 6–8 Mt, however this model does not account for changes in wetland extent or hydrogeology. A warming climate will likely lead to intensification of precipitation extremes¹²⁸ and the global water cycle.¹²⁹ In a warming scenario, changes in precipitation would be a dominant biophysical regulator of methane emissions in the Arctic wetlands and could amplify methane emissions.

Bohn et al.¹³⁰ modeled wetland emissions under various climate scenarios and report that the interaction of temperature and precipitation, through their effects on the water table depth, play an important role. Whereas higher temperatures alone increased methane production in saturated areas, they also caused those saturated areas to shrink, resulting in net methane emission reduction, but higher precipitation alone

raised the water tables and expanded the saturated area resulting in a net increase of methane emissions. An increase in temperature of 3 °C, in conjunction with a 10% increase in precipitation in the western Siberian wetlands, led to a doubling of annual methane emissions. In a simpler calculation, Archer¹³¹ estimates that if 20% of the peat reservoir gets converted to methane over 100 years, this would release 0.7 GtC/yr, doubling the atmospheric methane concentration.

Terrestrial Permafrost. Permafrost soils are one of the Earth's largest carbon pools, containing about twice as much carbon as the atmosphere.^{132–134} Of particular concern are the carbon-rich loess, or yedoma, soils. These are composed largely of plant roots and wind-blown dust deposited in the glacial Pleistocene era. The largest span of yedoma permafrost is in Eastern Siberia, but it also covers parts of North America, totaling about 1 million km² to an average depth of 25 m, and holding an estimated 500 Gt of organic carbon.¹³³ The submerged portion of this same formation comprises much of the organic carbon in ESAS sediments, discussed above.

As permafrost thaws, the labile organic matter can be metabolized either to CO₂ or methane. Even as CO₂, release of permafrost carbon is very likely a significant climate feedback.^{132,133} If the permafrost thaws into wetlands, lakes, or ponds, methane production is favored. The mechanism of methane release from permafrost is thus the same as for wetlands and lakes as described above. Accordingly, there is no characteristic methane release rate associated directly with permafrost in Figure 2; the release can rather be seen as an expansion of emissions from wetlands and lakes. Walter et al.⁹⁶ estimate that from 450 Gt of C in the East Siberian yedoma permafrost, about 49 Gt of methane will be released through lakes if the current thaw pattern continues. Another 23 Gt could be released from nonyedoma permafrost by the same mechanism.¹² The time scale of this release is not known, but may be centuries to millennia.^{12,96}

■ ASSESSMENT OF OPTIONS

Options for Arctic Sources. Because of its strong near-term warming effect, methane poses a special risk of triggering climate tipping points. In case of rapid methane release from one or more of the sources described above, we would very likely wish to deploy a mitigation measure to limit runaway climate change. A more likely scenario is that a combination of several sources' characteristic release rates (Figure 2b) doubles global methane emissions, which, although not the catastrophic case most feared, would have substantial ill effects and could warrant intervention. In this section we discuss potential methane mitigation measures in light of Arctic sources.

In cases where Arctic methane is confined in identifiable formations and susceptible to release, such as in pockets below thawing permafrost or trapped under winter ice in lakes, it may be possible to extract it in concentrated form. The range of technologies for confined sources could then be applied. Indeed, commercial interests have long viewed various formations in the Arctic as potential sources of fuel, and oil and gas are currently extracted at many Arctic sites.¹³⁵

On the other hand, trapped pockets of gas may be released in concentrated yet unpredictable bursts. Appropriate mitigation strategies have yet to be explored, but a system of remote detection and ignition might be possible. Remote detection of methane plumes can be achieved with infrared imaging.¹³⁶ The research on laser activation suggests one route to remote ignition.⁸⁹ Incendiary ballistics may be another route.¹³⁷

It is attractive to compare anthropogenic area sources (landfills, agricultural lands) with the Arctic area sources (wetlands, peatlands, and thawing permafrost), and consider applying the same technologies. The estimated current, average methane flux from Siberian wetlands (including peat) is 0.07 g CH₄/(m²·d),¹²⁵ several orders of magnitude smaller than the typical flux from landfills (~200 g CH₄/(m²·d)),⁷⁹ but in the range of fluxes from rice paddies (0.1–2 g CH₄/(m²·d)).⁴⁶ The areas involved are daunting; Arctic wetlands cover 0.6–1 million km²,¹²⁴ East Siberian yedoma spans about 1 million km², and highland permafrost extends over 22 million km².¹³³ Even though only a small fraction of the total area is likely to be active at a given time, such low emissions and large areas probably preclude an engineered cap of the type used for landfills. However, agricultural manipulations have been executed over comparable areas: globally, cultivated land covers 17 million km².¹³⁸ This suggests that soil aeration, water management, or cultivation of particular microbial or plant communities is possible, and that an analogy with biocovers and agricultural mitigation measures is instructive.

The affected areas of aqueous sources are similarly large: the water-covered portion of the ESAS is 2.1 million km²,¹¹⁹ estimated surface area of Arctic permafrost lakes is 0.8 million km²,⁹⁶ and estimated area of Arctic seas with vulnerable deep clathrates is 0.3 million km².⁹¹ Fluxes from lakes are also similar, with current, average fluxes from Siberian thermokarst lakes of 0.09 g CH₄/(m²·d). The current average flux over the ESAS is smaller at 0.003–0.004 g CH₄/(m²·d).¹²¹ However, in many cases, methane emissions are concentrated to a small fraction of the total area. For example, the ocean hydrates vulnerable at any given time lie in a relatively narrow band at the temperature and depth defining the GHSZ.⁹¹ Free gas release to the ESAS appears to be concentrated along fault lines.⁵⁷ Not all lakes will be affected at once, and within a lake, emissions tend to occur in "point sources" or "hot spots" along a particular edge, where new organic carbon is being exposed by thermal erosion.⁹⁶ Such patchiness of emissions suggests that targeted management of Arctic methane might be possible even with the vast geographical areas involved.

Few of the known mitigation measures appear applicable to large-scale aqueous sources. Again, the areas involved probably preclude engineered caps of the type used for manure ponds. Aeration or drainage (in the case of Arctic lakes) appear to be the most plausible strategies.

Other strategies specific to the Arctic have yet to be explored. Because of the prominent role of ebullition in many of the methane sources, various types of bubble management may be effective. For example, where bubble plumes are persistent or predictable, laying a screen or similar porous material over the sediment could reduce the size of bubbles, causing them to dissolve before reaching the surface. Reducing dissolved methane concentrations in the water column, such as by enhancing methanotrophic activity, would also reduce the height that bubbles can rise. Alternately, adding a surfactant to the surface of water with active bubbling can cause the bubbles to stick to the surface in a foam, which could subsequently be ignited or otherwise controlled.¹³⁷

Thermal management is another strategy specific to Arctic methane. Seitz¹³⁹ proposes generating hydrosols, micrometer-sized air bubbles, in water bodies to whiten them, reflecting sunlight and potentially cooling them by several degrees. Other types of surface coverings that increase albedo can also be imagined. In the case of ocean clathrates, manipulation of ocean

circulation to redirect warm currents or to cool certain deposits may help delay methane release.

As a more general approach to thermal management, injection of reflective particles into the atmosphere has been proposed to offset global warming.^{140–142} Some proposals focus on cooling the Arctic specifically via tropospheric particles and other means.^{140,143} It is unclear to what extent such “solar radiation management” could halt releases or whether they would continue by thermal inertia.

Options for Current Sources and Common Development Paths. Considering current sources of anthropogenic methane, global emissions can be substantially reduced by applying known mitigation technologies more widely. Mature technologies can address several of the larger sources (landfills, wastewater treatment, biomass burning), and options have been demonstrated for several more sources (coal mines, rice cultivation, manure management, natural gas systems). Enteric fermentation is the clearest exception. Of course, stronger policy drivers than currently exist will be required to deploy the technologies at the necessary scale.

Nevertheless, there are substantial opportunities for new technologies to expand the scope and reduce the cost of mitigating current emissions. Here, we suggest avenues of research that can jointly benefit current mitigation efforts and potential Arctic mitigation.

As previously discussed, leaks from natural gas production are of growing concern and uncertain magnitude. Systems of detection and quantification of methane emissions could help in two respects: (1) to understand the problem generally and (2) to identify specific releases for mitigation. Detection is possible through atmospheric samples, infrared spectroscopy, and other methods.^{126,144} Experience with such a system could be highly applicable to Arctic emissions in both respects.

A number of methane sources are difficult to utilize because they are small, remote from the gas or electric grid, or too low or variable in concentration. These include older landfills, abandoned coal mines, and new or exploratory oil and gas wells. Flares can be used in some cases but utilization would be preferable from an emissions standpoint. In other cases, the concentrations are too low or variable to sustain a flame. These applications call for portable, modular mitigation technologies. A device that converts methane to methanol, perhaps based on MMO or a derivative, could fill this need. Once developed, the technology might also be applied to localized Arctic sources.

Technology has been developed for coal mine VAM that can oxidize concentrations as low as 1000 ppm (see Table 1). An improved technology to attack lower concentrations, say 200 ppm, would open a new range of applications (animal feedlots and manure storage) and the largest, most stubborn slice of anthropogenic emissions. Technological advances that drive toward lower concentrations and room-temperature oxidation could lead to a solution for unconfined sources, Arctic or otherwise.

Finally, further efforts to understand the ecology of methanotrophs and methanogens, to reduce emissions from agricultural lands, and to better design biocovers and bioreactors all have potential to reduce current sources of emissions. For example, although the majority of emissions from landfills in developed countries are well-managed, they remain a significant source globally. Effective biocovers could reduce emissions in the developing world where engineered caps are often not affordable.⁷⁶ Research on such biotic systems

may also lead to a better understanding of Arctic sources and means to mitigate them.

■ CONCLUSIONS

We have reviewed the literature on methane mitigation and on Arctic methane release. On the former topic, we found a range of technologies available for mitigating the well-known sources of anthropogenic methane and some clear opportunities for advancement. New developments are especially needed to address emissions from agriculture and livestock, and to cope with the expected boom in unconventional natural gas extraction. Although nearly all of the mitigation literature focuses on specific source types, we identified instructive cross-cutting themes; notably, methane production and oxidation in biotic systems had many common features across sources. Also, confined-source technologies should be easily applicable across source types.

The need for methane mitigation is increasing dramatically as new research indicates that methane has greater climatic impact than previously thought and as global CO₂ mitigation continues to falter. It now appears that aggressive methane mitigation is not only a lower-cost means to reduce climate forcing, but a necessary component of any emissions pathway that avoids dangerous climate change.

In our review of Arctic methane sources, we found that significant gaps in understanding remain of the mechanisms, magnitude, and likelihood of Arctic methane release. No authors stated that catastrophic release of methane—e.g., hundreds of Gt over years to decades—is the expected near-term outcome. But until the mechanisms are better-understood, such a catastrophe cannot be ruled out. The evidence is strong that methane had a role in past warming events, but the particular source and release mechanisms of methane in past warming is not settled.

Whereas most authors indicated that a catastrophic release is unlikely, a chronic, climatically significant release of Arctic methane appears plausible. Such a release could undermine or overwhelm gradual emissions reductions made elsewhere, and thus warrants technological intervention.

Because methane capture from free air cannot be scaled to compete with natural sinks, and thus meaningfully reduce atmospheric concentrations, mitigation must focus at the sources. Depending on the mechanism and magnitude of release, there are a number of ways to frame Arctic methane mitigation. If releases are relatively small and localized, a mitigation program might be included in a carbon market, with mitigation considered like offsets, similar to flaring methane from abandoned coal mines. In case of a larger-scale, patchy release, a mitigation program might operate like a forest fire-suppression program. Both involve monitoring networks over large areas, and periodically deploying a team of specialized personnel and equipment to contain an environmental threat.

If mitigation measures take an ecological approach, Arctic methane mitigation might be viewed as an adaptation measure, similar to the way a nature preserve can be actively managed to maintain ecological viability in a changing climate.¹⁴⁵ Finally, if the release is very large or uniform over a large area, any mitigation measure might quickly look like geoengineering, and should be considered with appropriate caution.

The role of mitigation will become more clear as we come to understand the Arctic sources. Further effort is clearly needed to monitor and study Arctic methane. Still, mitigation technology can develop concurrently. In particular, we

identified four avenues of research and development that can serve the dual purposes of addressing current methane sources and potential Arctic sources:

1. methane release detection and quantification,
2. mitigation units for small and remote methane streams,
3. mitigation methods for <1000 ppm methane streams, and
4. understanding methanotroph and methanogen ecology.

Mitigation strategies specific to the Arctic should also be studied. Currently, there is no obvious solution to any of the Arctic sources. Considering the magnitude of potential consequences, it is only prudent to prepare some sort of response. Preparedness would have many components, including means of detecting and understanding a release of concern, a socio-political willingness and mechanism to respond, and the technological tools with which to respond. This paper has attempted to draw attention to the range of technologies and strategies that may be developed.

■ ASSOCIATED CONTENT

● Supporting Information

Table of values used in Figure 2b with specific references and calculations regarding the size of mitigation systems required for atmospheric methane capture. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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