Learn About ...

METHANE


FIGURE 1. Gas burner on a kitchen stove © Ulga / Adobe Stock

Methane (CH_4)

Boiling point, –164 °C

Melting point, –183 °C

Low water solubility

Natural gas is 70 to 90 percent CH_4, plus a mixture of other hydrocarbons: ethane (C_2H_6), propane (C_3H_8) and butanes (C_4H_{10}).

Methane, CH_4, the major component of natural gas, is a colorless, odorless, flammable gas. Almost all the methane humans use (usually as natural gas–see Section B) is burned for cooking (Figure 1), heating buildings, industrial heating, and as a major fuel for power stations generating electricity. Burning all this methane/natural gas produces carbon dioxide that escapes to the atmosphere where it is a greenhouse gas that causes Earth's temperature to increase. Methane is itself a greenhouse gas that is, in some ways, more potent than carbon dioxide (see Section C).

A. METHANE USE: POWER AND PERIL

The principal use of methane is as a fuel, because burning methane releases a large amount of energy.

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \quad \Delta H = -891\ \text{kJ/mol}$$

This is roughly twice as much energy as would be released by burning the same mass of coal. The energy released by burning methane, from natural gas, is used directly to heat homes and commercial buildings. It is also used in the generation of electric power. During the past decade natural gas accounted for a little over 1/5 of the total energy used for power generation worldwide, and up to about 1/3 in the United States. The use of natural gas for power generation is increasing and, in the United States, has overtaken coal (each at about 1/3 in 2016). This increasing use of natural gas (methane) and its consequences are discussed in Section B.

Some of the energy released in the combustion of methane is emitted as light, the luminous blue light you see in Figure 1. These emissions are from excited electronic states of molecular fragments (C_2 and CH, for example) formed at the high temperature of the flame. Because the hot gas flame is so much brighter than a burning wood or candle flame, gas became the primary source of lighting for streets and homes during the 19th century, especially in the Victorian period at the end of the century. Most of the gas was “artificial gas” produced by heating coal to drive off its volatile components, much of which is methane. Natural gas was also used when available in a few locations near a gas well. By early in the 20th century, electric lighting had replaced gas lighting. What remains is some decorative “faux gas” electric lighting, usually designed to evoke the earlier Victorian period.

Methane is nontoxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen inhaled. A tiny amount of smelly organic sulfur compounds (tertiary butyl mercaptan, $(CH_3)_3CSH$, and dimethyl sulfide, CH_3SCH_3) is added to give commercial natural gas a detectable odor. This is done to make gas leaks readily detectible, which is important because mixtures of about 5 to 15 percent methane in air are explosive. An undetected gas leak is dangerous and explosions are reported every year, causing lost lives and occasional spectacular property destruction.

A quieter natural gas hazard may be posed by gas kitchen stoves (Figure 1). When the gas flame heats the nearby air, some of the nitrogen and oxygen in the air react to give oxides of nitrogen. Among these, nitrogen dioxide, NO_2, is a particularly bad irritant for the lining of the nose and lungs. In addition, the flame can produce tiny, unburned particles that are also respiratory irritants. These emission from the stove can create an unhealthy indoor air environment, especially if the space is small and ventilation is poor. Such unhealthy indoor air has been studied for years as a possible cause of childhood asthma. An epidemiological statistical analysis, reported in 2023 (Ref. 1), concluded that about one-eighth “of current childhood asthma in the U.S. is attributable to gas stove use”. The most important way to limit the unhealthy air is good ventilation to get the emission outdoors. Such findings have added another argument for phasing out the use of gas stoves and furnaces.

In the chemical industry, methane is a raw material for the manufacture of methanol (CH_3OH), formaldehyde (CH_2O), nitromethane (CH_3NO_2), chloroform (CH_3Cl), carbon tetrachloride (CCl_4), and some compounds containing carbon and various combinations of fluorine, chlorine, and hydrogen, which are mainly used as the working fluid in refrigerators and air conditioners. Many of these have been banned because of their harm to the stratospheric ozone layer.

B. NATURAL GAS

Methane, CH_4, has a wide distribution in nature. Most of it is in natural gas, which occurs in reservoirs trapped beneath the surface of the earth by overlying layers of rock. It is often found together with petroleum deposits. These reservoirs are tapped by drilling through the rock. Before it is distributed, natural gas usually undergoes some sort of processing. Usually, heavier hydrocarbons (propane and butane) are removed and marketed separately. Non-hydrocarbon gases, such as hydrogen sulfide and water vapor, must also be removed. Another component of the crude natural gas mixture from most wells is helium. Helium is formed from alpha particles (helium nuclei) produced by radioactive decay of uranium and thorium in the Earth's crust. Like methane, helium is trapped by overlying rock layers and released when a bore hole pierces the rock.

The cleaned gas is then distributed throughout the country through more than 300,000 miles of pipeline, Figure 2. Local utility companies add an odorant before delivering the gas to their customers.

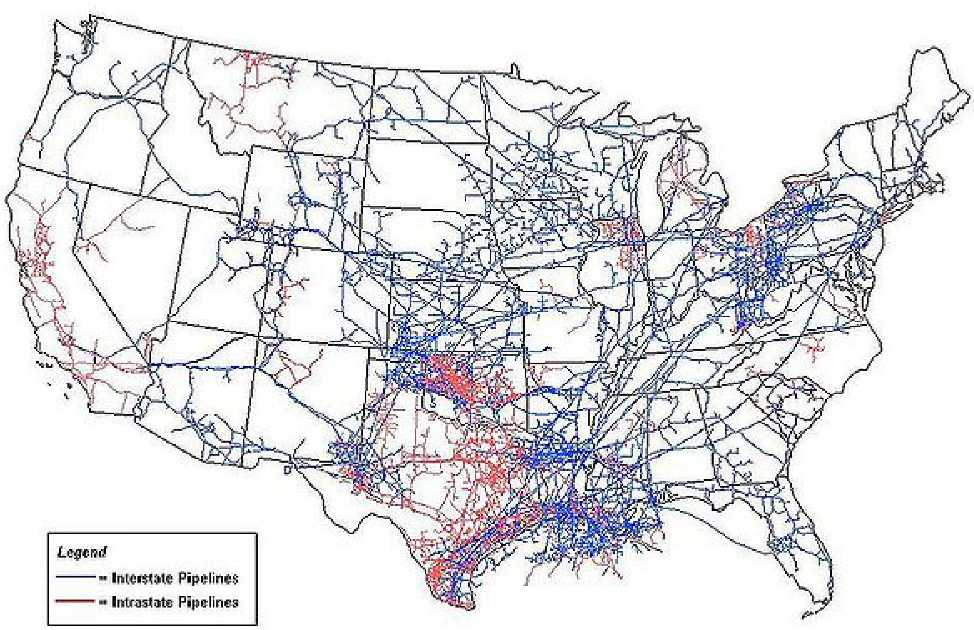

FIGURE 2. The network of pipelines that distribute natural gas through the United States. Source: Energy Information Administration, Office of Oil & Gas, Natural Gas Division, Gas Transportation Information System

There are both environmental and economic factors (often in combination) driving the use of natural gas in competition with coal for world and U.S. power generation. Because of the impurities in coal, especially bituminous coal (the majority of what is burned), the emissions from smokestacks can contain substances such as sulfur dioxide (leading to acid rain) and mercury (toxic to most organisms, including humans). In addition, unburned particulates that are harmful, particularly to those who suffer respiratory problems, are released. To clean up the effluent gases, power plants are required to install expensive scrubber technologies that add to the cost of the power produced, even if the coal itself is relatively inexpensive. Processed (clean) natural gas has almost none of these problems, so the expensive power plant scrubbers are unnecessary. In the United States, many coal-fired power plants have been or are being converted to natural gas, or have been shut down entirely, and new ones are gas-fired.

Helium (He)

Helium formed by alpha decay and recovered from gas wells is its only terrestrial source. The U.S. produces about 50 percent of the world's supply. Helium's major use, as the coldest liquid known, is cooling the superconducting coils of magnetic resonance imaging (MRI) instruments.

A pollutant that is common to burning both coal and natural gas is, of course, carbon dioxide, a greenhouse gas driving human-caused global warming, ocean acidification, and consequent climate disruption. In this regard, natural gas is promoted as a "clean" energy source. What does this mean? The comparison is based on the amount of carbon dioxide produced for the same amount of energy output from burning natural gas versus coal. Natural gas produces about 50 percent less carbon dioxide for an equivalent energy output. Thus, natural gas is "cleaner" than coal—the conversion to more gas-fired power stations is probably the major factor in the reduction of about 12 percent in U. S. carbon dioxide emissions from power generation since 2005. Cleaner than coal, but still a "dirty" fossil fuel contributing to increasing levels of atmospheric carbon dioxide and global warming. But, too often omitted in "clean" gas discussions and advertising, is the powerful greenhouse warming effect of methane itself (see Section C). Leakage at wells, in distribution systems, and at power plants themselves, could eliminate much or all of the advantage of gas compared to coal with respect to global warming. Although there are occasional massive releases of gas from large underground natural gas storage facilities (Refs. 2 and 3), most leakage is from localized sources (valves and piping, for example) that are scattered all over the world and are hard to monitor. This situation could be changed by the MethaneSAT satellite, conceived and constructed by a consortium of an environmental organization, universities, and industries and planned for launch in 2024. The satellite is designed to detect methane emissions and send their locations to the team on the ground, so they can act to try to get the problem fixed. Watch for news of the satellite and its mission.

Liquified natural gas (LNG)

Even with several hundred thousand miles of pipeline, Figure 2 shows there are areas of the U.S. that are not serviced by this network. One way to provide natural gas to these areas is to ship it there at high pressure as compressed natural gas (CNG) in heavy-walled metal containers. This works well, although somewhat inefficient, for shipment by rail or truck on land. But shipment of CNG by sea from gas producing countries to others with limited domestic sources can deliver only a relatively small payload of gas, which makes it economically unfavorable. The solution, initiated in 1964, is to ship natural gas as a liquid, so it can be stored and transported in insulated, light-walled containers at low temperature and pressure as LNG. Before liquefaction the heavier components (propane and butanes) are removed, so LNG is largely methane and some ethane at about –162 ºC, just below the methane boiling point. LNG dramatically alters the economics of exporting and importing natural gas. Beginning with the first tanker in 1964, in 2021 there were 700 LNG tankers, Figure 3, carrying the fuel from exporting to importing countries. Special exporting and importing LNG ship terminals have been and are being built around the world. The export terminals have facilities for liquefying and transferring the liquid to the tankers. The import terminals are equipped to gasify the liquid (for transport via pipelines) as it is removed from the tanker. The large investment by the fossil fuel industry in building and expanding this LNG infrastructure is one of their incentives for promoting the increasing use of natural gas, especially as hydraulic fracturing technology has made it much more available.

FIGURE 3. This example of an LNG tanker docking at an LNG ship terminal shows how the tanker resembles a hollowed-out oil tanker or container ship with the oil tanks or container holds replaced by well-insulated spherical LNG tanks.
Source: Aerial-motion/Shutterstock.com

Hydraulic fracturing (fracking)

The largest economic factor driving the recent use of natural gas as an energy source is the large increase in its availability due to *hydraulic fracturing* (*fracking*) technology. A great deal of natural gas is trapped in shale (and other rock) formations that the gas cannot pass through, unless the rock has fractures the gas can seep through. Naturally occurring fractures are too rare to make natural extraction of shale gas economically viable. The technology that makes shale gas more readily available is the ability to drill gas wells horizontally, so fracturing can be done over a large area of a horizontal shale layer.

To fracture the rock, a fluid is pumped into it at high pressure (the hydraulic part). The usual fluid is mostly water containing several percent of sand or some other particulate matter as a *proppant* (particles to keep the fractures in the rock *propped* open when the pressure is released). Small amounts of other chemicals, especially gelling agents that help to carry the proppants in the water and keep them in place in the fractures, are also part of the fracking fluid.

Fracking began in vertical wells, but is inefficient, because the fracturing effect extends only a few tens of feet from the bore hole. Many wells would be required to extract a large shale bed. With horizontal drilling, the vertical bore hole is drilled into the shale layer and then horizontal runs are extended into the layer for several thousand feet in many cases. Fracturing is done at intervals along the horizontal pipe and gas from the surrounding shale flows into the pipe when the fracking fluid pressure is released. Exploitation of horizontal fracking took off at the beginning of the 21st century, especially in the United States, which, in a decade and a half, became the world's largest producer of natural gas.

Environmental impacts of fracking

The most apparent environmental impacts of methane use are in the extraction of natural gas by hydraulic fracturing. The well-head sites require several acres to house the supplies and equipment necessary for the process and disrupt the land. A prodigious amount of water is required for the fracking fluid and usually has to be hauled into the drill site in convoys of tanker trucks. In locations where water is scarce, fracking can use a substantial fraction of water available for agriculture and other human use. The waste fluid from the well is contaminated and unusable for these purposes and often pumped back into the rock formation. There is some concern that underground fresh water aquifers might be accidentally contaminated. Disruption of large areas of the foundation on which the Earth's surface rests can lead to motion of the surface, tremors (small earthquakes). Oklahoma was a seismically quiet state where disruptions most often came from above the surface in the form of tornadoes and droughts, but now, with a large concentration of fracking, tremors have become a common occurrence.

C. METHANE CONTRIBUTES TO GLOBAL WARMING

The environmental effects of natural gas extraction are relatively localized, but the contribution of methane to atmospheric warming and climate change is a global effect. Burning the gas produces carbon dioxide that adds to that produced by burning other fossil fuels. At present, beginning of the third decade of the 21st century, about one-fifth of the carbon dioxide added annually to the atmosphere comes from the combustion of methane (natural gas). Further, methane is a greenhouse gas in its own right—even more potent, and, from a short-term viewpoint, perhaps more important, than carbon dioxide.

The overall atmospheric warming power of a greenhouse gas is a function of three factors:

- the strength of its warming effect, which is related to the amount of the Earth's emitted infrared radiation a given amount of the gas absorbs,
- the amount of the gas present in the atmosphere, and,
- the lifetime of the gas in the atmosphere. Some greenhouse gases remain in the atmosphere for a very long time. The most abundant greenhouse gas produced by human activities, carbon dioxide, remains for many centuries. Some other gases remain for relatively short times. The second most abundant anthropogenic greenhouse gas, methane, has an atmospheric half-life of about 12.5 years. The methane, CH_4, is oxidized by reaction with hydroxyl radicals, HO·. About 90 percent of the carbon ends up as carbon dioxide.

Global warming potentials (GWP) for greenhouse gases are conventionally calculated by comparison of their effect to that of an equal mass of carbon dioxide emitted at the same time. For example, an emission of methane has an immediate warming effect that is about 125 times larger than an equivalent mass of carbon dioxide emission. To put this another way, the emission of a given mass of methane, say one gigatonne, has the immediate effect as the emission of 125 gigatonnes of carbon dioxide. But the original mass of emitted methane begins to disappear, as it is oxidized. Thus, the original amount of emitted methane decreases with time. Since there is less of the methane from the original emission, its warming effect, compared to the initial equal mass of carbon dioxide that does not change, becomes less as time passes. This complicates the determination of its overall atmospheric warming effect.

Although somewhat confusing, the most common measure of GWP involves summing the decreasing warming effects of the decreasing amount of methane (and other anthropogenic greenhouse gases) from its initial release to later times, usually 20 and 100 years. These values of GWP are given as the amount of carbon dioxide that would have had to be emitted at time zero to produce the same warming as the greenhouse gas produced. For methane the 20-year GWP is in the range 80-90 (different models of the various feedback effects give slightly different warming effects). That is, it would require an 80-90 gigatonne initial emission of carbon dioxide to produce the same warming effect over 20 years as the emission of one gigatonne of methane. For the 100-year time horizon, the methane GWP range is 25-30.

After 100 years, all the initial emission of methane will have been oxidized, but about 90 percent of its carbon remains in the atmosphere as carbon dioxide. How much carbon dioxide is this? The molar masses of CO_2 and CH_4 are 44 and 16 grams, respectively, so equal masses of the two gases will contain 3.67 (= 44/16) times as many molecules of methane. If about 90 percent of these molecules are oxidized to carbon dioxide, that will yield about 3.3 times as many molecules as were in the comparative mass of carbon dioxide. Put another way, an initial emission of one gigatonne of methane will end up as at least three gigatonnes of carbon dioxide that will persist for centuries in the atmosphere. Warming resulting from methane emission never goes completely away (Ref. 4).

Even though an initial amount of methane is gone from the atmosphere in a century, its warming effect during its first couple decades is substantial. This means that global warming is faster than it would be if only carbon dioxide was in control of warming. The more rapid the warming, the less time natural systems have to adapt and the more disruptive the warming becomes. Natural sources of methane, mostly wetlands, are abundant on Earth's surface. For almost all the past 10,000 years, the mostly natural atmospheric methane concentration was about 700 ppb (parts per billion). But, since the Industrial Revolution, methane has risen to about 1,900 ppb (in 2022) as human activities added to natural sources. About 30 percent of overall global warming since the Industrial Revolution has been due to atmospheric methane. At present, atmospheric methane has about one-fifth the greenhouse warming effect as the atmospheric carbon dioxide, Figure 4.

The global warming properties of methane provide a target of opportunity for short-term slowing of global warming.

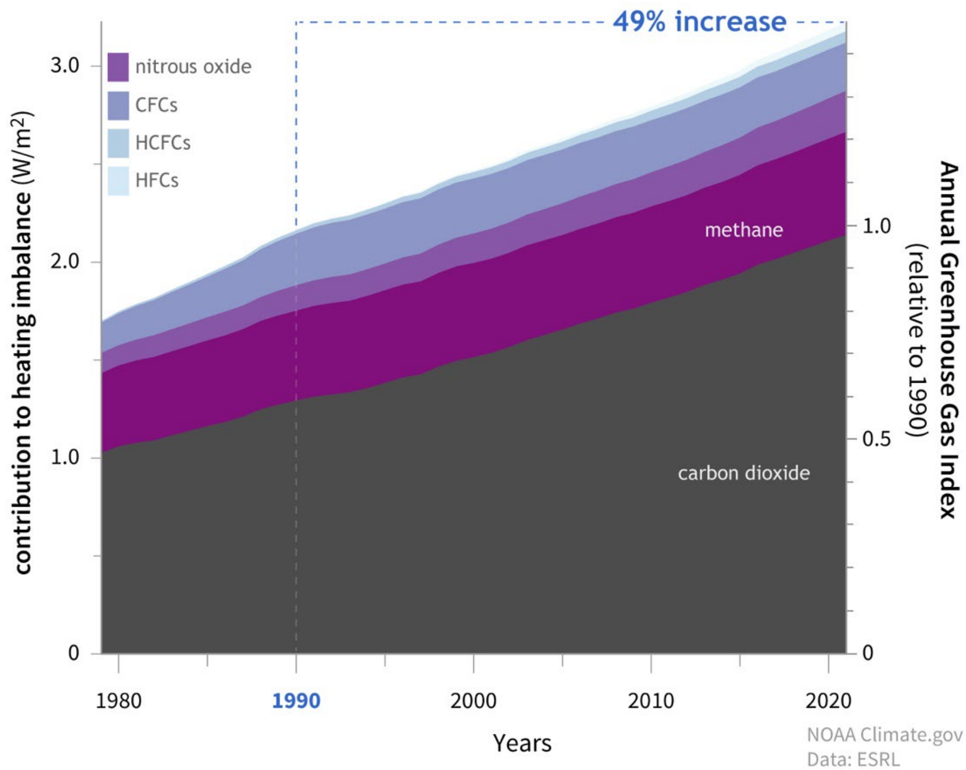

FIGURE 4. This graph shows the heating influence caused by the major human-produced greenhouse gases: carbon dioxide (gray), methane (dark purple), nitrous oxide (medium purple), chlorofluorocarbons (CFCs, lavender), hydrochlorofluorocarbons (HCFCs, blue), and hydrofluorocarbons (HFCs, light blue). Relative to conditions in 1750, today's atmosphere absorbs more than 3 extra watts of energy per square meter of Earth's surface. Source: Graph by NOAA Climate.gov based on data from NOAA Global Monitoring Lab.

The global warming properties of methane provide a target of opportunity for short-term slowing of global warming. The warming effect of methane is quite large during the first few decades after its emission. Therefore, reducing methane emission would have a fairly rapid effect on reducing the rate of global warming. To this end, at the 2020 United Nations Conference of the Parties (COP26) on climate change, the countries adopted a voluntary Global Methane Pledge to reduce emissions of methane to 30 percent below 2020 levels by 2030. By the time of COP27 in 2022, 130 countries had signed on to the pledge. If methane emissions are reduced soon, calculations suggest that there could be a quarter of a degree Celsius less warming by 2050 (Ref. 5). Of course, to mitigate long-term warming, we must also continue efforts to reduce carbon dioxide emissions, as well as removing the carbon dioxide we have already added to the atmosphere.

Anthropogenic methane sources

The "firedamp" of coal mines is chiefly methane. Anaerobic bacterial decomposition of plant and animal matter, such as occurs under water, produces marsh gas, which is another name for methane. About 33 percent of the methane emissions from the United States come from wetlands, about one-third of which is from rice fields that are flooded by humans, with the rest from natural marshes and bogs. Another 20 percent comes from fossil fuel extraction (coal mines and what is not captured from oil and gas wells) as well as leaks in the enormous natural gas distribution system, Figure 2. A further 20 percent is a result of raising large herds of cattle (for beef and dairy products). Cellulose makes up a great deal of the food, grass and grains, that cattle (and other ruminant animals like sheep, goats, and camels) eat. Animals cannot digest cellulose, but ruminants (and termites that also eat cellulose—wood) have digestive systems containing microbes that break down the cellulose for them. Unfortunately, one of the by-products of this process is a good deal of methane that the animals must get rid of and mostly they do this by burping, Figure 5. The solid and liquid waste all these cattle (and other agricultural animals) produce is often stored to decay in waste ponds, where the decay microbes produce more methane. Similarly, landfills produce methane as refuse decays. Some municipalities capture some of this methane and use it for heating and power.

FIGURE 5. Methane produced from their food is a waste of the carbon that could be used by cattle to make milk and meat. Research is going on all over the world to find ways to reduce the amount of this methane, both to keep it out of the atmosphere and to save its carbon for the animals. These cows in Ireland are fitted with devices that measure the methane they burp out to monitor changes as their diets are changed. Source: Moorepark Research Centre of Teagasc—The Agriculture and Food Development Authority of Ireland.

Methane hydrates (clathrates)

When water and methane are mixed at low temperature and elevated pressure, a soft solid is formed in which methane molecules are trapped in cages of water molecules. Methane hydrate is often called *clathrate* (a term from Latin meaning bars or a lattice and used to describe any inclusion solid like this). This mushy ice-like material can be ignited and the methane burned, so-called “burning ice,” Figure 6.

FIGURE 6. This image of the flame from ignited methane hydrate (white solid) is from "Burning Ice-Fire Ice-Methane Hydrate-(Dark room settings)" on YouTube.

Conditions for natural methane hydrate formation are found on sea floors and some bogs in the cold polar regions of the northern hemisphere. Methane formed by the action of anaerobic microbes on organic matter (or seeping from below the sea floor) is under pressure from the overlying water and/or soil and the environment is cold, favoring hydrate formation. These deposits of methane hydrate are widely distributed and there is no agreed upon estimate of the amount that actually exists. (A Japanese engineering study estimated that there is a deposit containing more than a trillion cubic meters of methane off the coast of Japan's main island and plans are afoot to extract this fuel.)

Natural gas is usually driven through the pipeline network under high pressure. A major reason for drying the gas during processing is to prevent the formation of methane hydrate, which will block the flow, if the gas passes through a cold pipeline. In 2009, the deepest oil well ever bored (almost seven miles deep) was drilled in the floor of the Gulf of Mexico. On 20 April 2010, the casing at the top of the well (on the sea floor at a depth of 4100 feet) failed and enormous amounts of crude oil and gas began to escape from the well head (continuing until finally capped on 15 July). One early attempt to capture the escaping material was to drop a "cage" over the well head with a tube leading to the surface where the effluent would be collected. Within a very short time of its deployment, the apparatus was completely clogged by methane hydrate and became useless.

An environmental concern about the methane hydrates scattered about the world is that they will become unstable in a warming world and break down releasing methane into the atmosphere. Because the methane would increase greenhouse warming, this is an example of a positive feedback in the climate system—a change that increases the effect that brought it about in the first place. The permafrost, underground deeply frozen damp soil in north polar regions, is beginning to melt (structures are collapsing and new bogs are forming). Methane is being emitted as hydrates melt and anaerobic microbes awake to also produce methane by decaying buried organic matter. The extent of this feedback is still unknown, because measurements of the methane releases are recent and do not provide enough history to tell how rapid or slow the process is (will be). Whether this is a minor or major effect, it adds to the burden of methane in the atmosphere and thus is a concern for global warming and climate disruption.

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