

Climate science of methane



2.1 Introduction

Methane is the most abundant reactive trace gas in the atmosphere and arises from both natural and anthropogenic sources. It is a valuable gas and is usable at a wide range of concentrations, down to 5%. In concentrated form it is flammable, representing an explosion risk in confined conditions.

The global atmospheric burden of methane (in 1998) was 4850 Mt(CH₄), equivalent to an average concentration of 1745 parts per billion (ppb). The global methane budget can be modelled by simply considering emissions as increasing the atmospheric burden of methane, with sinks removing methane from the atmosphere – the methane cycle. The concentration of methane in the atmosphere is thought to be increasing at a rate of 22 Mt/yr, due to the imbalance between estimated annual global emissions of 598 Mt and removals of 576 Mt (Figure 4).¹

It is therefore important to reduce global emissions to such a level that they are outweighed by methane sinks, so that the concentration of methane in the atmosphere decreases and its subsequent warming effect is reduced. A reduction of global emissions by just 22 Mt per year would result in stabilisation of methane concentrations in the atmosphere. Such a reduction represents just 3.6% of total methane emissions, or 6.1% of anthropogenic emissions. Such small reductions should be attainable. Obtaining a reduction in atmospheric methane concentrations would provide an encouraging example in the fight against global warming.

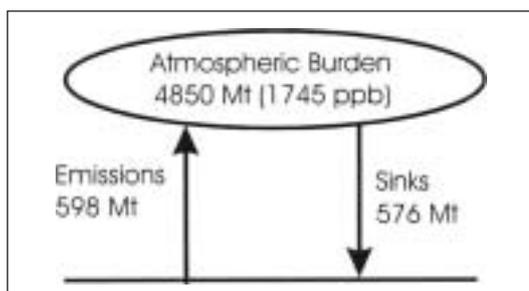


Figure 4: Global methane cycle

2.2 Methane sources

Methane is emitted from a range of natural and anthropogenic (relating to human activity) sources as a result of the anaerobic decomposition of organic matter, land use changes and fossil fuel related emissions (Table 2).

Table 2: Sources of global methane emissions

<i>Natural</i>	<i>Anthropogenic</i>
Wetlands	Agricultural livestock
Termite activity	Rice cultivation
Oceans	Waste practices
	Coal mining
	Natural gas distribution
	Biomass burning

Whilst the major sources of atmospheric methane have been identified, quantifying their individual contributions to global emissions has proved



Wetlands are areas of marsh, fen, peatland and water, representing approximately 6% of the world's land surface

Table 3: Emissions of methane (Mt) by source as quantified by different academic studies

Source	Fung <i>et al.</i> ¹⁴	Hein <i>et al.</i> ¹⁵	Lelieveld <i>et al.</i> ¹⁶	Houweling <i>et al.</i> ¹⁷	Mosier <i>et al.</i> ¹⁸	Olivier <i>et al.</i> ¹⁹	Cao <i>et al.</i> ²⁰	SAR ²	TAR ¹
Natural									
Wetlands	115	237	225	145			92		
Termites	20		20	20					
Ocean	10		15	15					
Hydrates	5		10						
Anthropogenic									
Energy	75	97	110	89		109			
Landfill	40	35	40	73		36			
Ruminants	80	90	115	93	80	93			
Waste Treatment			25		14				
Rice Agriculture	100	88			25-54	60	53		
Biomass	55	40	40	40	34	23			
Other				20	15				
TOTAL	500	587	600					597	598

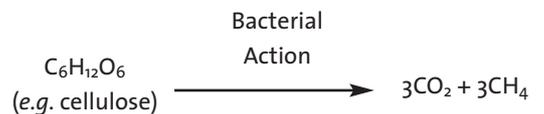
Source: IPCC, 2001¹

problematic.^{12,13} For many sources, emissions are highly variable in space and time. For instance, emissions from most types of wetlands can vary by a few orders of magnitude over just a few metres.¹

Based on a range of studies, the IPCC¹ estimates that global emissions of methane are around 598 Mt per year, but does not provide a definitive breakdown of CH₄ emissions by source. Other studies have attempted to classify this, but there are a wide range of estimates and definitions used for each sector (Table 3). This lack of accuracy and definitive emissions figures is a serious handicap to the design of practical policy and trading schemes.¹³

The role of bacteria

There are two classes of bacteria actively involved in the methane cycle. Methanogenic bacteria generate methane by breaking down organic matter in the absence of oxygen (anaerobically), releasing carbon dioxide and methane according to the reaction:



Conversely, methanotrophic bacteria oxidise methane to carbon dioxide. Methanotrophic bacteria are of two sorts; low affinity oxidation, where methanotrophs oxidise high concentrations of methane at the source of production (usually a population of methanogenic bacteria), and high affinity oxidation, which can oxidise methane present at atmospheric concentrations.

Natural sources

The main natural sources of methane are wetlands, termites and oceans. Wetlands are by far the largest source, accounting for 30% of total emissions (Figure 5), with methane being produced from the anaerobic decomposition of organic matter covered by water. Because this process involves the action of bacteria, the rate of methane production is strongly temperature dependent. Maximum methane production is experienced at temperatures between 37 and 45°C and so future increases in global temperature may enhance methane production from wetlands, thereby reinforcing the greenhouse effect.

Methane is also produced by the digestive processes of termites, resulting in the generation of around 20 Mt per year – approximately 5% of world methane emissions. This value is unlikely to change as termite populations are not expanding despite greater availability of biomass due to deforestation.²² Methane emissions from termites should be treated as a significant, but background, source that is likely to remain constant.

Oceans contribute approximately 2% to global methane emissions. The methane is produced by methanogenic bacteria within sinking particles in

surface waters. The production of methane from oceans is spatially dependent, with much methane arising from methanogenesis in marine sediments, particularly in nutrient rich areas such as estuaries. There is also an anthropogenic component to ocean emissions, with bacterial populations being increased by high nutrient levels from agricultural fertiliser run-off and waste treatment effluents.

Anthropogenic sources

Approximately 60% of emissions are related to human activities. The key anthropogenic sources of methane include fossil fuels, agriculture, landfill and the burning of biomass. Methane emissions arising from the fossil fuel industry form the largest anthropogenic source of methane, estimated to be between 80 and 100 Mt per year. The main sources of fossil fuel-related methane emissions are the release of natural gas from coal mining and leakage from gas processing and distribution pipes. Pockets of methane that have been trapped between layers of coal during its formation and methane within the coal itself are released once the coal is mined.

Agricultural practices also result in significant methane emissions, the two major sectors being rice production and the rearing of livestock. Paddy fields for rice production are essentially man-made wetland areas and are characterised by high moisture content, oxygen depletion and high organic substrate and nutrient levels.²³ As such, they provide ideal conditions for methanogenic bacteria and result in substantial emissions of methane of approximately 40 Mt per year. Up to 90% of this methane is absorbed by populations of methanotrophic bacteria, which convert the methane to carbon dioxide, but the remaining 10% escapes to the atmosphere. The production of 1 kg of rice corresponds to the emission of 100 g of methane.²⁴ It is worth noting that the accuracy of methane emissions estimates has improved substantially over the past decade, with current figures almost half previous estimates.¹

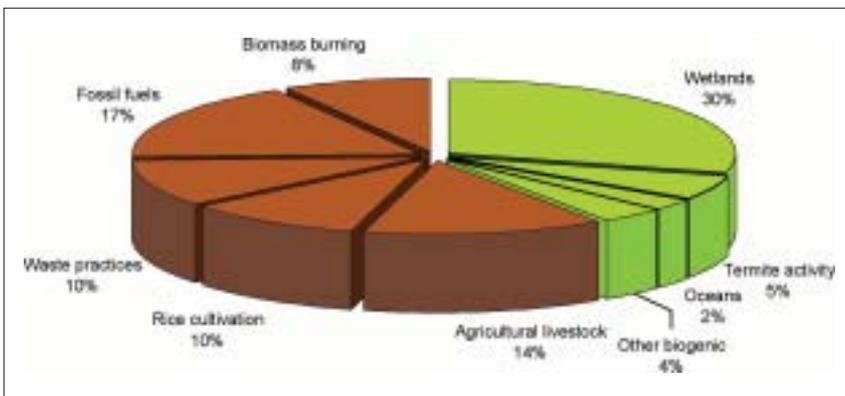


Figure 5: A representative distribution of worldwide anthropogenic and natural sources of methane

Source: Khalil, 2000²¹



Rice paddy soil is fully waterlogged for 4 months each year, creating an artificial wetland

Methane is produced as part of the natural digestive processes of ruminant animals such as cattle, sheep and goats. Food is broken down by bacteria in the rumen, aiding digestion, since stomach enzymes are insufficient to break down plant polymers. However, the action of these bacteria yields methane, carbon dioxide and ammonia as gaseous by-products. With an increasing global population, coupled with higher living standards, livestock numbers are increasing world-wide and contribute some 50-100 Mt per year to global methane emissions.

Landfill sites also provide an anaerobic environment where methanogenic bacteria break down waste organic materials. Somewhere between 40 and 60% of landfill gas is methane, depending on the composition of the waste. The remainder is mainly carbon dioxide with other trace gases. The amount of methane emitted to the atmosphere from a landfill site is strongly dependent on the design and operation of the site. Unchecked, the landfill gas will simply permeate through the waste or along cracks in the compacted waste or bedrock. Modern landfill sites use impermeable liners and a capping layer to control the movement of the gas, which may then be collected. However, even the best caps are only 85% efficient²⁵ with the remaining 15% of methane escaping through the cap.²⁶ This is offset by breakdown of up to 90% of the methane in the capping layer by methanotrophic bacteria (Section 5.1).

The burning of biomass releases around 40 Mt of methane into the atmosphere each year. Biomass burning results mainly in the production

of carbon dioxide, but if fires smoulder and combustion is incomplete, methane and other volatile organic compounds are released. The extent of methane emissions is dependent on the completeness of combustion and the carbon content of the fuel used.²⁷

Methane hydrates

Although currently neither a source nor a sink, methane hydrates are by far the largest store of methane on the planet and account for 53% of all fossil fuels on earth.²⁸ They are a crystalline solid mixture of water and methane (essentially methane trapped in ice) and are found in ocean floor sediments and arctic permafrost. Methane hydrates are stable compounds and are not part of the methane cycle described in this chapter.

The methane in ocean sediment hydrates is trapped by the high pressure deep in the ocean but is released above a depth of 400m as the pressure drops. The energy industry is keen to take advantage of this and mine these deposits.²⁹

Methane contained in arctic tundra, trapped within the frozen solid structure of the hydrate, is a more serious issue. Should temperatures rise, the methane hydrate will melt, releasing methane gas to the atmosphere. There is concern that, if rising global temperatures due to anthropogenic climate change cause the arctic permafrost to melt, massive quantities of methane would be released into the atmosphere, causing a catastrophic run-away greenhouse effect beyond even the upper 5.8°C estimate postulated by the IPCC. Such a process is believed to have occurred in the Palaeocene-Eocene Thermal Maximum,³⁰ some 55 million years ago, when average global temperatures increased by 5°C and which lasted for 150,000 years.

Is it renewable?

The question of whether methane is a renewable resource is central to determining its eligibility for strong financial incentives such as ROCs. Renewable energy technologies are defined as

Flaming ice: methane hydrates are essentially methane trapped in ice



relying on “natural energy flows and sources in the environment, which, since they are continually replenished, will never run out”.³¹

Agricultural emissions, being biogenic are clearly renewable. Methane from landfill is mostly derived from decomposition of plant-based material and once flared is approximately carbon neutral.³² It is also arguable whether waste streams are a ‘natural flow’, but it is assumed that societies will always produce some waste as a consequence of their activities. Landfill gas is therefore defined as a renewable resource. However, if the same waste stream is combusted to generate electricity, this does not count as renewable because fossil-fuel based plastics are incinerated.

Coal mine methane is certainly an energy flow within the environment, but is it a natural flow? As a resource, methane would not be released to the atmosphere were it not for human action, although the same could be argued for landfill gas, which does qualify for ROCs. However, landfill gas is carbon-neutral, whereas the release of coal mine methane must be considered an addition to the present carbon cycle. The DTI does not consider coal mine methane to be a

renewable resource.³³ Methane from the oil and gas industries is also considered non renewable.

Although the issue of what is classified as renewable is not straightforward, especially when considering landfill and coal mine methane, the separation assumed by policy makers is clear. If the methane is generated from biogenic sources, it is renewable. Conversely, if it is derived from fossil fuel sources, it does not count as renewable.

Future outlook

Both natural and anthropogenic sources of methane are likely to change the atmospheric burden over the forthcoming century.¹ There is considerable potential to reduce the anthropogenic sources of methane by improved waste management and changes in agricultural practice. However, these sectors are still prone to upward pressure due to an increasing global population with increasing energy, land and dietary demands. Natural emissions may also increase further as a result of global warming, as higher average global temperatures may stimulate microbial activity.^{2,20}

2.3 Methane sinks

Methane is removed from the atmosphere (*i.e.* converted to less harmful products) by a range of chemical and biological processes, which occur in different regions of the atmosphere. These include tropospheric oxidation, stratospheric oxidation and uptake by soils.

The troposphere is the lowest 15 km of the atmosphere. As colder air lies on top of warmer air in this section of the atmosphere, the troposphere is well mixed vertically by convection currents. The methane is therefore present at a constant concentration of approximately 1.7 ppm throughout the troposphere. Because atmosphere decreases in density with increasing altitude, over 75% of the atmosphere, and therefore by far the majority of methane, is contained within the troposphere (Figure 6). Oxidation of methane in the troposphere is the

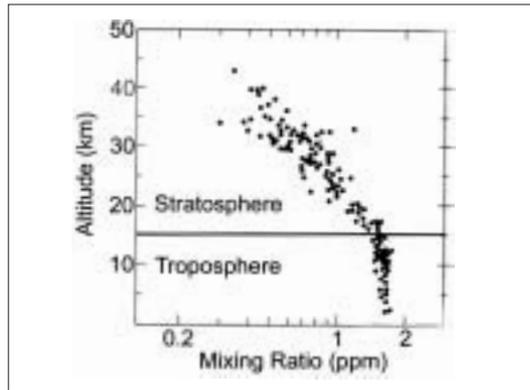


Figure 6: Relative concentration of methane in the atmosphere

Source: Warneck, 1988³⁴

largest methane sink, removing 506 Mt of methane per year from the global methane burden (Table 4). It is therefore changes to the chemistry and composition of the troposphere that will dominate the future environmental impact of methane emissions.

Above the troposphere lies the stratosphere. The stratosphere is less dense than the troposphere and is not mixed vertically by convection, as warmer air lies on top of colder air in this region. Methane enters the stratosphere from below and is consumed by chemical reactions, so the relative concentration of methane decreases with altitude. Stratospheric oxidation of methane consumes 40 Mt per year.

The third process for removal of methane from the atmosphere occurs at the ground-atmosphere interface. Bacteria present in soils can also oxidise methane, thereby removing it from the atmosphere.

Table 4: Sinks of methane

Mechanism	Methane removal (Mt)
Tropospheric oxidation	506
Stratospheric oxidation	40
Soil uptake	30
Total	576
Emissions	598

Tropospheric oxidation

The predominant mechanism for removal of methane from the earth's atmosphere is oxidation within the troposphere by the hydroxyl radical (OH). The hydroxyl radical is responsible for the breakdown and removal of a host of trace gases, including methane, and for this reason is known as the 'cleanser of the atmosphere'. In essence, atmospheric OH effects a low-temperature combustion of 'fuels', such as methane and other hydrocarbon species, by eventually oxidising methane to carbon dioxide, as would happen if methane were burned.

Reactions between methane and the hydroxyl radical initiates a chain of possible reactions that produce other species, such as carbon monoxide, nitrogen dioxide and hydroperoxide, which can then be removed from the atmosphere. This is a complex process with numerous feedback loops. A more detailed discussion of these reactions is provided in Appendix I.

The overall rate of removal of methane is dependent on the rate of the initial reaction between methane and hydroxyl. This, in turn, is dependent on the concentrations of these species in the atmosphere. This has two important consequences.

- Reaction between methane and hydroxyl removes both species from the atmosphere. As the concentration of hydroxyl reduces, the rate of methane removal will slow down. Increasing atmospheric methane concentrations removes hydroxyl from the atmosphere and so slows its own removal.
- Because the hydroxyl radical - the cleanser of the atmosphere - is capable of reacting with many species, methane is not the only influence on its concentration. Sources of hydroxyl (mainly ozone) are roughly constant, but it may be removed from the atmosphere by reactions with carbon monoxide (CO), nitrogen dioxide (NO₂), hydroperoxide (HO₂) and volatile organic compounds. In particular, the reaction between carbon monoxide and hydroxyl proceeds very rapidly, so carbon monoxide

scavenges hydroxyl from the atmosphere. Increased anthropogenic emissions of carbon monoxide (from transport), coupled with the further carbon monoxide produced from oxidation of methane, can cause significant hydroxyl concentration reductions and so slow the rate of methane removal.

As the rate of methane removal slows, its lifetime in the atmosphere and therefore its GWP will increase. Methane will become a more potent greenhouse gas over time if hydroxyl concentrations continue to decrease. In terms of policy, it is more effective to reduce methane emissions now while hydroxyl concentrations remain relatively high. Delaying action to reduce methane emissions, until a time when hydroxyl concentrations are lower, will result in the emitted methane being more potent.

Furthermore, successful methane emission reductions, preferably accompanied by lower anthropogenic carbon monoxide emissions, could result in an increase in hydroxyl concentrations and a subsequent lowering of the GWP of future methane emissions. This beneficial positive feedback loop is a further reason for encouraging methane emissions reduction in the short term.

Stratospheric oxidation

Some of the methane present in the troposphere passes into the stratosphere. Approximately 40 Mt of methane are oxidised in the stratosphere, representing 7% of all methane removal. The chemistry of methane in the lower stratosphere is identical to that in the troposphere, with hydroxyl radicals oxidising methane in the same manner. Indeed, oxidation of methane to carbon dioxide and water is the source of approximately 50% of stratospheric water vapour.

In the upper stratosphere, methane decomposition can be initiated in two other ways: by reaction with chlorine radicals or oxygen atoms. Chlorine atoms are produced by decomposition of CFCs and related compounds by the high intensities of ultraviolet light found in

the upper stratosphere. Oxygen atoms are similarly produced by the decomposition of ozone (O_3) in uv light; it is this reaction in the 'ozone layer' that prevents harmful ultraviolet radiation reaching the earth's surface.

When chlorine or oxygen atoms react with methane, they initiate the same chain reactions that occur in the troposphere, resulting in overall oxidation of methane and removal from the atmosphere.

Uptake by soils

Approximately 30 Mt of methane are removed from the atmosphere annually by uptake in soils. Soils contain populations of methanotrophic bacteria that can oxidise methane, by a process known as 'high affinity oxidation'. These bacteria consume methane that is in low concentrations, close to that of the atmosphere (<12 ppm). The bacteria favour upland soils, in particular forest soils.²⁴ Surprisingly, the bacteria responsible for high affinity oxidation processes remain largely unidentified. It is known, however, that exposure of soils to high ammonium concentrations leads to a loss of methanotrophic bacteria and a subsequent reduction in the rate of methane oxidation. The use of artificial fertilisers containing ammonia is therefore detrimental to the removal of methane.²⁴

2.4 Methane in the atmosphere

The atmospheric concentration of methane is thought to have increased by a factor of 2.5 since pre-industrial times, reaching 1745 ppb in 1998.¹ This rate of increase far exceeds that of carbon dioxide, concentrations of which are only 30% higher than in pre-industrial times. In fact, information is sufficient for the IPCC to assert that the current methane concentration has not been exceeded in the last 420,000 years.¹

Ecosystems may not be able to adapt to a rapid rate of climate change



How much heat is being trapped?

The amount of 'extra' energy being held within the earth's atmosphere because of the rise in atmospheric GHG concentrations is termed radiative forcing, measured in units of watts per metre square (W/m^2). Radiative forcing is the change in radiation balance due to a change in greenhouse gas concentrations over a quoted timeframe. The total radiative forcing of the well-mixed greenhouse gases since pre-industrial times (1750) is $2.43 W/m^2$. Of this, the radiative

forcing of methane is $0.48 W/m^2$. It is important to note that this is not the radiation absorbed by the 1745 ppb methane in the atmosphere. Rather it is the radiative forcing of the extra 1045 ppb methane present in the atmosphere since 1750. Essentially the radiative forcing is the difference in rate of heat capture now versus then.

Table 5: Radiative forcing of selected greenhouse gases

	CO_2	CH_4	N_2O
Pre-industrial concentration (ca. 1750) ppb	280,000	700	270
Concentration in 1998 (ppb)	365,000	1745	314
Relative concentration 1998/1750	1.30	2.49	1.16
Radiative forcing (W/m^2)	1.46	0.48	0.15
Atmospheric lifetime (years)	5-200	12	114

Source: IPCC, 2001¹

From Table 5, it can be seen that carbon dioxide is the most important greenhouse gas, with a radiative forcing of $1.46 W/m^2$. Methane is the second most important anthropogenic greenhouse gas, contributing 20% to the total radiative forcing, proportionally far greater than expected according to atmospheric concentrations of the gases. The explanation lies in the considerable potency of methane as a greenhouse gas.

Global Warming Potential

The different greenhouse gases vary in both potency and their lifetime within the atmosphere. On emission, different greenhouse gases have different abilities to absorb radiation. However, the radiative forcing of the emitted gas decays exponentially as the gas is removed from the atmosphere over time and the concentration

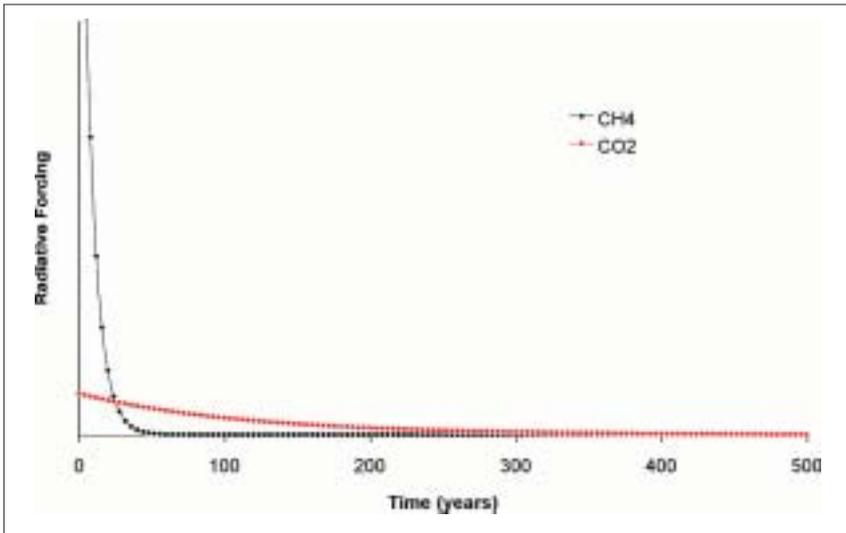


Figure 7: Radiative forcing of methane and carbon dioxide

decreases (Figure 7). The rate of this removal is dependent on the atmospheric lifetime of the species involved. It is therefore difficult to determine an absolute measure of the relative effects of one tonne of each gas, because these will vary over time. In fact, it is impossible to combine the two influences of potency and lifetime into a single definitive figure that reflects the properties of a greenhouse gas. However, it is useful to have one single parameter that reflects the influence of different gases, especially under multi-gas abatement schemes such as the Kyoto Protocol and other emissions trading schemes.

Table 6: Global Warming Potentials for the greenhouse gas ‘basket’

Gas	Lifetime (years)	Global Warming Potential (time horizon in years)		
		20 years	100 years	500 years
CO ₂	5-200	1	1	1
CH ₄	12	62	23	7
N ₂ O	114	275	296	156
HFCs	0.3-260	40-9,400	12-12,000	4-10,000
PFCs	2,600-50,000	3,900-8,000	5,700-11,900	8,900-18,000
SF ₆	3,200	15,100	22,200	32,400

Source: adapted from Table 3, IPCC 2001¹

The Global Warming Potential (GWP) is the parameter that has been adopted.

The GWP of a greenhouse gas is defined as “the [cumulative] radiative forcing from the instantaneous release of 1 kg of a trace substance relative to that of 1 kg of a reference gas”.¹ The reference gas is almost always carbon dioxide and so its GWP is always unity (Table 6). In visual terms, this is the relative area under the curves in Figure 7, up to a certain time limit. Short-lived gases such as methane have higher GWPs under short time-horizons. Conversely, long-lived species such as SF₆ have higher GWPs under long time-horizons. Table 6 shows the Global Warming Potential of the basket of six greenhouse gases over three different timeframes.

The effect of different time horizons poses interesting questions with regards to policy. Which value of GWP should be used to assess the relative importance of methane emissions versus carbon dioxide? The Kyoto Protocol and other key policies use the 100-year time horizon, although these are currently based on the old GWP for methane of 21 given in the IPCC’s Second Assessment Report. This will be updated to 23 for the second commitment period (2013-17). The IPCC most frequently quotes the 100-year GWPs, although has made no policy recommendations as to which GWP timescale to use.

Calculating CO₂ equivalent emissions

It proves useful to measure the potency of greenhouse gas emissions in one set of units: tonnes CO₂ equivalents (t CO₂e). To calculate the impact of methane emissions, the mass emitted is multiplied by the 100-year GWP. One tonne of methane is deemed equivalent to 23 t CO₂e.

It is also important to note that GWP is defined in terms of mass of emitted gas, not volume. Care must be taken if GHG emissions are measured as volumes – one litre of carbon dioxide weighs 2.75 times as much as one litre of methane. So one litre of methane is 8.4 times (23/2.75) as potent as one litre of carbon dioxide.

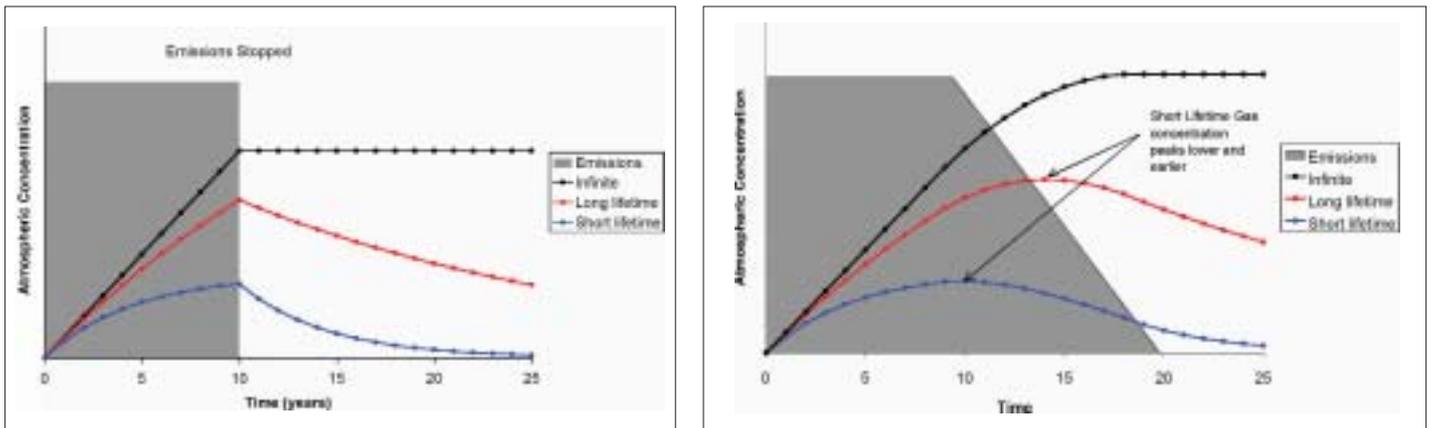


Figure 8: Effect of emissions cessation (a) and gradual reduction (b) on atmospheric concentration

The influence of lifetime

The Global Atmospheric Lifetime of methane in the atmosphere is defined as the atmospheric burden (concentration) divided by the sink strength (annual removal).

$$\text{Global Atmospheric Lifetime of CH}_4 = \frac{\text{Atmospheric burden}}{\text{Sink strength}} = \frac{4850 \text{ Mt}}{576 \text{ Mt}} = 8.4 \text{ years}$$

However, the chemistry of methane in the atmosphere contains several feedback loops affecting the concentration of other atmospheric species such as O₃ and OH, which slows the removal of GHGs (including methane itself) from the atmosphere. This feedback effect is included in the Perturbation Lifetime, which is longer than the Global Atmospheric Lifetime and is equal to 12 years. The Perturbation Lifetime is the standard figure used.

For constant emissions, species with a short lifetime do not reach such high atmospheric concentrations because they can be removed more rapidly from the atmosphere. If emissions

are stopped completely, as shown in Figure 8a, the atmospheric concentration of a short lifetime gas will drop away much more rapidly than a gas with a long lifetime.

A sudden stop in emissions of a particular gas is an unlikely scenario, so Figure 8b looks at the effect of gradually reducing emissions over a period of time. It can be seen that the concentration of the short lifetime gas reaches its peak earlier and also drops away more rapidly after this point. This means that policies targeting short-lived gases, such as methane, will rapidly lead to tangible atmospheric concentration reductions. Gases with a longer lifetime reach higher atmospheric concentrations and experience a longer lag between emissions reduction and atmospheric concentration reductions. Reducing emissions of short-lifetime potent gases such as methane is therefore a valuable means of rapidly slowing global temperature rise.