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Xiaoli Chai
Tongji University

David J. Tonjes
Department of Technology and Society, david.tonjes@stonybrook.edu

Devinder Mahajan
SUNY Stony Brook, devinder.mahajan@stonybrook.edu

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Methane Emissions as Energy Reservoir: Context, Scope, Causes and Mitigation Strategies

Chai Xiaoli[1], David J. Tonjes[2], Devinder Mahajan*,[1]

[1]State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science & Engineering, Tongji University, Shanghai, China.

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Climate change; methane emissions; fugitive methane; renewable methane; energy production; renewable fuels; municipal solid waste; landfills; landfill gas; biogas; waste water; oil & gas operations; agriculture waste; anthropogenic methane; gas-to liquids (GTL); electricity from renewables; renewable energy policies; GHG emissions; carbon dioxide emissions.

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*Corresponding author: Advanced Energy Research and Technology Center (AERTC), Stony Brook University, Stony Brook, New York 11794-2275, USA; [1]State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science & Engineering, Tongji University, Shanghai, China. Tel.: +1-631-632-1813; E-mail:devinder.mahajan@stonybrook.edu (D. Mahajan).
[2]Technology and Society, Stony Brook University, Stony Brook, New York 11794-2275, USA

ABSTRACT

Methane (CH_4) is now considered a bridge fuel between present fossil (carbon) economy and desired renewables and this energy molecule is projected to play an important role in the global energy mix well beyond 2035. The atmospheric warming potential of CH_4 is 28-36 times, when averaged over a 100-year period, that of carbon dioxide (CO_2) and this necessitates a close scrutiny of global CH_4 emissions inventory. As the second most abundant greenhouse gas (GHG), the annual global CH_4 emissions were 645 million metric tons (MMT), accounting for 14.3% of the global anthropogenic GHG emissions. Of this, five key anthropogenic sources: agriculture, coal, landfills, oil & gas operations and wastewater together emitted 68% of all CH_4 emissions. Landfills are ranked as the third highest anthropogenic CH_4 emission source, behind agriculture and coal mines, and emissions from the waste sector are expected to reach almost 800 million metric tons CO_2equivalent(MMTCO_2e) in 2015.

The two largest economies spewed out 42% (14% (U.S.) and 28% (China)) of the world's total greenhouse gas (GHG) emissions; these two countries are also the largest producers of municipal solid waste (MSW). The United States averages 250 MMT of MSW annually, of which about 63% enters landfills. In 2015, there were 2434 landfills in the United States and CH_4 from these landfills accounted for 138 MMTCO_2e released into the atmosphere and represents 17.7% of all U.S. CH_4 emissions. China had 580 landfills and treated 105MMT of MSW in 2013. Methane produced from landfills contributes about 13% of total CH_4 emissions in China. Almost 50% of landfills in China did not install efficient LFG collection and reuse system to make them manageable so a great deal of CH_4 and CO_2 GHGs are emitted without intervention. Recent data show that globally, 45 bcm of CH_4 or 282 million barrels of oil equivalent (boe) was annually released from landfills into the atmosphere. Managing methane emission from landfills is a global challenge, though China lags behind in managed landfills that contribute to adverse health effects on the population. Moreover, the rich organic content of MSW in China indicates that CH_4 emissions there may be underestimated. The China unmanaged landfill scenario is further duplicated in developing as well as in least-developed countries.

This review starts with a dialog on CH_4 emissions and climate change and the chemical changes the CH_4 molecule undergoes in the atmosphere (Section 1). Section 2 deals with identification of global CH_4 emissions from key sources, particularly anthropogenic, among

those are agriculture, coal mines, landfills, oil & gas operations and wastewater. Though each of these sources is descriptive on their own, the focus of Section 3 is on landfills with particular emphasis on the United States and China, two largest producers of waste. The quantitative measurement of CH_4 emissions is still uncertain so Section 4 is devoted to various CH_4 estimation models, such as United States Environmental Protection Agency (US EPA) LandGEM, the United Nations Intergovernmental Panel on Climate Change (IPCC) and others that are under development. The key landfill emissions data bases and the collection methodologies such as those used in the United States and recently released by the Chinese government are highlighted. Section 5 describes chemistry of pathways that produce CH_4 from various sources. Section 6 reviews potential of CH_4 as an energy source for combined heat and power (CHP) production as well as and pathways for conversion of CH_4 into renewable gaseous fuel for use as compressed natural gas (CNG) and clean liquids that could be used as either drop-in replacement (gasoline, diesel, jet fuel hydrocarbons) or advanced oxygenated fuels such as methanol, a versatile precursor to fuels and chemicals, and dimethylether (DME), a clean diesel substitute. Section 7 describes in-place government policies to deal with CH_4 emissions from specific sectors. These policies vary from country to country but the Unites States and the European Union (EU) countries are well ahead in curbing methane emissions while China is now playing close attention to its increasing global share of emissions. The last section (Section 8) identifies science and technology and needed policy challenges to manage fugitive methane; this includes identification of technological intervention that China and other countries would need to capitalize on this wasted resource by efficiently harvesting this energy source, needed government policies and science and technology issues that researchers have to deal with to help combat climate change. The overall review provides a comprehensive description that could lead a coherent picture to harvest global CH_4 emissions for useful energy, a sensible solution.

Last year marked a milestone in the U.S.-China relations when the White House announced that the United States intends to achieve an economy-wide target of reducing its emissions by 26%-28% below its 2005 level in 2025 while China intends to achieve the peaking of CO_2 emissions around 2030 and intends to increase the share of non-fossil fuels in primary energy consumption to around 20% by 2030. In another 2014 initiative, the United States also identified fugitive methane from oil and gas operations, agriculture, and landfills to maintain respective post-2020 actions on climate change, recognizing that these actions are part of the longer term efforts to transition to low-carbon economies, mindful of containing the global temperature increase goal of 2℃, also known as two-degree scenario (2DS). These commitments by the United States and China were evident in the successful agreement at the culmination of the recently concluded COP21 event in Paris. This review is written to start a dialog among researchers that tetrahedral CH_4, the simplest among all organic compounds, plays such a complex role in climate change that as its use increases, it will rival carbon dioxide (CO_2) in GHG effect in the coming decades if no attempt is made to contain its emissions.

Contents

1. Global methane emissions

Methane (CH_4) is the most common organic compound in the atmosphere [1] and its 2013 globally averaged atmospheric concentration was 1824 parts per billion by volume (ppbv), a value that has been increasing about 0.5% per year over the past 30 years (Fig. 1) [2]. Current estimates, which tend to converge, are the product of four independent research communities [3], using flask grab samples analyzed by gas chromatography with flame ionization with a precision of ± 2ppb. Atmospheric concentrations in the Pleistocene Epoch have varied from 350 ppbv for glaciated periods to 700 ppbv for more ice-free periods, according to polar cap ice core sample analyses [4]. These modern values are considerably less than the estimated 1-10 parts per million by volume (ppmv) concentrations in the abiotic Hadean Eon and 100-1000 ppmv in the anoxic Archean Eon [5], although maximum concentrations then may have been 3500 ppmv [6]. Following the onset of photosynthesis but before complete oxygenation of the atmosphere, concentrations probably were reduced to 100-300 ppmv [7]. Oxygenation of the atmosphere caused order of magnitudes reductions in CH_4 concentrations. The maximum estimated concentration of 750 ppbv for the pre-Industrial Revolution Pleistocene is elevated a little compared to interglacial averages, probably because of anthropogenic land use changes over the past 10,000 yrs [8] [9]. Methane concentrations over the past 250 years have increased by approximately 250%, increasing more than carbon dioxide (CO_2) concentrations (which doubled over the same period) (Fig. 2) [4] [1] [10].

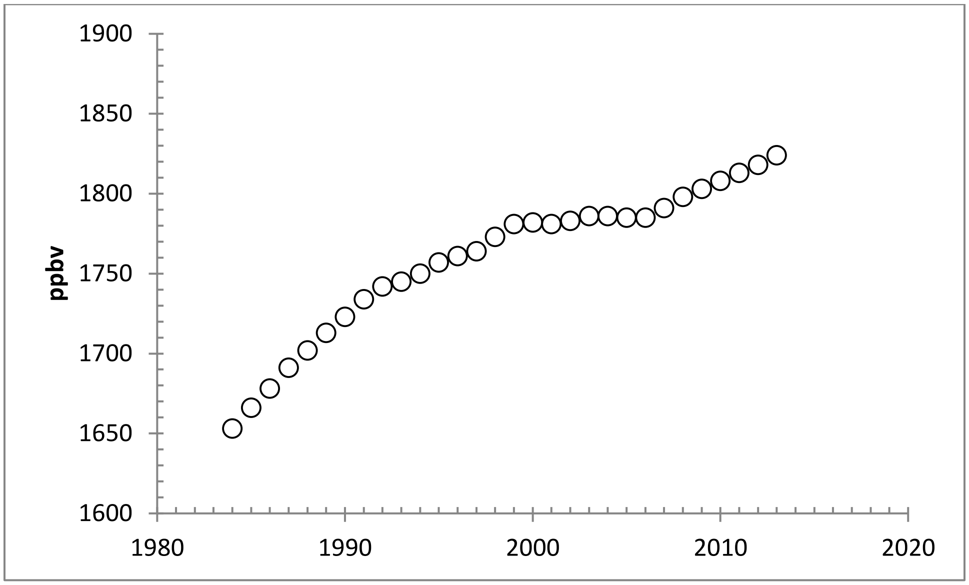


Fig 1. Recent trends in globally-averaged atmospheric methane concentrations (adapted from ref. 2)

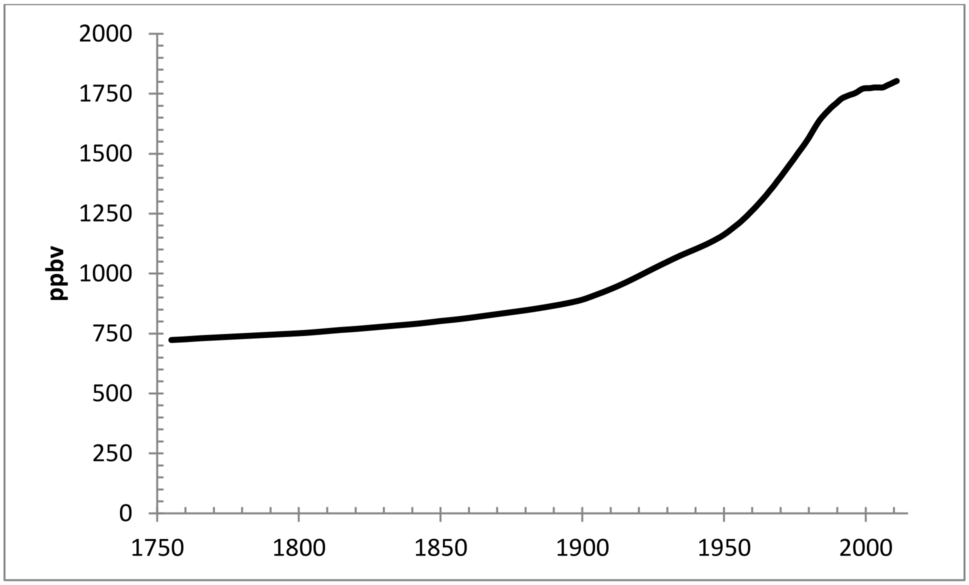


Figure 2. Atmospheric methane concentrations over the past 250 years (data from ref. 11)

Atmospheric CH_4 decays to CO_2 and water (H_2O), primarily due to reactions initiated by the hydroxyl radical (OH·) [10], especially under strong sunlight in the tropics [4]. The reaction pathway (Fig. 3) is not simple and involves several feedbacks, and some soluble intermediate compounds can be removed by precipitation. The most important feedback is linked to the OH· reaction pathway (Fig. 4); atmospheric CH_4 tends to consume OH· but the linkages between compounds that create OH· and the CH_4 cycle mean it is not always the case that the destruction of CH_4 requires consumption of OH· [12]. Still, one reaction pathway for CH_4 with OH· results in CO; this produced CO is then oxidized by more OH·, so one molecule of CH_4 results in the consumption of two molecules of OH·. Therefore, as CH_4 concentrations increase, there are somewhat fewer OH· to react with, thus slowing the destruction of CH_4 – a positive feedback where more CH_4 results in a longer CH_4 atmospheric lifespan. In this way, CH_4 plays an important role in determining the overall oxidizing capacity of the atmosphere and its ability to remove many pollutants, as OH· is involved in many reactions that determine the fate of common air pollutants [1].

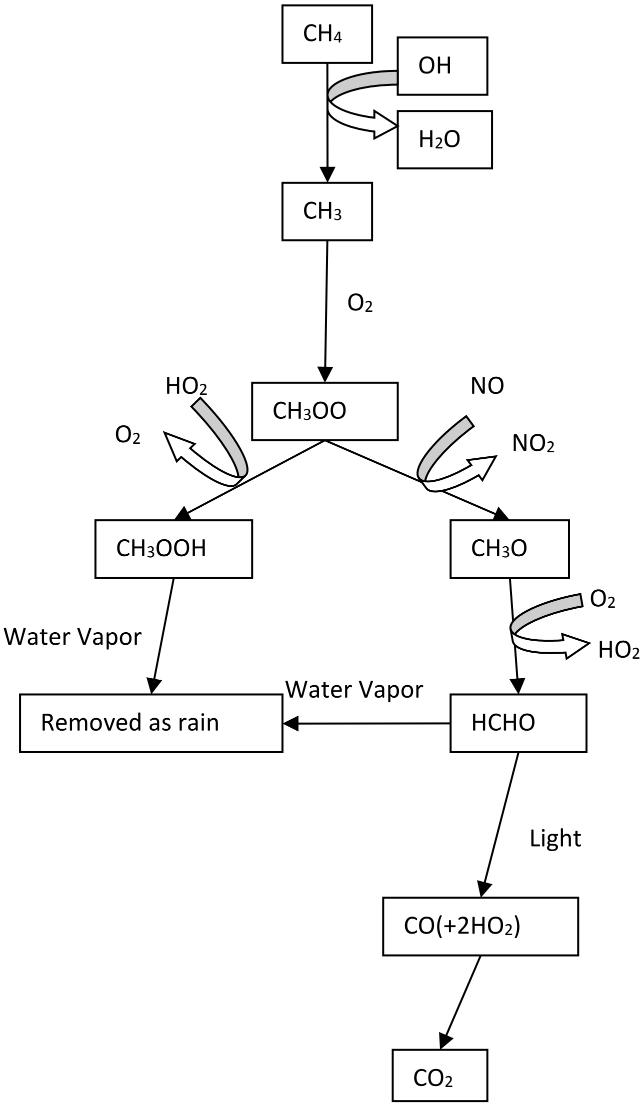
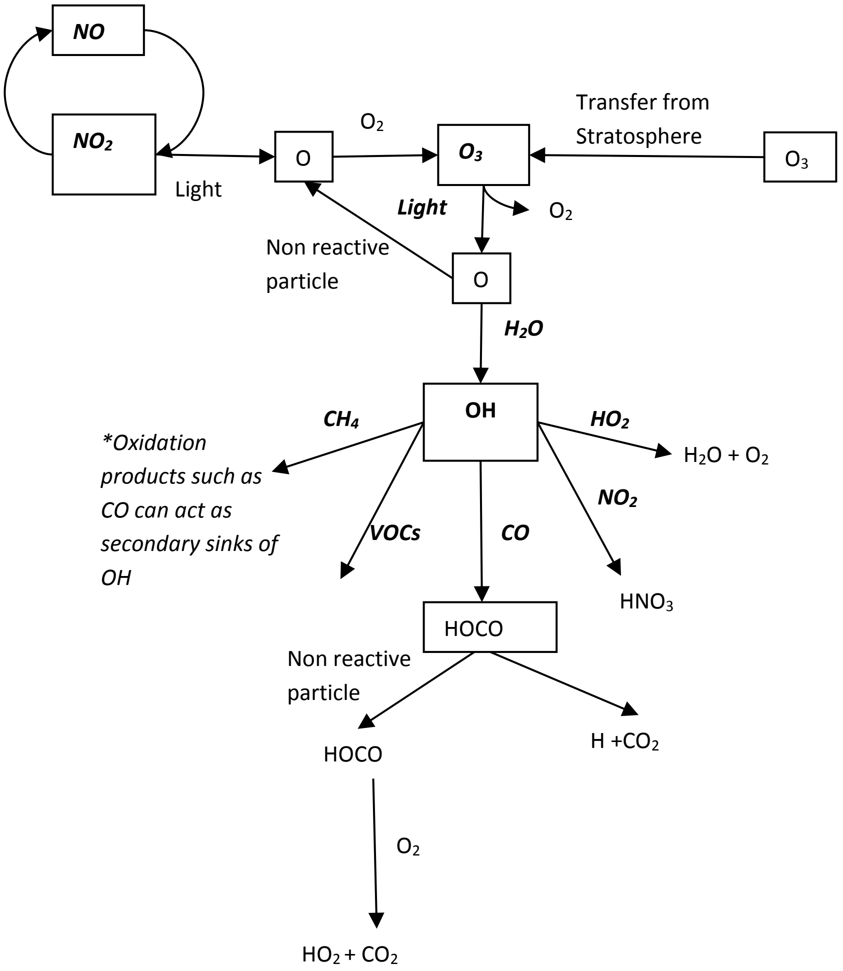


Figure 3. Atmospheric decay pathway for methane (adapted from ref. 12)



****Sources and Sinks are italicized***

Figure 4: Atmospheric decay pathway for the hydroxyl ion (adapted from ref. 12)

On average, molecules of CH_4 have an eight to nine yr atmospheric life span [13] [4] (given as 9.1 yrs in [10]), calculated as the atmospheric content divided by the removal rate. However, because of feedbacks that slow its removal, the lifespan of CH_4 is often given as its perturbation lifetime. Values for the perturbation lifespan are usually in the range of 12 yrs [12], with IPCC [10] using 12.4 ± 1.4 yrs, but may be as much as 14.4 yrs [14]. The OH· is the primary means of removing CH_4 from the atmosphere [10]; one general estimate found the OH· decay process accounts for 90% of CH_4 removals; soil oxidation by bacteria removes 4% more, stratospheric reactions with chlorine and oxygen radicals remove 3% more, and chlorine radicals present at the sea-air interface remove the remaining 3% [3]. Because OH· reactions dominate, small changes in its concentration can cause variability in atmospheric CH_4 concentrations [4]. Nonetheless, interannual and interdecadal variability of CH_4, while poorly constrained, is surmised to be due to changes in wetlands releases [15], and probably driven by precipitation differences [3]. Higher concentrations of CH_4 have been measured in the northern hemisphere compared to the southern hemisphere over the past 1000 years, with the difference increasing from 30-60 ppbv to 150 ppbv in the twentieth century [1]. Seasonal variability at particular measurement sites appears to be driven by changes in tropical wetlands releases as mediated by differences in global dispersion of the released gas [13]. Methane greenhouse gas (GHG) effects are spatially differentiable from those from CO_2, and so these two gases need to be separately determined in order to model GHG effects [1].

Methane is a potent GHG; long-wave heat radiation (infra red light) from the earth's surface is absorbed by the vibrations of the carbon-hydrogen bonds of CH_4 at wavelengths clustered at 7-13 µm (wave numbers of 1200-1400 cm^{-1}), with the most important feature at 7.66 µm (1306 cm^{-1}), preventing radiation from escaping to space and thereby maintaining the earth's surface at temperatures above its "black box" values [16] [1]. Methane increases cause increasing GHG effects with the square root of concentration due to partial saturation [1], although since the wavelengths at which CH_4 absorbs radiation are not entirely saturated each additional molecule of CH_4 adds to the GHG effect [17]. Changes in CH_4 concentrations correlate well with changes in temperature over the past 500,000 years. It is not clear if temperature changes cause CH_4 concentration changes, or if changes in CH_4 concentrations cause temperatures to change, as the resolution of the signals is not temporally sharp enough to discriminate [1].

The strength of GHGs is conventionally compared to CO_2; this is because recent increases of the atmosphere's greenhouse effect are primarily due to increasing CO_2 concentrations. Because the lifespan for CH_4 is much less than that of CO_2 (CO_2 is relatively inert, and is removed from the atmosphere by coming into equilibrium with the ocean, a process that requires ~1000 years to complete due to slow deep water turnover) [18], the CO_2-relative GHG impact of CH_4 (sometimes called global warming potential, "GWP") varies depending on the time horizon that is considered (Table 1). The 100-year horizon is the most commonly considered value. However, although the conversion of CH_4 to CO_2 is already accounted for in the GWPs, indirect effects associated with its atmospheric decay cycle can double impacts listed in Table 1 [1]. IPCC [10] distinguishes between fossil CH_4 and general CH_4 emissions, as fossil CH_4 emissions contribute net "additional" CO_2 to the atmosphere on decay. The sum of CH_4 emissions accounts for ~20% of current GHG radiative forcing; CO_2 creates about 70% of the forcing, and other gases account for the difference [10].

Table 1. Global warming potential for methane relative to carbon dioxide

	Forcing (W m^{-2})	Time Horizon		
		20 yrs	100 yrs	500 yrs
[19] direct effects (indirect effects)			15 (30)	
[14]	0.65			
[1]	0.47-0.55	62±20	24±7.5	7.5±2.5
[20]		105	33	
[12]		62	24	7
[21]			25	
[22]			21	
[23]			21	
[24]			21	
[25]			25	
[26]			21	
[27]			25	
[28]		62		8
[29]			21	
[30]			23	
[10] (for 2005)	0.47			
[31]			25	
[10]	0.48±0.05	84	28	
[10] "fossil methane"		85	30	
[10] with feedbacks		86	34	

Many assessments of non-CO_2 GHGs express the amounts of these GHGs as CO_2-equivalents (CO_2e) because such units allow for more direct comparisons of the potential effects associated with the compounds. However, conversion of release amounts or atmospheric concentrations requires adopting a particular time frame and GWP value. As Table 1 shows, the standard (IPCC) values have drifted upwards over several decades for CH_4, and some researchers prefer different values and time scales as appropriate measures of relative impacts. This suggests that older CO_2e values require adjustment to be considered alongside more recent evaluations; it also implies use of CO_2e units requires explicit identification of the time scale and conversion factor being used. Note that for CH_4 especially, indirect effects are usually not included in the valuation factors. Indirect effects include that oxidation of CH_4 causes increases in water vapor, and its oxidative consumption of OH· results in other GHG gases not being oxidized in their turn [1].

Based on a "steady-state" atmospheric concentration of 700 ppbv and a similar-to-present lifespan of CH_4 of ~9 yrs, pre-Industrial Age emissions to the atmosphere were estimated to be on the order of 215 Tg yr^{-1} [4]. Most current emission estimates range from a little less than 500 Tg yr^{-1} to just more than 600 Tg yr^{-1} (Table 2). Some estimate the values to be higher – for instance, Kirschke et al. [3] set their bottom up generation value at 678 Tg yr^{-1}. Models of monitored air concentrations ("inverted" source determinations) sometimes find large discrepancies from government organization-reported values [32], although Kirschke et al. [3] presented arguments that summed bottom-up values resulted in overestimates. To account for increasing atmospheric concentrations, consumption of CH_4 must be about 0.5% less than the generation estimates. Note that IPCC in its most recent assessment [10] has adopted values and assessment techniques from Kirschke et al. [3].

Table 2. Estimates of methane generation and consumption rates

Source	Methane Generation Rate (Tg yr^{-1})	Methane Consumption Rate (Tg yr^{-1})
[13]	545±20	
[15]	525	506
[10] top-down	553 (526-569)	550 (514-560)
[10] bottom-up	678 (542-852)	632 (592-785)
[3] literature values (bottom up)	526-569	514-560
[3] literature values (top down)	542-852	592-785
[3] bottom up estimate	678	632
NATO-IRW [33]	510	
[1] range (best estimate)	410-660 (503)	430-660 (515)
[12]	598	576

Most global estimates of CH_4 generation are "bottom up": they are based on summing individual source category estimates. Uncertainties arise due to variability across space and time for point-source source estimates, which then need to be applied across many source areas, which also may not be well-defined [1]. Consumption is even more difficult to determine, as measurements of OH· concentrations are not accurate nor well distributed. Most estimates of consumption use various atmospheric chemistry models. It is also possible to determine CH_4 concentrations from a "top-down" modeling approach, using the model outputs to assess variability in monitoring station data, and then fitting presumptive sources to those outputs [3].

Methane emissions are usually classified into source categories. One way is to classify CH_4 into biogenic (from microbial processes), thermogenic (from geologic sources), and pyrogenic (from incomplete combustion) classes, because each of these has a different stable carbon (δC^{13}) isotopic signature [3] (Table 3). This can enable verification of estimates based on source categories, by comparing measured isotopic values for atmospheric CH_4 to modeled values based on source signatures [3] [4]. However, most broad assessments of CH_4 generation commonly parse the releases into different groupings, mostly based on whether the emissions are anthropogenic (agriculture, waste management, land use, fossil fuel industry) or naturally caused (wetlands, termites, seeps) [10] [27]. Our sources assessment (see below) follows this convention, as it is most amenable to identification of potential mitigation of fugitive releases

Table 3. Isotopic signatures of methane by source [3]

Category	Source Exemplars	$\delta^{13}C$ (‰)
Biogenic	Wetlands, rice paddies, dam impoundment sediments, termite and ruminant digestive systems, manure, landfills, sewage treatment systems	-55 - -70
Thermogenic	Fossil fuels: marine and terrestrial seeps, mud volcanoes, oil and gas extraction well leaks, pipeline leaks, coal gas	-25 - -55
Pyrogenic	Fossil fuels, wildfires, biofuels	-13 - -25

Methane is produced biologically by single-celled organisms in Archaea, where CH_4 is a waste byproduct from metabolic consumption. There are three distinct redox reactions. For the simplest, CO_2 is reduced and hydrogen gas (H_2) oxidized; energy is produced, water is created, and CH_4 released as a waste gas. The reactions are catalyzed by nickel compounds and are dependent on intracellular thiol cofactors [34] [35]. In detail, complicated organic molecules need to be simplified before they can be metabolized by methanogens. This is usually conceptualized as a three-step process. First, organisms use hydrolysis to convert carbohydrates to simple sugars, proteins to peptides and amino acids, and lipids to long-chain fatty acids. Next, other organisms ferment these products either through acidogenesis to volatile fatty acids, alcohols, ammonia, CO_2 and H_2, or through acetogenesis to acetate. The presence of methanogens often suppresses concentrations of H_2 and formate so that other degradative pathways that are more energetically favorable are not followed. The class of methanogenic organisms then follows three distinct pathways to produce CH_4. Reductive methanogens convert CO_2 and H_2 to CH_4 and water. The methyl groups in organic compounds associated with acidogenesis pathways are coupled to coenzyme M and then demethylated, producing CH_4 and water with H_2, as was the case for the reduction of CO_2. Only a few genera of aceticlastic methanogens convert acetate to CO_2 and CH_4 [36]. Methanogens tend to be poisoned by O_2 or by reaction products of O_2, and so are considered to be strict anaerobes. Microenvironments may exist in otherwise oxygenated settings to allow production of CH_4 [36]; the mechanisms that allow for oxidative production of CH_4 from terrestrial plants is not known [37]. Methanogens are found in a variety of anaerobic environments: waste facilities such as landfills and sewage treatment plants, the guts of certain primary consumers (notably termites and cattle), rice paddies, and natural wetlands [10].

Because intermediate reactions catalyzed by other classes of organisms are necessary for methanogens to use most organic compounds, it is not likely they were among the first organisms on early Earth, and they produce less energy per mole of carbon than any other strand of Archaea, so that they are outcompeted when other electron donors are not limited [36]. Nonetheless, by the mid-Archean they are likely to have been important in maintaining the early atmosphere, partly because atmospheric residence of CH_4 would have been closer to 1000 yrs absent oxidizing agents and would have been key in keeping the early Earth ice-free [5]. Based on isotopic data, it seems likely that “recent” differences in glaciated and warm-period CH_4

concentrations in the Pleistocene are due to greater wetlands production of CH_4 by bacteria when glaciers are less extensive [4]. Generally, warmer temperatures in the late Cenozoic Era are related to higher CH_4 concentrations [38] [39] [40], and positive excursions in CO_2 concentrations at other times in this era also seem likely to have been caused at least partly by increased CH_4 generation, although the source of the CH_4 may have been geologic rather than biotic [41].

Wetlands release between 60% [4] and 70% [1] of non-anthropogenic CH_4. Variations in Cenozoic and early Holocene CH_4 concentrations have been linked to wetlands expansion and contraction [1], and even much of changing concentrations over the past several millennia appear to be linked to changes in wetland area although anthropogenic effects on atmospheric concentrations are detectable [9]. Tundra and higher altitude bogs emit one-third of wetland CH_4 [4], but tropical South America and Africa are the greatest sources, with large emissions also coming from southeast Asia and temperate South America [3]. This creates latitudinal and seasonal signals in emissions [42] [3]. The saturated soils of wetlands, which typically have high carbon loading and slow water circulation, tend to be anoxic. This supports anaerobic decay of organic matter. Where redox conditions allow, methanogenesis occurs. The wetland water interface may be a region of intense CH_4 oxidation, but often more CH_4 is produced than can be consumed. Modern agriculture is usually assessed as being the greatest single source of CH_4 [42], but wetlands are the second largest single source. Changes in rainfall in tropical South America and/or Africa has consequential impacts on wetland release rates, and therefore these climatic conditions dominate interannual variability in atmospheric CH_4 concentrations [3] [10].

In the mid-2000s there was flurry of excitement regarding an unexpected source term for CH_4. Frankenberg et al. [43] identified high emission levels from tropical forests through space-based observations. The amounts (30 Tg yr^{-1}) were within model budget uncertainties (50-100 Tg yr^{-1}). Incubation experiments in the field and laboratory suggested that some unidentified methanogenetic process in forests could cause CH_4 releases from live plants as well as fallen litter. Field experiments were partly confounded by the unavoidable presence of atmospheric CH_4, but laboratory work in CH_4-free settings suggested aerobic methanogenesis was occurring, and because of the depleted δC^{13} signatures of the resulting gases, pectin was probably the plant material being consumed. Global emissions were estimated to be 62 to 236 Tg yr^{-1}, with approximately 10% from litter and the remainder coming from living tissues [44]. The deviation in δC^{13} values was seen as validating excursions measured in ice cores in pre-Industrial times [45]. The large potential output was quickly reduced: to less than 125 Tg yr^{-1} through three independent CH_4 budget modeling exercises [46], to 20-69 Tg yr^{-1} by reconsidering assumptions made in the original global output estimate [47], and to potentially as low as 0 Tg yr^{-1} through reconsideration of ice core δC^{13} values (although uncertainties associated with biomass combustion mean that substantial emissions of more than 100 Tg yr^{-1} were still considered possible) [48]. Confirmatory experiments sometimes found emissions, and sometimes did not, although a consensus seems to be that woody plant pectins under UV-light could produce CH_4 through an undetermined mechanism [37]. Lichens and bryophytes [49] and wheat farming [50] have been found to cause some methane emissions, too, although one study suggested aerobic agricultural soils are a net sink and not a source of CH_4 [51]. Recent global budgets do not include aerobic methanogenesis from terrestrial plants as a substantial source of atmospheric CH_4 (see [10] and [3]) and IPCC [10] described it to be "unlikely" to be a significant contributor. Linked to this is the "ocean methane paradox," where the surface ocean is saturated with both CH_4 and O_2; most budgets estimate the oceanic contribution to atmospheric methane at 5-25 Tg yr^{-1}. Research suggested that at least some of these releases were from methylphosphonate decomposition to generate phosphate (under low phosphorus conditions) in the surface ocean saturated in O_2 [52]. In addition, thawing permafrost, because the carbon made available in this process is likely to be under anaerobic conditions, is expected to be a potentially large CH_4 source in the near future, although it is not a significant element in current CH_4 budgets [53].

Submarine seeps and mud volcanoes are the largest geologic point sources of CH_4 [54]. A great deal of ocean sediment-sourced CH_4 is oxidized before it reaches the open ocean [55]. Some abiotic CH_4 is also produced by volcanic outgassing. Spreading ridges create serpentine rocks, which tend to exclude ferrous minerals. Serpentine oxidizes to magnetite, which leads to the reduction of CO_2 to CH_4 [5] [56]. Other CH_4 classed as abiotic production occurs with the burial of organic carbon fixed by autotrophs, which is then diagentically released as CH_4 either as direct gas seeping to the atmosphere or through volcanic releases [35]. Release of CH_4 from oceanic hydrates can also be perceived of as an abiotic CH_4 release [41], although it is likely most CH_4 in hydrates was originally produced through methanogenetic organisms. Thermogenesis typically results in much higher ethane and propane to CH_4 ratios than biotic methanogenesis, and δC^{13} values are smaller [36].

Fossil fuels are a source of CH_4. Fossil fuels too are diagenetically altered organic carbons, present as solids (coal), liquids (petroleum), or gas (natural gas). Methane is a component in all of these carbon states, and is a byproduct release associated with the harvest, transport, and use of these resources [10] [20] [1]. Natural fossil fuel sources include diffuse but widespread microseepage from petroleum-containing sedimentary basins [54]. Incomplete combustion of wood, fossil fuels, and other carbon-containing materials is also a source of CH_4 [10] [1] [3].

Release of CH_4 to the atmosphere from many environments can be inhibited and greatly reduced because of methane oxidizers. This is especially true in sedimentary environments [36]. Methane oxidizing bacteria will be discussed thoroughly in Section 4.

2. Methane emissions from key anthropogenic sources

This section describes CH_4 emissions to the atmosphere from four key anthropogenic sources: agriculture, coal mines, gas systems (including other petroleum system sources), and wastewater management. Landfills are discussed separately and more completely in Sections 3-5. These five sources are the dominant anthropogenic sources (Table 4) and so offer opportunities for control of CH_4 impacts regarding climate change. Table 5 lists natural sources of methane.

Table 4. Anthropogenic sources of methane (Tg yr^{-1}) (*/**: considered together) ([1] livestock manure only) ([2] includes manure)

	Agriculture	Biomass Combustion	Coal	Landfills	Gas	Wastewater	Other	Total (Tg yr^{-1}) Percent of Total Emissions
[57]	190	55	35	40	45			365 68%
[33]	159	50	46	22	30	25	30	360 70%
[28]	155	50	50	25	30	25	30	365 70%
[1]	141		103*	61	103*			355 70%
[21]	50%	4%	6%	11%	20%	9%		
[15]	121±19	50±8	47±10	55±11*	63±9	55±11*		
[10]	200 (187-224)	35 (32-39)	96* (85-105)*	75**[2] (67-90)**[2]	96* (85-105)*	75**[2] (67-90)**[2]		331 (304-368) 50%-65%
[3] (top-down)	209 (180-241)**	30 (24-45)	96 (77-123)*	209 (180-241)**	96 (77-123)*	209 (180-241)**		335 (273-409) 61%
[3] (bottom-up)	200 (187-224)**	35 (32-39)	96 (85-105)*	200 (187-224)**	96 (85-105)*	200 (187-224)**		331 (304-368) 49%
[58]	167	11	37	46	101	29	18	325
[59]					60			
[22]	140	152*	152*		152*			357.9

Table 5. Natural sources of methane (Tg yr^{-1})

	Fires	Seeps	Termites	Wetlands	Other	Total (Tg yr^{-1}) (Percent of Total Emissions)
[57]		5	40	115	15	175 32%
[33]	2		20	110	16	150 30%
[28]			20	110	20	150 30%
[1]			20	115	25	160 30%
[15]			23±4	147±15	19±6	
[10]	3 (1-5)	(42-64)	11 (2-22)	217 (177-284)		347 (238-484) 35%-50%
[3] (top-down)				175 (142-208)	43 (37-65)	218 (175-273) 40%
[3] (bottom-up)	3 (1-5)	54 (33-75)	11 (2-22)	217 (177-284)		347 (238-484) 51%

There is variability in the assessment of sources. Part of the differences comes from definitional issues (such as whether wildfires are considered separately from biomass combustion for energy purposes), but most of the differences come from the use of models primarily based on area emission rates. There are only a few aggregate estimations based on collecting measurements from the dispersed and numerous locations of CH_4 releases, even when only one or two kinds of CH_4 sources are being considered (e.g. [59]). Note that most sectoral estimates of natural CH_4 generation are less than pre-anthropogenic influence budget estimates of 215 Tg yr^{-1}, but that IPCC [10], following the lead of Kirschke et al. [3] in their bottom up estimates, sees natural sources as generating much more (75% more) CH_4 than the budget model determined [4].

All but one current assessment find that most CH_4 releases have anthropogenic sources, so that most find circa two-thirds of all CH_4 is now released because of human activities; this ignores secondary effects associated with climate change, such as increased forest fires [60] and termite activity [61]. Although short-term variations in CH_4 concentrations are most probably due to climatic effects on wetlands, the overall trend of increasing CH_4 concentrations is being driven by human-caused releases to the atmosphere [10] [15] [3].

IPCC [11] notes that assessments of CH_4 sources are more uncertain than assessments of CO_2 sources. Kirschke et al. [3] estimated that uncertainties in CH_4 quantifications are being reduced, but are still substantial: 50% for wetlands and perhaps 100% for other natural sources; 60% for biomass burning, and 30% for waste, fossil fuel, and agriculture anthropogenic source terms. Brandt et al. [62] estimated that emissions as estimated by the US Environmental Protection Agency (USEPA) in its inventory reports are at least 50% too low in sum, and that errors are greater for certain source categories (as surmised from isotopic analyses). In addition to scaling issues discussed above, errors accumulate because samples are not representative of sources (i.e., whether or not fracking effects are not accurately accounted for), samples are too few in number, may be biased because of selection of cooperative sites, data uncertainty is not properly accounted for, and distributions of sources are likely to have “heavy tails,” which when coupled with insufficient sampling, means large sources are not well represented in the data sets.

2.1. Agriculture

Agriculture is usually assessed as the largest category of anthropogenic CH_4 releases, and the single largest source of CH_4 to the atmosphere. The predominant sources have long been understood to be rice paddies and livestock (either from manure or rumen releases, or both) [63] [64] [65], and that is still the current understanding [10]. Rice cultivation is a much smaller source than livestock, with estimates for rice cultivation about 40 Tg yr^{-1} and ruminants approximately double [4] [10], although Bloom et al. [66] estimated rice emissions to be about 66 Tg yr^{-1} (using a scaling for combined rice-wetlands releases), which was similar to data compiled by Wuebbles and Hayhoe [1]. USEPA [58] estimated agriculture as being 25% greater than many estimates (~160 Tg yr^{-1}) but found rice a smaller contributor (24 Tg yr^{-1}) and livestock thus five times greater a source than rice. Kirschke et al. [3] thought agriculture was a much greater source than others (200 Tg yr^{-1} by bottom-up estimates, 209 Tg yr^{-1} by top down estimation), about twice as much as all fossil fuel sources. World Bank [22] estimates are that agriculture is approximately the same scope as energy sources for CH_4 releases; many assessments [22] [58] [10] find poorer countries (especially the poorest) have a much higher proportion of agricultural sources than wealthier countries, so that the relative proportion is likely to change with increasing global affluence and increased energy use.

Agricultural lands cover approximately 50% of the global land surface, and because of population growth, agricultural effort and outputs have been increasing. Flooded tropical rice paddies create near optimal conditions for CH_4 production: low redox conditions, large labile organic inputs, and elevated temperatures, all of which are found just below the water-soil interface [67]. Methane is released at specific times in the rice cultivation process, meaning it is not a constant source even when cultivated year round [66]. Flooding is the key element, as it creates the anoxic conditions necessary for methanogenesis. Plant height is also important, as the rice plant itself is the main transport means of CH_4 from sediments to the atmosphere [67]. Soil water CH_4 volatilizes in the root cortex, and then is transported through intercellular spaces and aerenchyma to pores in the leaves; this pathway means CH_4 is not oxidized in the paddy, thus making it the primary route for CH_4 releases [68]. Soil types mostly change the timing but not the amount of CH_4 generation (acidic soils delay gas generation). Most other factors (such as tillage, transplanting versus seeding, and other farming practices) do not have consistent signals in CH_4 generation rates [67]. Because rice began to be cultivated ~8000 years ago [69], it has played a long-term role in the increase of atmospheric CH_4 concentrations [8]. Methane releases from rice paddies have decreased per tonne of rice produced, due to greater yields and more use of inorganic fertilizers [28] [70]; inorganic fertilizers may reduce CH_4 releases by a third.

Draining flooded fields at some time during the year also reduces gas emissions [1]. Increasing use of composts and other humified carbon sources may be useful to maintain good soil qualities; they should produce less CH_4 emissions than traditional "green" manures [67]. Methane releases from rice paddies is mostly determined by the area of rice being cultivated, rather than the intensity of use. Therefore, because of increased efficiency in rice production, the amount of CH_4 associated with rice farming has not been increasing as quickly as many other anthropogenic sources [28]. A rough approximation of average rice paddy CH_4 emission rates is 300-500 mg m^{-2} d^{-1} [63], more than is emitted from landfills generally (see below, Section 5). The amount of CH_4 produced in rice paddies is actually ten times greater than what is emitted; 90% of production is consumed by methanotropic bacteria at the sediment-water interface and in the water column of a flooded paddy [12]; increasing the activity of these methanotropes mitigates CH_4 production [71]. Methanotropic bacteria are discussed in Section 5.

Increasing incomes lead to less consumption of starchy food and more consumption of meats, dairy, and fish [72]. There has been increasing consumption of protein and energy rich foods, and convenience foods, and decreases in rice consumption, especially in Asia [73]. IPCC [11] reports that changes in diet could increase non-CO_2 emissions from agriculture by a factor of three. Because modern diets include more meat, ruminant numbers have increased more than human population has. Grazing systems now occupy 30% of ice-free land surface [74]. Ruminants (primarily cattle but also sheep and goats) harbor bacteria in their digestive system that aid in the degradation of fodder; the animals absorb organic compounds released as breakdown products from the bacteria, but the bacteria also produce CH_4, ammonia, and CO_2 as waste gases, which the animals emit [12]. The primary point of production is the foregut, which allows the animals to further digest the microbes and non-gaseous waste compounds and breakdown products produced by this fermentative process [64]. The output of manure and gas from rumens is generally proportional to the number of animals, although lower quality feed increases both rumen releases and manure production slightly (approximately 5%) [75], and approximately 50% of ruminants graze on lower quality feed on grasslands [74]. As much as 90% of methane releases from animals is from the rumen releases [63], although one study making direct measurements of contained animals found liquid manure a greater contributor [76]. Field-dried manure may not produce much CH_4 at all [1]. Increased use of liquid manure systems has caused a doubling in US manure-related CH_4 emissions over 20 years [24]; EIA [27] found releases from enteric fermentation to still be three times greater than animal waste-related gases, and, for the US, found swine and cattle manure were about equal in emissions. Although cattle generate most enteric CH_4, sheep, goats, and water buffalo also are major ruminant producers of CH_4; camels, horses, mules, and pigs are minor emitters. Wild animal foregut ruminants include deer, but they produce much less CH_4 per unit feed than cattle. Wild animal hindgut fermenters, mostly minor CH_4 emitters, include most birds, fish, and reptiles, rats, rabbits, and elephants [64]. Many other organisms harbor methanogens in their digestive system, including half of all humans. It is thought methanogens grow too slowly to exploit potential substrates in most digestive systems and so cannot maintain their populations except under special conditions [36]. Herrero et al. [74] found two-thirds of CH_4 releases due to animals was from ruminant outgassing. In the US, rumen gases and manure account for nearly 40% of all anthropogenic CH_4 releases [24]. India is the greatest single source of ruminant CH_4 due to its exceptionally large population of cattle, although most are not being raised for direct consumption [10].

2.2 Coal mines

Methane (and CO_2) are incorporated in coal deposits, and therefore can escape to the atmosphere when coal is mined [77], making it an important source of CH_4 releases. This source is declining (absolutely and relatively) for two reasons: increased use of controls to reduce releases, and declining use of coal as an energy source as it is replaced by natural gas. Natural gas is a greater source of fugitive CH_4 than is coal currently [10]; in the US, EIA [27] estimated the ratio at about 2:1. This difference will grow with greater use and exploitation of natural gas resources.

Methane is often released from coal directly, but also from nearby strata, because more CH_4 is generated during coalification than can be stored in the coal seams themselves. Mining disturbance of the surrounding rocks and coal seams releases the gas from its storage. In open pit mines, the CH_4 escapes directly to the atmosphere, but in underground mines the gas seeks means to escape, including shafts and tunnels, although to maintain safety for miners concentrations in these areas are actively sought to be minimized. Because open pit mines usually exploit younger and shallower coal seams, it is thought that they hold less CH_4 per tonne of removed coal, and it is also assumed that the overlying strata are not significant sources of gas

[78]. Gas is intentionally ventilated from underground mines for safety reasons, and CH_4 evolves from stored coal [79].

Because it is difficult to measure releases from open pits and there are numerous means for gas to escape underground mines, estimates of CH_4 produced by coal mining tend to use indirect measurements based on mining rates. Inactive mines are therefore usually not accounted for, and variations in coal types and particularities of mining operations, all of which affect the rate of release of gas, are usually not addressed [78]. In the US, abandoned coal mines were estimated to release about 10% of the amount that active mines do [24]. In China, 48% of active mines are classified as "gassy" [80]. Reasonable estimates of underground mine CH_4 degassing can be made where occupational safety measures are in place, as CH_4 represents a major threat of explosion in mines. Aggregating data across different reporting bodies make it hard to accurately use these data, however [78].

Nonetheless, estimates of coal mine CH_4 releases amount to between 8% and 12% of all anthropogenic CH_4 in the atmosphere [78] [10] [81]. The greatest producers of coal (China, US, India, Russia) also emit the most CH_4, although the use of horizontal and vertical wells to recover coal gas from coal seams and surrounding rocks (respectively) is increasing, especially in the US and China [81] [80]. Coal mining was estimated to produce about 25% of all US anthropogenic releases [24]; reductions in coalbed CH_4 releases not only decrease CH_4 emissions and therefore help the environment, they provide an opportunity for energy recovery, and increase miner safety [80].

2.3. Oil and gas systems

Methane is the primary constituent of natural gas (they are sometimes considered to be synonymous); thus it is not surprising that natural gas (its mining, processing, shipment, and use) should result in fugitive CH_4. Methane is also one of the volatile hydrocarbons released from petroleum, and natural gas is often co-located with petroleum. Therefore it is also released in the mining, processing, transport, and use of petroleum, although the scale of those releases is much smaller than releases associated with natural gas operations. In the US, oil operations release about 25% as much CH_4 as natural gas systems [24], although note EIA [27] estimated that releases from petroleum were only about 15% of natural gas emissions.

“Conventional” estimates of fugitive gas releases are less than 2% of natural gas production [1] [82]; Larsen et al. [59] estimated the impact at 60 Tg yr^{-1} (approximately 3% of all natural gas produced), more than 15% of all anthropogenic releases; other estimates are up to 50% greater [3]; IPCC [10] ranges of releases are higher, as well, suggesting oil and gas systems are responsible for 30% or more of anthropogenic fugitive CH_4. In the US, EIA [27] found natural gas was responsible for about one-third of all anthropogenic CH_4 releases.

Official data on “methane leakage” (CH_4 that escapes during drilling, production, and venting at the exploitation site) for the US, Russia, and Canada are similar in scope, but other major producers tend to report much lower release rates (sometimes only one-twentieth of the “Big Three”) [59] which may explain why data based on these statistics is lower than other estimates. Some studies find potential releases from conventional well head sites may be as much as 6%, and for fracking the upper end estimate was nearly 8% of produced gas [20]. Pneumatic devices (55-150 fittings or so per well) and storage facilities are the major contributors [59] [20]. One sampling program at 190 representative sites in the US found relatively low loss rates, equating to an estimate of 0.42% of production [83]. USEPA [24] found that production releases are declining with time because of technology substitutions that leak less. However, Allen et al. [83] estimated 75% more leaks from equipment than USEPA, and a study of seals and compressor packing found emissions that were about 10 times greater compared to standard emission factors [84]. On-shore systems leak more than off-shore systems [59]. Brandt et al. [62] note that high emissions sites (estimated to be 0.05% of all wells) are the source of over 50% of the total US leakage, so that sampling that may include such a well site would be biased upwards; conversely, a sampling set that did not include such sites would be biased low. Another potentially large source of CH_4 is transportation losses, because of compressors and pneumatic devices [59]; USEPA [24] found that changes in piping have reduced leaks in this part of the industry as well. Estimates for large producing countries are that 0.5%-0.7% of total production is lost in transportation, although 2.5% to 10% of all transported gas cannot be accounted for. These numbers include thefts and poor input-output accounting as well as leaks, and may be biased by maintenance issues in Russia at the turn of the millennium [20]. Compressors are the source of most leaks at processors [59]. Processors are commonly thought to be small emissions sources, ~0.2% of production, although measurements in Canada resulted in 1% estimates [20]. Samples from 130 sites that gather and process natural gas in the US found that the two processes appear to lose about 0.47% of production [85]. One study of the impact of pipeline losses found that the rate of losses was great enough to more than offset increases in CO_2 emission efficiency gains, if natural gas use were to replace gasoline or diesel fuel use, over significant time frames [86]. Increases in fracking for both oil and gas may increase production losses, because of estimates that fracking has two orders of magnitude greater releases in the drilling phase [20]; USEPA [24] found that fracking had increased overall industry-wide production emissions by 25%; contrariwise, the large sampling effort reported by Allen et al. [83] found flow-back releases of CH_4 to be much lower than USEPA [24] estimates.

2.4 Wastewater

Methane is produced in the processing of human sanitary wastes (generally, wastewater) when anaerobic conditions exist [87]. This can be deliberately induced or be the result of happenstance, or may be due to error. Most large sewage treatment plants operate aerobically to treat inputs, which should not result in methanogenesis. Some systems, particularly anaerobic lagoons and constructed wetlands, intentionally use anaerobic consumption of organic matter as a primary treatment process, causing CH_4 emissions. On-site sanitary systems for houses (cesspools and septic systems) tend to operate anaerobically and so produce CH_4. Latrines also decay wastes anaerobically [24].

Sludge collected at waste water facilities is often intentionally digested anaerobically to stabilize it [24]. Digesting sludge reduces the mass of material, makes dewatering residues easier and decreases their odor potential. Anaerobic digestion is less susceptible to poisoning than aerobic digestion, but takes much longer. The produced CH_4 may be utilized for energy [88].

Wastewater is a relatively insignificant source of fugitive CH_4 in the US, estimated at less than 3% of all anthropogenic releases [24]; this is less than the 5% to 10% worldwide estimates reported in Table 4 (above). USEPA [24] estimated that about 40% of US emissions were from industrial wastewater facilities in 2010, up from one-third in 1990. Paper pulp plants and meat and poultry waste treatment plants are the two largest industries, and collectively are responsible for 90% of US industrial waste water CH_4 releases [27]. RTI International [89] provides a methodology to determine the amount of CH_4 generated by anaerobic processing at wastewater treatment plants. According to USEPA [24] data, on-site systems, privies, and latrines produce approximately the same amount of CH_4 person^{-1} d^{-1} (10.7 g) as do sewage treatment plants (from sludge) (11 g person^{-1} d^{-1}), although all of the CH_4 is released from the on-site systems, and much less is released from most sludge digesters – one estimate is that CH_4 releases are only 10% of production [1]. RTI International [89] provides a methodology to estimate CH_4

generation at any sludge digester, but does not estimate how much may be released to the atmosphere. During standard operations, only 4% of produced CH_4 was released from one Japanese plant, but during operational troubles (such as foaming in the digester) release rates could be more than 30% [90]. Measurements at a French sewage treatment plant found most CH_4 releases come from pretreatment of wastes, or from leaks at sludge digesters; in general, the range of releases from sewage treatment plants was reported to be 0.1-0.9 g person^{-1} d^{-1} [91]; it was found that three-quarters of CH_4 releases from sewage treatment plants is from digesters. Better operation of ventilation systems can reduce off-gassing [92].

Materials other than human sanitary wastes are anaerobically digested [93] [94] (also see Section 5.2). In the EU in 2010, “biogas” (CH_4) was produced from landfills (27%), sewage sludge (10%), and from agricultural residues (often a mixture of crops and animal manure) and solid waste [95]. In 2012, 202 on-farm digesters for manures and crop residues were in operation in the US [96]. Leakage from these plants should be less than sewage treatment plants, as a portion of the attributed CH_4 releases from sewage treatment plants is not from sludge processing but rather is due to direct atmospheric venting, either from plants operated anaerobically or from aerobic plants experiencing process upsets.

3. Methane emissions from landfills

Landfills release CH_4 to the atmosphere because much of the waste buried in them is organic. Biological degradation of the organic matter consumes interstitial O_2, and the waste pile becomes anaerobic. When redox conditions support methanogenesis, CH_4 is released as a waste gas [97]. Although landfill surfaces are sometimes sealed from the environment in developed countries, and landfill surface soils may host methanotropes, some CH_4 is released to the atmosphere. Global releases appear to be on the order of 40-75 Tg yr^{-1} (Table 4) (see [98], estimating 54 Tg yr^{-1}, but [99] reporting 30-35 Tg yr^{-1}). Reports are also spatially variable; as of the mid-2000s, for instance, field measurements showed release rates from sanitary landfills ranged over seven orders of magnitude, from 0.0004 g m^{-2} d^{-1} [100] to >10,000 g m^2 d^{-1} [101]. Reports also include negative values (where landfill soils consume atmospheric CH_4).

Not all generated landfill methane is emitted into the air; some is stored in the landfill in voids and part is oxidized to CO_2 by microbes in landfill soils. Variations in stored CH_4 were found to be considerable, resulting from variable leachate levels, changes in internal geometries, dissolution into and out of leachate, changes in gas extraction rates, and relative changes in atmospheric pressures and temperatures [101].

Since CH_4 releases in solid waste management are generated almost entirely by landfills, and landfills are the dominant means of waste disposal worldwide, CH_4 generation should correlate to waste generation rates [98] [99]. IPCC collects country-specific data for greenhouse gas releases, including reports on landfill emissions, and requests annual updates. Instructions to produce the reports were released in 1994 and revised first in 1996 [102] and again in 2001 [103]. USEPA, which generates comprehensive world estimates of GHG releases, uses the IPCC data as a starting point; USEPA uses other data sets to adjust IPCC values, and to determine data where none were reported to IPCC [23]. Many reporting countries assume gas generation is proportional to waste generation, and use some conversion factor to transform whatever waste data may be available to a CH_4 release value [104]. The IPCC estimation uses Equation 1 [105]:

$$M_e = ([MSW_t * MSW_f * MC_f * DOC * DOC_f * F * (16/12)] - R) * (1 - OX_f) \quad \text{(Eq. 1)}$$

with

M_e = methane emitted (Tg yr^{-1})
MSW_t = total MSW generated (Tg yr^{-1})

MSW_f = fraction of MSW landfilled in an engineered landfill
DOC = fraction of biodegradable organic carbon in MSW
DOC_f = fraction of organic carbon converted to CH_4 or CO_2
F = fraction of CH_4 in landfill gas
R = recovered CH_4 (Tg yr^{-1})
OX_f = fraction of CH_4 oxidized at the landfill

However, differences in waste management processes mean that is a too simplistic conceptualization to be useful to generate meaningful national and regional CH_4 generation and release rates. Alternatives to landfilling of wastes are common: recycling diverts waste, both by organized programs in developed countries, and through more informal sectors in the developing worlds. Waste may not be collected for management in some areas. Collected wastes may be dumped in unofficial disposal sites, or at unengineered disposal points (dumps) [106]. Sanitary landfills (engineered structures intended to mitigate some environmental impacts of landfilling) may or may not collect gases produced in the fill. Dumps, depending on climate, thickness of waste deposits, quality of materials, and whether or not they were set on fire to control odors and vermin, may or may not produce gas [98] [107]. Kirschcke et al. (2013) characterize uncertainties associated with landfill CH_4 generation rates at about 30%. IPCC estimates for worldwide releases, using two alternative estimation means, also narrowed the gap between them to 30% for 2005 [104]. There is some skepticism regarding the accuracy of these kinds of data, however [62]; the latest IPCC report [11] notes that the poor quality of waste data affects the value of GHG estimates derived from them.

Table 6 shows estimates of CH_4 releases from landfills worldwide, by various regional definitions, using some of the more comprehensive global accountings. The values in Table 6 are less than many of the broader sectoral estimates presented in Table 4. This may partially stem from more specific assessments accounting for mitigation of methane generation better, or from rounding errors in assessments with larger scopes.

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Table 6. Regional landfill methane emission estimates (Tg yr^{-1})

	1990		**1995**			**2000**			**2005**			**2010**			**2012**
	[58]	[108]	[58]	[108]	[109]	[58]	[108]	[109]	[58]	[108]	[109]	[58]	[110]	[109]	[109]
Africa	2.60	3.50	3.14	3.92		3.71	4.38		4.14	4.83		4.55	4.82		
Cent. & South America	2.13	3.42	2.49	3.80		2.96	4.11		3.14	4.41		3.34	3.40		
Middle East	1.55	1.63	1.79	1.89		1.94	2.15		2.17	2.44		2.40	3.20		
Asia													6.34		
China/Cent. Pacific Asia		2.05		2.18			2.29			2.37					
SE Asia		4.12		4.21			4.10			4.54					
Non-OECD Asia	18.66	17.85	19.09	16.98		17.49	14.24		17.04	13.44		17.78			
Europe													4.15		
EU	8.37		7.98			6.98			5.77			5.24			
EU 27					6.60			6.11			5.20			4.25	3.91
EU 15					6.35			5.82			4.77			3.69	3.32
OECD 90 & EU	5.70		6.28			7.08			7.53			8.02			
Non-OECD Europe & Eurasia	2.99		3.19			3.48			3.80			4.23			
Non-EU East. Europe		0.58		0.57			0.60			0.63					
Non-EU former USSR		3.11		3.11			2.90			2.94					
Eurasia													2.66		
N. America													0.97		
OPEC	1.75		2.03			2.15			2.80			3.06			
World Total	33.62	36.26	35.97	36.65		36.66	34.78		37.81	35.59		40.32	40.32		

As mentioned, IPCC has required member nations to estimate CH_4 releases under various source categories through annual reporting. For landfills, IPCC has created an estimation methodology that depends on data for landfilled wastes over time (because landfills emit CH_4 from buried wastes over decades). IPCC inventories show that landfills are approximately 2% of worldwide emissions. Approximately 4%-5% of CH_4 releases from developing countries come from landfills, although per capita landfill CH_4 emission rates tend to be much lower (because much smaller amounts of wastes are managed through landfills) [31]. Transition from unmanaged wastes to a modern waste management system can increase CH_4 emissions by a factor of five [58]. Releases of CH_4 from the most developed countries are declining on a per capita basis due to growing controls on landfill releases, and, for some EU countries, are declining absolutely due to compliance with the EU Landfilling Directive (see Section 7, below)

The data in Table 6 generally show increasing releases in all areas of the world, and so the world summaries show ~10% increase from 1990-2010. This is twice as great as the atmospheric increase over the same time period. The one area of the world with decreasing landfill CH_4 releases is Europe. The European Union has passed legislation (see section 7) reducing the delivery of organic wastes to landfills. As shown just below in section 3.3, some of the decreases for particular member states are very dramatic.

3.1 United States landfill emissions

US landfill release values in the annual USEPA Greenhouse Gas Inventories were generated based on a FOD model specified by IPCC (in 2006). The model estimates CH_4 generation based on waste inputs. USEPA modified the model to match results from a survey of 52 US landfills, which were found to be affected by rainfall. Therefore US landfills were stratified into three climate categories (high rainfall, medium rainfall, low rainfall), with CH_4 generation rates dependent on the climate and waste inputs. The total amount of CH_4 generated was reduced by data specifying gas combusted to produce energy or flared prior to release, with a 10% reduction additionally applied to account for methanotrope consumption of CH_4 at the landfill-atmosphere interface [25]. The data are also affected across the reports by changes in USEPA modeling of solid waste generation. USEPA adjusts previous years' estimates when it alters the overall model, and so part of the changes in the data has to do with the changes in waste generation created by waste model alterations.

An independent estimate of total landfill gas (LFG) production based on summing reports from individual landfills estimated that 9 Tg yr^{-1} were generated. This is 50% greater than the 2012 USEPA estimate of 6 Tg yr^{-1}, which was based on the BioCycle estimate of US waste generation, and nearly twice as large as the USEPA estimates based on the USEPA waste generation model. According to this paper, more gas was used for beneficial purposes (39%) than was flared (27%), but 34% of the available gas was emitted to the atmosphere (even allowing for CH_4 oxidation in cover soils) [111].

US landfill CH_4 emission estimates are presented in Table 7.

Table 7. Estimates of US landfill CH_4 emissions (Tg yr^{-1})

Source	1990	1995	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
[108]	8.20 8.20	7.73 7.73	6.22 6.22					6.22 7.46								
USEPA 2012c	7.02	6.64	5.32					5.36					6.18			
[110]													6.18			
[111]															9	
[25]	7.45											6.32	4.87	4.85	4.61	4.59
[24]	6.54							4.68			4.77	4.81	4.55	4.43	4.21	
[112]	6.54							4.70		4.65	4.53	4.72	4.40	4.22		
[113]	6.53							4.71	4.66	4.65	4.55	4.62	4.45			
[114]	6.52		4.73					4.70	4.67	4.64	4.60	4.92				
[115]	6.61	6.31	5.13					5.32	5.39	5.36	5.09					
[116]	6.61	6.32	5.21					5.43	5.55	5.67						
[117]	6.60	6.27	5.10	4.93	5.05	5.30	5.15	5.20	5.29							
[118]	7.12	6.88	5.62	5.41	5.54	5.74	5.61	5.60								
[119]	7.61		5.94	5.79	5.94	6.05	5.96									

The data in Table 7 show that more recent model outputs tend to report fewer releases, comparing year to year. However, the models also tend to show decreasing releases over time. This is due to changes in landfilling rates, but also because more gas is being captured and flared, or used to produce a form of energy. There is not great confidence in USEPA waste generation estimates (see [120] [121]; the nearly 100% difference between government and independent estimates for 2012 underscores how larger estimates of waste generation lead to much larger estimates of US landfill emissions. This difference in the estimates is nearly 1% of total world CH_4 emissions.

3.2 China landfill emissions

China waste management numbers are uncertain. In 2006, it was estimated that annual per capita waste generation in urban areas was a little over 500 kg [122]. One evaluation used those values to suggest urban waste generation was ~340 MT, and about two-thirds was collected [123]. The official collection rate ("harmless treatment") for 2010 was 77.9%. Suburbs and exurbs of the cities usually have little to no collection. Amounts of wastes are growing nearly 6% a year: partly due to increasing per capita generation, but partly due to increased collection efforts [124]. With recycling rates less than 5%, and incineration estimated at 15% in 2010, nearly all (~80%) managed urban waste was landfilled [123].

Rural waste is different in quantity and quality. Waste generation is about 400 kg person^{-1} yr^{-1}. There are low collection rates (~25%). Rural areas have lower incineration rates, and less recycling, so that about 90% of the managed wastes are landfilled [123]. This suggests urban per capita landfilling rates are ~300 kg, and rural per capita rates are somewhat less than 100 kg. Most of the remaining waste is dumped, either informally as a form of litter or in unregulated sites [123].

Waste generation is not only different on an urban-rural axis, but according to geography. Waste composition in the north of China is very different from that in the south, due to differences in food consumption, but also because of domestic use of coal. Coal ash can comprise up to 70% of northern MSW at times in winter, although substitution with other fuels (predominantly natural gas) is leading to rapid change [124].

Cai et al. [125] found about 75% of “safely disposed” MSW was landfilled in China in 2012. The number of sanitary landfills has decreased from a peak value in 2001, but the tonnage of waste landfilled has steadily increased. A scoring system established by the Ministry of Housing and Urban-Rural Construction classifies the nation's landfills: scores greater than 85 is Class I and between 70 and 85 is Class II, with 190 out of 365 landfills rated as Class I or II in 2005, with 300 landfills reaching Class I or II in 2008 [126].

It is not clear what source for MSW generation data was used to drive the gas release models, but it appears it was the same for all of the US reports, and is likely to be the official government estimate of waste generation. One independent assessment used data from 2007, with site-specific waste generation and climatic information used to drive a first order decay (FOD) model (see Section 4), with different degradation rates for a number of organic waste fractions. The work divided China into seven regions to differentiate waste composition. Three different classes of landfills were identified based on tonnages managed, and data from 2,107 landfills were used (630 sanitary landfills, 1,477 “simple” landfills). The model predicted 1.186 Tg CH_4 emissions [125].

China landfill CH_4 emissions data are presented in Table 8. The data show slowly increasing emissions, with the rate of increase about 5% decade^{-1}.

Table 8. Estimates of China landfill CH_4 emissions (Tg yr^{-1})

Source	1990	1995	2000	2005	2007	2010
[108]	1.94	2.05	2.13	2.19		2.24
[58]	1.92	2.03	2.12	2.19		
[110]						2.24
[125]					1.19	

3.3 Other key countries landfill emissions

In India, MSW "generation" data was said to be 6 MT in 1947, and 48 MT in 1997 [127], with 0.5-0.7 kg person^{-1} d^{-1} generated in urban areas [128]. These data most probably refer to the amount of managed MSW; data from Rathje's work with Mexico City households in the 1980s suggests less developed countries generate approximately the same amount of MSW as developed countries (2-3 kg HH^{-1} d^{-1}), although the composition is very different [129], and it is clear many developing countries do not have any organized means to manage the generated wastes. IEA [130] set India urban waste generation at 42 MT, and said 50% to 90% is sent to uncontrolled dumps with the remainder left as litter or sent to absolutely uncontrolled sites. Sampling of urban wastes find they contain a high level of putrescible material, largely food wastes, which means when collection is provided it must be frequent -- as often as every day. However, street sweepings and construction and demolition debris in wastes mean that much of landfilled waste is inert (20-45%). Most recyclable material is scavenged before disposal (or at the disposal site, before burial) [131].

Tremendous rates of recycling are achieved through the informal sector; there is little to no source separation. Most wastes are disposed of as litter or at informal dumps. Composting is also widely practiced, but the end product is often low quality due to physical contaminants (plastics, glass, metal) in the feedstock [131]. Jha et al. [128] cited reports that 70-90% of India's landfills, managing three-quarters of its waste, were "non-scientifically managed ... open dumpsites." Local funding is used for municipal waste management, and obtaining capital for large projects is considered to be difficult [131].

Application of the earliest IPCC methodology, which assumed all CH_4 was emitted in one year of waste deposition, resulted in an initial nationwide landfill emission rate of 0.334 Tg yr^{-1} for 1990-1991, and, using revised data, an increasing rate of 0.263 Tg yr^{-1} (1980) to 0.502 Tg yr^{-1} (1999). A revised, "triangular" approach (a linear approximation of the FOD methods) estimated release rates of 0.119 Tg yr^{-1} to 0.4 Tg yr^{-1} over the same period [132]. Estimates by others of CH_4 generation around 2000 ranged from 0.33 to 1.80 Tg yr^{-1}, plus an unknown amount from "open dumping and improper landfilling" [127]. Joseph [131] suggested that releases nationwide range from 0.5 to 1.5 Tg yr^{-1}. A comparison of integrated fluxes based on field measurements at open dumpsites to IPCC modeling estimates for the sites found the IPCC methodology outputs were at least two orders of magnitude greater [128].

The other countries reviewed here (Table 9) were selected to provide a diversity of data sets. Indonesia, for instance, has a much smaller population than India (by a factor of 5), and is developmentally similar. Nonetheless, reported emissions are much greater than India emission rates. South Africa is also a developing country. Its emissions on a per capita basis far exceed Indonesia's. Brazil and Mexico are similar developmentally, but Mexico has 40% fewer people. Mexico's landfill emissions are twice as great as Brazil's, and sometimes were found to be greater than Russia's -- a country that is much more developed and has a somewhat greater population. In 1990, Germany's landfill emissions were on a par with Russia's. Now Germany emits a tenth of what Russia landfills do. This is due to aggressive implementation of the EU Landfill Directive in Germany, which aims to divert degradable organic wastes from landfills. On the whole, the table shows increasing CH_4 emissions from landfills (with the notable exception of Germany) -- a trend that makes intuitive sense, given increasing populations in these countries and also generally increasing affluence, and perhaps improving methods of waste management. However, the disparities in the comparative generation rates make it seem likely that the same estimation processes are not being applied evenly among these different states.

Table 9. Estimates of some key country landfill CH_4 emissions (Tg yr^{-1}) (2013 population estimates from [133])

Country	Population (M)	1990	1995	2000	2005	2010
Brazil [108]	200	0.79	0.92	1.06	1.10	1.18
[58]		0.62	0.69	0.74	0.79	
Germany [108]	81	1.84	1.73	1.13	0.68	0.33
[58]		1.50	1.20	0.68	0.43	
[110]						1.42
India [108]	1250	0.54	0.59	0.59	0.60	0.63
[58]		0.51	0.58	0.66	0.76	
[132]		0.37	0.44			
[132]		0.30	0.35			
[127]				0.33-1.80		
Indonesia [108]	250	0.91	1.02	1.13	1.24	1.35
[58]		0.37	0.40	0.43	0.46	
Mexico [108]	122	0.78	1.23	1.55	2.34	2.69
[58]		1.24	1.36	1.47	1.58	
[110]						2.69
Russia [108]	144	1.34	1.48	1.65	1.90	2.25
[58]		1.80	1.80	1.67	1.63	
[110]						2.25
South Africa [108]	53	0.67	0.73	0.78	0.82	0.85
[58]		0.67	0.72	0.78	0.80	

4. Methane emission estimation models

LFG modeling is the practice of forecasting gas generation, emissions, and recovery based on past and future waste disposal histories and estimates of collection system efficiency [134]. Modeling is relied upon due to complexities and uncertainties associated with methane production (methanogenesis), consumption (methanotrophic oxidation) and LFG transport processes. These combine to result in field measurements of landfill methane emissions that range over seven orders of magnitude (less than 0.0004 g m^{-2} d^{-1} [100] to more than 10,000 g m^{-2} d^{-1} [101]). Site precipitation, preferential flow paths within the waste mass, the distribution of methanotropes in cover soils, and underlying waste quality and history all affect measurements at a particular place at a landfill. Barometric pressure has also been identified as a key environmental control on measurements of release rates [135]. Although approaches to integrate areal site releases are available (see Section 4.4), the most common means to estimate a site's gas emissions is through a model [121]. Therefore, the quantification of methane generation and emission rates for a given field site requires a reliable model which considers spatial and temporal variability of waste inputs and local conditions.

Mathematical models have been designed to simulate bio-chemical and physical processes governing the microbial degradation of organic material and the subsequent generation and transport of LFG, and the emission of LFG from landfill surfaces [134] [136]. USEPA and IPCC have developed the most widely applied methodologies for determining methane generation, and provided default values for model input parameters for sites and areas lacking specific input data. Model results do not always match well with real world results. For instance, Terraza and Willumsen [137] estimate gas collection projects underperform by 20% to 90% compared to expected values based on standard models.

4.1 USEPA model (LandGEM)

The Landfill Gas Emission Model (LandGEM) is an automated estimation model with a Microsoft Excel interface used to calculate CH_4 and non-methane organic compound (NMOC) emission rates from MSW landfills. LandGEM relies on a FOD approach for quantifying emissions from the decomposition of MSW. The model is simple and flexible. LandGEM is best when site-specific climatological and waste disposal data are available, but has default values based on the country the model version is designed for. The base model was developed for US sanitary landfills. LandGEM 3.02 was released in 2005 [138]. It is based on a simpler model, the Scholl Canyon model developed by Emcon Engineering in 1976, which used an exponential decay equation to estimate gas generation over time [137].

LandGEM uses Equation 2 to simulate emissions, using a 0.1 year time increment; the model assumes CH4 generation is at its peak shortly after initial waste placement (after a short time lag while anaerobic conditions are established). The model also assumes that the rate of CH_4 generation decreases exponentially as organic material is consumed by bacteria [138] (also see Section 5).

$$\mathrm{QCH}_4 = \sum_{i=1}^{n}\sum_{j=0.1}^{1} kL_0\left(\frac{\mathrm{M}_t}{10}\right)e^{-kt_{ij}} \tag{Eq. 2}$$

where:

QCH_4 = annual CH_4 generation (m^3 yr^{-1})
i = 1 year time increment
n = (year of the calculation) - (initial year of waste acceptance)
j = 0.1 year time increment,
k = methane generation rate ($year^{-1}$)
L_0 = potential methane generation capacity (m^3 Mg^{-1})
M_i = mass of waste accepted in the ith year (Mg)
t_{ij} = age of the jth section of waste mass M_i accepted in the ith year

The value k, the degradation rate constant, is key to accounting for different conditions at different sites, or for area considerations. It determines how quickly mass is converted to CH_4 [139]. Higher values of k result in higher initial CH_4 generation amounts, which then decline more quickly as the waste mass ages. The default value for k is 0.04. Values of k used at US landfills range from 0.003 (for landfills in arid regions) to 0.70 (for wet bioreactor landfills); the typical input value is 0.05 [140]. The factors affecting k that are either easily measurable or approximated are precipitation, temperature, biodegradable fraction of the waste, and the depth of the fill. LandGEM models applied at 32 North American landfills were tuned using fuzzy logic, resulting in somewhat consistent predictions compared to estimated gas generation ($r^2 = 0.791$, with predictions tending to underestimate output (Δ ranging from -18% to + 0.4%) [141].

Another key parameter is L_0 (potential CH_4 generation capacity), defined as the total amount of CH_4 potentially produced by a metric ton of waste. L_0 depends on waste composition, although the potential for waste decay is also lower in dry climates where the lack of moisture limits CH_4 generation. The higher the organic content of the waste, the higher the value of L_0. The default values for L_0 is 170 m^3 Mg^{-1} for NMOC emissions and 100 m^3 Mg^{-1} for CH_4 generation (96 m^3 Mg^{-1} for a bioreactor). USEPA [142] notes values of L_0 at particular sites vary from 6.2 m^3 Mg^{-1} to 270 m^3 Mg^{-1}.

LandGEM models can provide more data than just CH_4 emissions. Although LandGEM will forecast lifetime emissions on an annual basis, it also forecasts standard pollutant outputs (the user must specify a NMOC concentration; LandGEM will speciate the projected emissions) [140].

Some country specific variants of LandGEM have been created: China, Columbia, Ecuador, Mexico, Philippines, Thailand, and the Ukraine (Table 10). A Central American version has also been made (it is linked to on the Dominican Republic country area of the Global Methane Initiative website).

Table 10. LandGEM country-specific models

	Default adjustments			Calibrated
	Climate	Waste Characteristics	Landfill Practices	
Central America [143]	3 precipitation amounts	7 countries	Landfill type, waste depth	
China [144]	3 zones	Coal disposal	Frequent fires, gas collection	
Columbia [145]	5 topographical-climatic regions + rainfall data (Regions 2/3)	5 regional def.	Landfill type, waste depth, history of fires, gas collection	Yes
Ecuador [146]	5 rainfall amounts	Food waste percent	Saturation, gas collection	
Mexico [147]	5 climate regions	State or climate region	Landfill type, waste depth, history of fires, gas collection	
Philippines [148] and Thailand [149]	1 zone, some outliers		History of fires, gas collection	
Ukraine [150]	4 precipitation amounts		Landfill type, waste depth, severity of fires, gas collection	

The China model has three climate variations which resulted in default values for k: cold and dry ($k = 0.04$), cold and wet ($k = 0.11$), and hot and wet ($k = 0.18$). A combination of climate and waste disposal practices was used to set default values for L_0. In dry climate zones, the default $L_0 = 70$ m^3 Mg^{-1}, and in wet climate zones the default $L_0 = 56$ m^3 Mg^{-1}. If significant coal ash is disposed (defined as >30% of waste inputs), L_0 was decreased. For landfills in cold and dry climates with significant coal, the default $L_0 = 35$ m^3 Mg^{-1}, for cold and wet $L_0 = 35$ m^3 Mg^{-1} ($k = 0.11$), and for hot and wet $L_0 = 42$ m^3 Mg^{-1}. A fire discount value was assigned if observed, frequent fires are seen at a site (30% of overall gas generation). Gas collection efficiency was discounted depending on site management: lack of waste compaction, absence of a working face, ineffective leachate management, shallow depth of waste, absence of daily-intermediate-final cover, and absence of the gas system in areas of the fill. Otherwise, the default gas collection efficiency was 85%. Although four landfills were surveyed to test the model, insufficient information was available to calibrate the model [144]. The model and manual are available in Chinese.

The Columbia model has five geographical zones based roughly on topography and climate. In addition, five rainfall regimes (dry to very wet) were defined; these are applied in Zone 2 and Zone 3. Five categories of waste were defined (based on waste samples from 51 cities) and these had default percentages assigned for the zones. Values of k vary based on climate and the four degradable waste categories (so there are 20 different default values). L_0 values were defined for each zone, using the IPCC calculation method (see below), based on the assumed waste composition of the region and IPCC default values for the other elements of the equation. Gas generation rates were discounted depending on four types of non-sanitary landfills and the depth of waste (greater or less than 5 m), and a history of fires. Similar to the China model, gas collection efficiency was discounted depending on specifics of site management: lack of waste compaction, absence of a working face, ineffective leachate management, shallow depth of waste, absence of daily-intermediate-final cover, and absence of the gas system in areas of the fill. An additional discount was assigned for general poor site management. Model results were compared to gas measurements at two Columbia landfills [145]. The model and manual are available in Spanish.

The Ecuador model set default k values based on four rainfall amounts (0, 250, 500 and 1000 mm yr^{-1}) and two categories of food waste percentages (<50% or > 65%). It seems likely the k values are meant to be interpolated if they fall between the set rainfall and food waste parameters. Default L_0 values were based on only three rainfall amounts (0, 250, and 500 mm yr^{-1}) and the two food waste categories. Gas collection efficiency was based on the type of landfill gas extraction well used, how the landfill was capped, and the mass of waste excluded from the gas collection area. The model was not calibrated [146]. The model and manual are available in Spanish.

The first version of the Mexico model was developed in 2003; it was re-done in 2009. The 2.0 Mexico model uses regional climate and waste generation data to set default k and L_0 values. Five categories of waste were defined, four of which are organic and decay at varying rates. A landfill is assumed to have either the specific state waste composition, if data are available, or the regional waste composition. Default k values were created for each region for each of the four degradable waste categories (they varied by a factor of three from 0.1 to 0.3); an overall default k value for each site can be computed based on waste composition. A similar process was used to determine L_0, although L_0 was set to one value nation-wide for the quickest (69 m^3 Mg^{-1}), medium slow (214 m^3 Mg^{-1}), and slowest (202 m^3 Mg^{-1}) decaying wastes. Gas generation and collection efficiency were discounted similarly to the Columbia model (above). The model was not calibrated [147]. The model and manual are available in Spanish.

The Philippines model classified all of the country as hot and wet, although it was recognized some isolated sites might be classified as dry (rainfall < 1000 mm yr^{-1}). The default value for k was set at 0.18 (a dry landfill would use k = 0.10). The default value for L_0 was 60 m^3 Mg^{-1} (70 m^3 Mg^{-1} for dry locations). A methane generation discount factor was applied to sites with a history of fires, and methane collection efficiency was adjusted similarly to the way it was for China (see above). The model was not calibrated [148]. The model and manual are available in Spanish; there was no link to the model from the Methane-to-Markets Philippines Partner Country page.

The Thailand model is structured exactly like the Philippines model, and it was not calibrated [149]. The model and manual are available in Thai; there was no link to the model from the Methane-to-Markets Thailand Partner Country page.

The Ukraine model is structured similarly to the Mexico 2.0 model (above), using similar factors to determine k and L_0. The rainfall amounts are different; default k values across the categories 0.011 to 0.15. Waste composition was based on 12 studies, and national default values were determined for each of the four degradable categories: very fast (L_0 = 69 m^3 Mg^{-1}); medium fast (L_0 = 126 m^3 Mg^{-1}); medium slow (L_0 = 214 m^3 Mg^{-1}); and, slow (L_0 = 201 m^3 Mg^{-1}). Gas generation rates were discounted depending on four types of non-sanitary landfills and the depth of waste (greater or less than 5 m), and the severity of any site fires. Similar to the China model, gas efficiencies were adjusted based on site management. The model was not calibrated [150].

The Central America model was created for Belize, Costa Rica, El Salvador, Guatemala, Honduras, Nicaragua, and Panama, and assumes most of the area receives high amounts of rain (>1000 mm yr^{-1}), but has adjustments for moderate rainfall and dry regions. Values of k depend on waste composition. Two types of waste are defined. One is fast decaying wastes (food and yard wastes) which have high default k values: 0.23 for high rainfall, 0.20 for moderate rainfall, and 0.18 for dry areas. All other organic wastes receive low default k values, which vary by country and by rainfall category, and are almost an order of magnitude lower (ranging from 0.020 - 0.033). Each country has an assigned waste composition, so the model can calculate a set k for any landfill in each country. Default L_0 values were defined for each country, using the waste composition for the two types of waste (fast and slow degrading). Gas generation rates were discounted depending on four types of non-sanitary landfills and the depth of waste (greater or less than 5 m). Although data from two landfills were collected to test the model, they were insufficient to calibrate the model [143]. The model and manual are available in Spanish. The Dominican Republic page at the Methane-to-Markets webpage also links to the Central America model. Since none of the countries the model was created for are partners in the Methane-to-Markets program, none of them have pages there to link to the model.

An adaptation of LandGEM 3.02 was made specifically for Finland by researchers. It was calibrated to data collected at a large landfill, and the integrated decay factor of 0.18 yr^{-1} was much larger than the default value for LandGEM of 0.05 yr^{-1}, and on the high end of the US range of 0.003-0.21 yr^{-1} [151].

LandGEM was used with redefined k values for waste classes, based on data from landfills and laboratory mesocosm experiments, creating an overall k value for landfilled US waste generally. An additional factor w, a measure of the biodegradation state in the landfill, was added to the LandGEM model to reduce gas generation when conditions were not optimal. The intention was to better forecast and control t_{max}, the time of greatest gas generation. Enhancing degradation conditions affected t_{max} more than changing the composition of the wastes [152]. Similarly, LandGEM has been coupled with measured waste, gas, and leachate factors to create a decision-support model to determine whether or not gas collection was likely to be economically viable. It was hypothesized that comparisons of site measurements to literature values for methanogenic landfill conditions could determine whether landfill wastes were decomposing "as expected," or if gas production model estimates should be adjusted. Sites where landfill dynamics were different than expected might have problems meeting gas production forecasts [153].

4.2. IPCC models

IPCC has developed two methodologies (Tier 1 and Tier 2) for estimating CH_4 generation and emissions from landfills. The Tier 1 method calculates CH_4 emissions based on annual solid waste disposal quantities, whereas Tier 2 method is a FOD method [102] [103]. Due to the quality and quantity of available data, developed countries tend to apply the FOD method while developing countries rely on the Tier 1 method [105].

The Tier 1 method is the default methodology for quantifying annual CH_4 emissions from solid waste disposal. Similarly in concept to LandGEM, landfill CH_4 generation is calculated based on MSW generation data (either measured or calculated), the landfilled fraction of generated waste, and the potential CH_4 generation capacity, except calculated not on a site basis but for a country or part of a country, and based solely on a single year's data – no accounting is made for previously landfilled wastes (Equation 3, Equation 4). Net CH_4 emissions are determined by subtracting CH_4 recovery and oxidation (Equation 5).

$$\mathrm{QCH_4} = \mathrm{MSW_t} \cdot \mathrm{MSW_f} \cdot \mathrm{L_0} \qquad \text{(Eq. 3)}$$

$$\mathrm{L_0} = \mathrm{MCF} \cdot \mathrm{DOC} \cdot \mathrm{DOC_f} \cdot \mathrm{F} \cdot \frac{16}{12} \qquad \text{(Eq. 4)}$$

$$\mathrm{QCH_4} = (\mathrm{QCH_4} - \mathrm{R}) \cdot (1 - \mathrm{OX}) \qquad \text{(Eq. 5)}$$

Where,

QCH_4 = CH_4 generation (Tg yr^{-1})
MSW_t = MSW generated (Tg yr^{-1})
MSW_f = fraction of MSW landfilled
L_0 = potential CH_4 generation capacity
MCF = landfilled fraction of MSW which decomposes anaerobically
DOC = fraction biodegradable organic carbon in landfilled MSW
DOC_f = fraction DOC actually converted to CH_4 and CO_2 in LFG,
F = fraction of CH_4 in landfill gas (v/v),
R = recovered CH_4 (Tg yr^{-1}) using active extraction systems
OX = fraction of CH_4 oxidized by methanotrophs.

For areas where more detailed data are available, the Tier 2 method is applied. Tier 2 uses the concept of FOD, with the quantity of waste landfilled in each year used to estimate CH_4 generation for the base year, and then decaying the methane generation over time. The amount generated for each area is integrated over time (Equation 6).

$$\mathrm{QCH_4} = \sum_{i=1}^{n} \mathrm{MSW}_{ti} \cdot \mathrm{MSW}_{fi} \cdot L_{0i} \cdot \left(1 - e^{-k}\right) \cdot e^{-k(n-i)} \qquad \text{(Eq. 6)}$$

Where,

i = year time increment
n = (year of calculation) - (initial year of waste acceptance)
MSW_{ti} = MSW generated in year i (Tg yr^{-1})
MSW_{fi} = fraction of national MSW disposed in a landfill in year i,
k = CH_4 generation rate ($year^{-1}$) and
L_{0i} = potential CH_4 generation capacity in year i (m^3 Mg^{-1}).

For countries with very good data sets, “Tier 3” methods based upon FOD methods applied to specific landfills, or actual data on CH_4 emissions from sites, can be substituted for the broader methods discussed here. So, for instance, US landfill release values generated by USEPA in the annual Greenhouse Gas Inventories are generated based on the FOD model. USEPA modified the model to match results from a survey of 52 US landfills, which were found to be affected by rainfall. Therefore US landfills were stratified into three climate categories (high rainfall, medium rainfall, low rainfall), with CH_4 generation rates dependent on the climate and waste inputs. The total amount of CH_4 generated was reduced by data specifying gas combusted to produce energy or flared prior to release, with a 10% reduction additionally applied to account for methanotrope consumption of CH_4 at the landfill-atmosphere interface [25].

In Finland, sampling at a large landfill resulted in a k value of 0.18, which is twice as large as the default value for wet boreal and temperate climates. The landfill’s production of CH_4 was therefore twice as great over an 18-yr time period than the IPCC model predicted [151].

4.3 Other models

There are some other models that are variants on the LandGEM and IPCC models. The Belgium model is very similar to LandGEM, and the German EPER model is similar to the IPCC model. A validation study of all of these models and the Scholl Canyon model found LandGEM typically underestimated CH_4 generation, by 10% on average but the other models tended to over predict gas outputs, sometimes by average multiples of 3 (especially for higher values of waste DOC) [154]. Still, most accounts assume LandGEM and the IPCC approaches successfully track overall trends if not absolute outputs in CH_4 generation. It is understood they do not account for variable waste characteristics and uncertainties associated with changeable environmental conditions. The models almost always use default oxidation rates of 10%, established in 1996 based on data from one site [155], although site specific rates are known to vary widely from that rate. Therefore, IPCC itself recognizes the accuracy of CH_4 estimations is poor, with deviations as much as 200% [156].

One variant to LandGEM introduced differential decay rates for specific portions of the waste stream. This model could be used to estimate future impacts to gas generation (and collection) associated with changing waste composition, due to differences in materials use and diversion programs (such as declining paper discards due to the newspaper industry's decline) in the OECD, and forecasts of increasing food waste diversions. It can be tuned so that relative decay rates for each organic component can equal in aggregate the decay rates assumed for waste as a whole. It matches LandGEM for initial gas generation rates, of course, but differences develop over time, due to forecast changes in incoming wastes and also differences in the composition of residual landfilled materials (gas generation falls off more quickly because the model decays more degradable materials first) [157].

Better models would include factors such as characteristics of landfill covers, specific methanotrophic CH_4 oxidation rates, and meteorological conditions [158]. A model that includes these factors is the California Landfill Methane Inventory Model (CALMIM). CALMIM is a field-validated one-dimensional methane transportation and oxidation model that estimates landfill methane emissions. CALMIM does not rely on a first order model for methane generation, but rather works with data on the major processes that control emissions: (1) surface area and properties of the daily, intermediate, and final cover materials; (2) the percentage of surface area for each cover type with engineered gas recovery; and, (3) seasonal methane oxidation in each cover type as controlled by climate factors. CALMIM incorporates two climate-related factors, meteorology and soil microclimate, which are automatically accessed according to the site location and physical properties of cover materials. In addition, CALMIM calculates daily emissions for each cover type which are summed to provide an annual total for the site [158].

However, CALMIM itself excludes important elements in CH_4 generation processes: (1) it does not include trends of LFG generation; (2) it does not include gas transport mechanisms other than diffusion, such as convection, ebullition, plant-mediated transport; (3) it does not assign LFG recovery efficiency. Nonetheless, CALMIM has been validated at several landfills [158].

It should be noted it has only been validated at landfills with LFG collection systems. Its effectiveness is unknown if it were applied in developing countries. In China, for instance, although larger, more recent landfills have installed gas collection systems, LFG recovery rates even at these sites are low, generally below 30% [159] [160], which are well below efficiency values used in CALMIM.

A gas generation model developed at the University of Texas the (CLEEN model) requires input data for waste composition, rainfall, and temperature. k values were developed through parameterization of different types of waste by means of laboratory mescosm experiments. The model was calibrated using data from 11 landfills, and a multi-variate regression on the three input variables for the calibrated model had $r^2 = 0.79$. When its outputs were compared to those from the IPCC and LandGEM models and to site data, the CLEEN model outperformed at four of six sites [161].

The Clean Development Mechanism (CDM) allows a signatory to the Kyoto Protocol with a commitment to reduce carbon emissions to sponsor or otherwise support a carbon reduction project in a developing country, and apply a credit for the developing country's reduction to its own commitment through standardized emission offsets (CERs) [162]. In order to claim a CER, it must be demonstrated that the project would not have proceeded otherwise. This most often means the activity must not be mandated [163]. For CDM credits, a special model needs to be used. The model is driven by Equation 7 [164]:

$$\mathrm{BE_y} = \varphi \cdot (1 - \mathrm{f}) \cdot \mathrm{GWP_{CH_4}} \cdot (1 - \mathrm{OX}) \cdot \frac{16}{12} \cdot \mathrm{F} \cdot \mathrm{DOC_f} \cdot \mathrm{MCF} \cdot \sum_{x=1}^{y} \sum_{j} W_{j,x} \cdot DOC_j \cdot e^{-k_j (y-x)} \cdot \left(1 - e^{-k_j}\right) \qquad \text{(Eq. 7)}$$

where

$\mathrm{BE_y}$ = avoided CH_4 emissions, year y
φ = uncertainty correction factor (default == 0.9)
f = fraction of generated CH_4 captured
GWP = Global Warming Potential of CH_4 (in 2006, set at 21)
OX = oxidation factor
F = proportion of CH_4 in LFG
$\mathrm{DOC_f}$ = fraction of DOC that degrades
MCF = correction factor for the facility type (a dump vs. a sanitary landfill, primarily)
j = waste type
W_{jx} = organic waste of type j disposed in year x (T)
DOC_j = organic fraction of waste type j
k_j = decay rate of waste type j
x = year (crediting period)
y = year (methane emissions calculations)

This model is intended to allow a standard calculation for CDM credits. Verification of model outputs (compared to actual gas production at China landfills) found the model under-predicts gas generation. Analysts believe this is because decay rates (k) are too low; it also could be that the default values for the gas capture efficiency (f) are incorrect. For China, they were originally set at 30% or 40%, and were raised to 60%; but there had been no field verification of actual capture efficiency [164].

4.4 Techniques to Monitor Methane Emissions

Measurement of LFG emissions is often carried out by the flux chamber method, especially in settings where more complicated experimental approaches appear difficult to install such as in less developed areas (c.f., [165] [166] [128] [167] [158] [127]), or where power supplies are unavailable [168], but also still commonly at many North American and European landfills [169] [170]. They are non-intrusive and portable, and allow for repeated measurements with relative ease. A container is set, sealed to the atmosphere, on the landfill surface. For the static chamber, gas accumulates due to emissions from the landfill surface, and its constituents and their concentrations can be determined at an exit port. For a dynamic flux chamber, a controlled flow of gas flows through the chamber and mixes with the emissions, and flows out exit ports. The mixed gas can be analyzed and then emission rates calculated from the results [171]. Negative values can result, and suggest the soil microbes have consumed atmospheric CH_4 [167]. Sensitivity is approximately 1 µg m^2 s^{-1} [169], which means data at controlled sites may not be as accurate as desired: quantified emissions for landfills range from hundreds to thousand s of µg m^{-2} s^{-1} at uncontrolled landfills, and fractions to hundreds of µg m^{-2} s^{-1} at sites with gas control [100] [101] [172]. Results are spatially variable at any particular site, often by many orders of magnitude, and it becomes labor intensive to generate extensive coverage of a site [173]; instruments are subject to measurement drift, and maintaining seals on rough surfaces is sometimes an issue [169]. The measurement variability means that extrapolation across one site or to other sites is often approached hesitantly [101]. An important aspect of the closed chamber method is the analytic approach taken to reify the readings made over the sampling period. Short time scales mean the variations approximate a linear regression, but longer sampling periods appear to require more complicated approximation means [168]. Flux chambers are very good at quantifying localized gas releases; static chambers can have biased results at higher flow rates due to the generation of back pressure which can inhibit outflows from the soil [170], or even force some of the emitted gas back into the soil [169]. As mentioned earlier, measurements from the flux chamber methods vary over seven orders of magnitude: from less than 0.0004 g m^{-2} d^{-1} [100] to more than 10,000 g m^{-2} d^{-1} [101].

Mass balance methods have been developed. Two perpendicular to the wind transects are established (upgradient and downgradient), and a planar value for CH_4 is determined for both. The difference is the landfill output. The methane integrals are usually measured by either Fourier transform infra-red (FTIR) spectroscopy [174] or Tunable Diode Laser Adsorption Spectroscopy [172]. These create one-time estimates of CH_4 emissions, and are difficult to replicate because of high labor requirements and changes in particular measurement topographies because different wind conditions require changes in the locations of the transects [135]. The modeling approach was developed to measure gas releases over flat ground, and so has been modified to work on landfill settings that often have steep slopes; often these adjusted modeling results did not meet QA/QC expectations [172]. However, by creating an average CH_4 concentration over a large area, variability associated with point measurements can be ignored, and all emissions from an area can be accounted for [169], and using multiple beam paths to generate data makes the measurements more robust [174]. The availability of FTIR equipment in many technical laboratories makes it attractive and it has been used in a number of instances to generate emissions data (e.g., [165] [167] [175]); it has also been identified as a good means of monitoring large but distinct areas at a site, which can be differentiated if the wind is in the right direction [170]. As suggested by the mass balance label, two measurement sets are created: one for upgradient conditions, and one for the site. Upgradient gas amounts are subtracted to generate net emission values (which can also account for consumption of atmospheric CH_4 by landfill soils) [172]. To address variability of FTIR measurements at a site in Canada, a multivariate ANOVA was used to generate a statistical model incorporating temperature, barometric pressure, and precipitation effects to interpolate releases when measurements were not being made [175]. One set of emissions data, for US landfills with intermediate cover (not considered to limit emissions much), ranged from 4-140 g m^{-2} d^{-1}, with a maximum reading of 210 g m^{-2} d^{-1}[172], the equivalent of 60 µg m^{-2} s^{-1} to 1.5 mg m^{-2} s^{-1} , with the maximum = 2.2 mg m^{-2} s^{-1}. Capped landfills were at least an order of magnitude less than the lowest value for intermediate cover, and as much as three orders of magnitude less [172].

Tracer methods for whole landfill gas emission measurements have been developed. Inert tracers, most often SF_6 (but sometimes N_2O and/or CO [170]) are released across the landfill at known rates. At an appropriate distance from the landfill (determined by air modeling) where the tracer should be well-mixed, samples are taken. The ratio of LFG constituents to the tracer indicates the release rate of LFG. General topography should be flat near the landfill, weather is an important variable, other sources of LFG constituents (feedlots, sewage treatment plants, etc.) can interfere with single source determinations, and the LFG release rate often needs to be high to ensure detectable amounts are measured downgradient [173] [101] [170] [135].

Spokas et al. [101] reported good agreements ($r^2 = 0.81$) between tracer and closed chamber sampling; Heroux et al. [175] reported better agreement between FTIR and closed chamber sampling ($r^2 = 0.91$). There was good correspondence (±10%) between FTIR and closed chamber sampling in one sampling instance in Taiwan, but in a second sampling effort, atmospheric concentrations measured by FTIR were higher than closed chamber data, and varied directly with organic carbon content in the samples [167].

Eddy covariance has also been used to measure fluxes from landfills. Measurements are made of gas concentrations at a certain distance above the landfill, and using theories regarding turbulent mixing, are compared to wind speeds over a set time period (30 to 60 min). This method generates release estimates integrated over an upwind distance equal to 10 times the height of the instrumentation, therefore creating a large areal footprint for the flux, which is useful at a landfill [135].

Eddy covariance was used to continuously monitor CO_2 and CH_4 and emissions at a capped but vented Nebraska landfill for more than 3 years. The ratio of CO_2 to CH_4 was significantly greater in summer than in winter, suggesting greater activity by soil methanotropes in summer, and emissions were higher in winter than summer. Increasing barometric pressure (for instance, a passing front) could suppress CH_4 emissions within minutes, although when pressure changes were averaged out over longer periods of time, emissions were stable, attributed to the landfill maintaining near constant internal temperatures. There was some uncertainty over whether barometric or wind direction changes was the primary driver of emission variance, but a spectral analysis of the data sets suggested a monitoring period of at least 10 days would be required to capture 90% of the emission data variance. It appears that "soil pumping" is the process driving the changes in releases (which is primarily but not entirely a phenomenon caused by changes in atmospheric pressures) [135].

Remote sensing (aircraft or elevated towers) can be used to measure atmospheric CH_4 and determine regional variations. The variations can then be attributed to sources, including landfills. These techniques can support large-scale screening projects, and have been used to refine considerations regarding major contributors to CH_4 emissions [176].

A modeling estimation technique has been developed for the US, where the regulatory requirement to measure ambient air for NMOCs quarterly generates repeated, robust data sets. Crosswind and downwind variations in concentrations are analyzed using standard gas dispersion equations. The resulting NMOC data are then related to CH_4 emissions. The technique also accounts for spatial and temporal variability in emissions, and compared well to concurrent FTIR surveys at a Florida landfill [177].

Sometimes very simple techniques can be used to survey landfills. PID-FID meters and hand-held methane gas monitors can be used to quickly assess potential point sources, and PID-FID meters have been used along transects to create emission estimates. Often, careful observations may suffice, as landfill gas often smells bad, and major release points can be identified by smelling them [176].

5. Chemistry of methane generation

5.1 Landfill gas (LFG)

Open dumping has been practiced by civilizations for millennia, using the principle of "out of sight, out of mind". Wastes in open dumps are often burned to control odors and reduce vectors, or perhaps catch on fire accidentally. Wastes are not inspected or otherwise controlled. They are not compacted or placed using any engineering concepts. Managed dumps are somewhat more organized: wastes may be inspected, dumping areas identified, stormwater management and basic cover materials provided [163]. The first sanitary landfill (a fill engineered to control the progression of filling, and using cover materials to reduce waste exposure to the environment) is thought to have been in Britain, in 1916 [178]. In the twenty-first Century, low income countries typically have "low technology sites," with open dumping, middle income countries have some landfills with controlled filling and environmental controls (managed dumps), and even some sanitary landfills, and high income countries exclusively use sanitary landfills with extensive environmental control systems [106].

Landfills (and dumps) do not have aeration systems and receive a loading that contains a great deal of organic matter. Near the surface, organics are oxidized aerobically [98]. However, slightly below the surface of the landfill air circulation from the atmosphere is minimized, and anaerobic digestion of organic material occurs, which rapidly becomes dominated by methanogenesis [107]. Wastes are typically quickly buried at the working face of a sanitary landfill, minimizing exposure to aerobic conditions. Once methanogenetic conditions exist, the process has a positive feedback, since the production of CH_4 and CO_2 as microbial metabolic waste gases makes the landfill a net source of gas to the atmosphere and surrounding subsurface, making infiltration of atmospheric gases into the waste mass more difficult. LFG migrates primarily by a combined mechanism of diffusion and convection; convection results from pressure gradients induced within the fill by differential outgassing from microbes, mediated by differences in pressure between the fill and the surrounding atmosphere. Typically, a dry, uncapped landfill will be in equilibrium with the atmosphere; however, a landfill with a saturated surface will not, although elevated pressures will develop in phase with changes in atmospheric pressures [107]. There tends to be more gas release from landfills at low atmospheric pressure times, therefore, and the differences can be sharp [135]. Diffusion exists because of unequal concentrations of gas, caused by differences in generation rates along with subsequent advection patterns [179]. Landfill gas, which is composed of approximately equal parts CH_4 (0.656 kg m^{-3}, lighter than air) and CO_2 (1.977

kg m^{-3}, denser than air), is approximately the same density as the atmosphere (1.225 kg m^{-3}). Therefore, since it has approximately neutral buoyancy, it will migrate along paths of greatest conductivity: sideways or downwards through the subsurface or upwards through the fill. At closed landfills with no or incomplete liner systems, putting an impermeable cap on the fill can cause all gas migration to be forced laterally, increasing off-site, subsurface migration [179]. Gas collection systems, however, appear to minimize if not eliminate lateral migration [101].

The development of gas production in a fill has been classically defined as having five stages [97] (Figure 4). Modern landfills (with effective liners and impermeable caps) have not been operated long enough to determine with certainty when gas production will cease. Sanitary landfills with less effective liners and cap systems appear to generate gas at high levels for approximately 20 years after being capped, and continue to produce gas for at least 50 years [24], although descriptions of degradation within fills vary widely, ranging from 3-10% [129], up to 50% [180] to “most” [181] through 20 yrs. Complete consumption of organic material in a sanitary landfill may take centuries or millennia, depending on cap effectiveness and the time to eventual cap and liner failure [182]. However, in the short term atmospheric gases (80% N_2, 20% O_2) are replaced within the fill by increasing amounts of CO_2 as aerobic respiration consumes organic matter; there is a brief time of H_2 production; methanotropes consume produced H_2 and replace it with increasing amounts of CH_4. Methane slowly grows so that it has slightly greater concentrations than CO_2 (see below) as methanogenesis dominates the degradation of organic materials, although some descriptions find their concentrations to be about equal. Eventually, methanogenesis will cease and the fill will aerate again. Some models suggest that if the fill dries out prior to consumption of all labile carbon, eventual failure of the cap and liner systems will re-initiate the sequence described in Figure 5, which may then continue until all consumable organic matter that remains in the fill has been depleted [182].

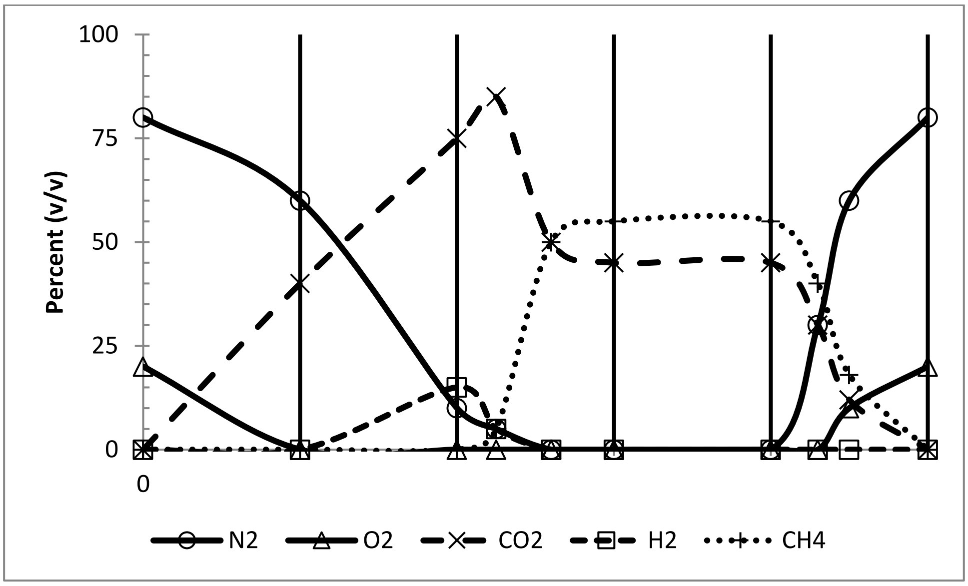

Figure 5. Gas composition with a landfill; the five delineated stages are not of equal duration (adapted from ref. 97)

The degradation of organic matter has classically been described using reduction-oxidation (redox) chemistry [183]. Table 11 shows the chemistry of the reactions on generalized organic matter. This description is drawn from marine sediments, where the zonation is often well-defined. In landfills, the zonations are indistinct, and it may be that micro-environments form where one process dominates over the others due to availability of electron acceptors [184] [185], which act as limits to methanogenesis. Aerobic decomposition of matter releases an order of magnitude more energy than methanogenesis, and, except for sulfate reducers, other anaerobic oxidation pathways produce much more energy, too [36].

Table 11. Redox description of the degradation of organic matter (adapted from ref. 183)

1. Aerobic oxidation of organic material $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (x+2y)O_2 + (y)HCO_3^- \rightarrow (y)NO_3^- + (z)H_3PO_4 + (y)H_2O + (x+y)H_2CO_3$ $\Delta G^0 = -3190$ kJ mol^{-1} (glucose) (Eq. 8)
2. Manganese reduction $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (2x+1.5y)MnO_2 + (3x+3y)H_2CO_3 \rightarrow (2x+1.5y)Mn^{+2} + (.5y)N_2 + (z)H_3PO_4 + (2x+3y)H_2O + (4x+3y)HCO_3^-$ $\Delta G^0 = -2920 - -3090$ kJ mol^{-1} (glucose) (Eq. 9)
3. Nitrate reduction (3a. oxidation to N_2) $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (.8x+.6y)NO_3^- + (.6y)H_2CO_3 \rightarrow (.2x)CO_2 + (.4x+.3y)N_2 + (z)H_3PO_4 + (.6x+1.3y)H_2O + (.8x+.6y)HCO_3^-$ $\Delta G^0 = -3030$ kJ mol^{-1} (glucose) (Eq. 10a) (3b. org. N released as NH_4^+) $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (.8x)NO_3^- + (y)H_2CO_3 \rightarrow (.2x)CO_2 + .4(x)N_2 + (y)NH_4^+ + (z)H_3PO_4 + (.6x)H_2O + (.8x+y)HCO_3^-$ $\Delta G^0 = - 2750$ kJ mol^{-1} (glucose) (Eq. 10b)
4. Iron reduction $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (2x)Fe_2O_3 + (7x+y)H_2CO_3 \rightarrow (4x)Fe^{+2} + (y)NH_4^+ + (z)H_3PO_4 + (4x)H_2O + (8x+y)HCO_3^-$ $\Delta G^0 = -1330 - -1410$ kJ mol^{-1} (glucose) (Eq. 11)
5. Sulfate reduction $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (.5x)SO_4^{-2} + (y)H_2CO_3 \rightarrow (y)NH_4^+ + (.5x)H_2S + (z)H_3PO_4 + (x+y)HCO_3^-$ $\Delta G^0 = -380$ kJ mol^{-1} (glucose) (Eq. 12)
6. Disproportionation (Methanogenesis) $(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (y)H_2CO_3 \rightarrow (.5x)CO_2 + (.5x)CH_4 + (y)NH_4^+ + (z)H_3PO_4 + (y)HCO_3^-$ $\Delta G^0 = -350$ kJ mol^{-1} (glucose) (Eq. 13)

Phase I (Aerobic) is the initial adjustment phase, also known as the aerobic phase because of its high oxygen concentration. Carbohydrates, hydrogen sulfide, and ammonium are oxidized and volatile fatty acids (VFA) are gradually produced [97]. The main reaction can be described as Equation 8. The duration of aerobic decomposition is under dispute, with the standard model suggesting buried wastes remain aerobic for a few hours to one week [97]. Those who believe landfills release more CH_4 than is generally said to be the case ascribe to the shortest time period for Phase I. Some who believe landfills are more benign describe longer aerobic periods, which can be months long. Variations from site to site may account for some of these differences in opinion. Staley et al. [186] suggested that uneven distribution of moisture, as a strong control on microbial activity is a determinant of whether or not degradation proceeds rapidly or not.

Phase II (Anaerobic but Non-Methanogenic) is a transition phase. Once oxygen is generally less than 5-10% (v/v), facultative and anaerobic bacteria are activated in places in the fill [97]. Under anaerobic condition, nitrate and sulfate (as well as iron and manganese in saturated zones) become terminal electron acceptors (Eq, 9, 10a, 10b, 11, and 12). The reduction of nitrate produces ammonia and the reduction of sulfate produces hydrogen sulfide. This phase may last six months, although some reports document 90% CO2 gas concentrations after 40 days [171].

Phase III (Unsteady Anaerobic Methanogenic) is an acid formation phase. Anaerobic hydrolytic microorganisms increase rapidly, resulting in the generation of volatile organic acids (VOA) and H_2. Acidogenic bacteria grow in numbers, consuming the VOA. Bacterial growth reduces the availability of nutrients. Carbon dioxide is predominant waste gas released by organisms within the fill. The accumulation of VOA and CO_2 tends to reduce pH in the fill; values as low as five have been reported. Peak production of H_2 occurs in this phase, and methanogenesis begins [97], despite reports from other environments such as peat that nlow pH values can entirely inhibit methanogenesis [187]. This phase lasts months to several years; two years is the most widely used estimate (c.f., [24]), but values of less than 1 yr are also widely cited [171]. Those believing landfills rapidly produce CH_4 will assign much shorter time periods to the non-methanogenic phases.

Cellulose and hemicellulose are believed to be the predominant degradable portions of wastes [188]; lignin has been found to be much more recalcitrant. Concentrations of cellulose and hemicellulose were called “reasonably consistent” in samples of fresh wastes in North Carolina, and except for food wastes, VFA were absent from the wastes as they were landfilled. Different fractions of wastes have different proportions of the key components, with leaves enriched in lignin and paper enriched in cellulose [186]). In waste samples, fresh waste can have a 4:1 ratio of cellulose to lignin, whereas older degraded samples tend to have a ratio of less than 1. At one California landfill, sample ratios for older wastes were all less than 0.1. The implications are that cellulose degrades in landfills, but lignin does not. There is additional evidence that lignin actually impedes cellulose degradation [188]. Note a study in the UK found that the age of waste (from 1 year to several decades) did not have an effect on CH_4 emissions -- which is not exactly the same as CH_4 generation rates [169].

Microbes causing degradation do not appear to be transported much within the fill, due to uncertain and irregular water flows associated with low hydraulic conductivity in much waste, and the development of preferential flow paths, and so are assumed to be present but inactive in the delivered wastes [186]. Water flows are also likely to be the best means to transport nutrients and organic substrates [189], so wastes outside of flow paths or isolated from other wastes inside plastic bags are unlikely to degrade quickly, if at all. Since collected wastes are mostly aerobic, the microbial communities must either be facultative or able to survive long exposures to oxic conditions. However, the microbial community structure of fresh waste, which is strongly influenced by food waste species composition, is very different from that of degraded waste [186]. Initiation of methanogenesis, as tracked by mesocosm experiments, requires the presence of VOA, and occurs at relatively low pH (as low as 5.5). VOA are produced when hydrolytic bacteria degrade cellulose and hemicellulose faster than acetogens and methanogens can convert the VOA to CH_4 [188]. Degradation of the cellulose appears to be accomplished by a varied set of thermophilic, motile bacteria, comprising at least four distinct isolates in samples from an English landfill [190]. Methanosarcina barkeri appeared to be the dominant methanogenic organism in the first stage of methanogenesis. As CH_4 concentrations increase, higher pH values were found in saturated areas of mesocosms, creating an advancing front of methanogenesis [187]. The Archaea methanogens are able to outcompete organisms found in aerobic communities, due to better fit with environmental conditions. The dominant methanogens are Methanomicrobiales and Methanosarcinales. Organisms found in leachate samples, however, are not similar to those found in waste samples [186]; in fact, samples from a Taiwan landfill leachate found that although these same two lineages were the dominant methanogens, they represented only 2% of the total community (as measured by oligonucleotide probes, which represent population numbers only approximately) [191].

Phase IV (Steady Anaerobic Methanogenic) is the methane fermentation phase. During this phase, intermediate VOA are consumed by methanogenic bacteria and converted into CH_4 and CO_2 [97], shown as Equation 13. In addition, CO_2 can be consumed if H_2 is present, producing CH_4 and water (Equation 14). Since some of the CO_2 in turn is consumed to produce more CH_4, most landfills have LFG that is 50-60% CH_4 and 40-50% CO_2 (v/v). Sulfate continues to be reduced, as well. The fill pH rises due to the bicarbonate buffering system; since methanogens need higher pHs to thrive, this is a positive feedback resulting in relatively more CH_4 production. The duration of this phase in unknown, but appears to be at least 10 years, and probably is at least 50 years [24], and may be more. Availability of water within the fill is an essential consideration. Note that Themelis and Ulloa [98] believe data show 50% of all labile organic matter is turned into CH_4 within one year.

$$CO_2 + H_2 \rightarrow CH_4 + 2H_2O \qquad \text{(Eq. 14)}$$

Phase V represents the stabilization of the waste mass, when it no longer degrades. When LFG generation ceases, atmospheric gases will permeate back into the landfill, and oxidized chemistry will re-appear.

The overall conversion from organic compounds to methane and carbon dioxide may stoichiometrically be expressed as Buswell formula (Equation 15) [192]:

$$C_nH_aO_b + (n - a/4 - b/2)H_2O \rightarrow (n/2 - a/8 + b/4)CO_2 + (n/2 + a/8 - b/4)CH_4 \qquad \text{(Eq. 15)}$$

All-in-all, LFG production is sensitive to moisture, temperature, oxygen, hydrogen, pH/alkalinity, sulfate, nutrients, and various inhibitors [97] [193], although temperature may not be important [135]. Moisture is key; maximum gas production appears to occur at 60-80% wet weight moisture content. Dry climate landfills experience spikes in gas production after rainfalls, but in temperate climates heavy rainfalls appear to temporarily inhibit gas production, possibly by filling preferential flow pathways [171]. Temperature has also been identified as a controlling variable. One consideration for waste degradation was Equation 16:

$$h_d = 0.014T + 0.28 \qquad \text{(Eq. 16)}$$

where

h_d = fraction of biodegradable wastes eventually degraded
T = temperature of waste mass (ºC)

Under mesophilic (~35 ºC) conditions, the efficiency is expected to reach ~75% [189]. The state of the wastes, including differing origins (industrial, commercial, residential) and whether or not they are shredded will affect degradation [189]; recent preferences in the US for tightly baled and wrapped bundles of wastes that enhance transportability is likely to suppress degradation, as well.

Barlaz [186] estimated gas generation (based on laboratory landfill reactors, with shredded biomass and constant water inputs) at 0.153 g CH_4 g biomass^{-1}. USEPA [24] has modeled a 21% reduction in decomposable material being landfilled (1990-2012), partly due to recycling and partly due to changes in materials use; USEPA has modeled a related 30% decrease in CH_4 generation at landfills. Other developed nations are probably experiencing similar trends; waste disposal trends in developing nations are probably different, as growing affluence is likely to increase paper and overall discards [106].

USEPA modeling [24] assigns a 40% reduction factor for dumps compared to sanitary landfills. Most nations under the IPCC protocols appear not to count dumps or informal disposal sites in CH_4 generation inventories.

It is generally understood that most carbon placed in landfills does not degrade [24], although this is not universally agreed to. Scheutz et al. [176] asserted LFG is generated until "the majority" of wastes has been degraded, which was said could take several decades. But, tremendous odors occurred when 2000 year old Roman waste were uncovered [194], indicating degradation may not have completed over a short time period. Rathje [131] was able to date landfilled wastes in the US by reading newspapers (often 30-40 years old), and reported finding intact items such as bananas and hot dogs 30 years after burial. Rathje's opinion was that yard waste and food degraded in many landfills, but most other organic matter did not. Landfill settlement rates are often less than expected. Maximum settling of landfill surfaces may approach 40%, but only about 40% of total settling (15% of the original thickness) is expected to be from waste decomposition. The remainder of the settling is due to waste consolidation and mechanical creep [195]. Sanitary landfills can more than 100 m thick but rarely settle more than 10-20 m. This failure for landfills to "disappear" supports the concept that most degradable materials are preserved in sanitary landfills.

Experimental tests show waste degrades. The Barlaz laboratory, working with mesocosm landfill analogs for several decades, has shown ground, moist organic material will degrade under landfill conditions [196]. Food was shown degrade rapidly and readily although CH_4 inhibition occurred with a subset of samples, apparently due to high VOA [197]; grass samples nearly all degraded, and over half of corrugated cardboard and office paper was degraded to CH_4, so that about 50% of all degradable MSW was gasified [196]. But not all constituents degrade even under these optimal anaerobic conditions [198]. In landfills, with plastic wraps, differential and uneven exposure to water, and other factors, it is clear that most degradable compounds do not evolve into CH_4 in sanitary landfills [188], at least partly due to isolation from water flows carrying nutrients [189], so that, in a sense, landfills constitute a carbon sequestration vehicle for time periods of decades to centuries [198]. It has been argued eventually the organic matter will decay, although it may take millennia [182]. Operating a landfill as a bioreactor to increase degradation rates (recirculating and potentially supplementing leachate to keep wastes wetter) can approximately double the decay constant, but does not ensure appreciably greater degradation of the landfilled material; it may just shift decay earlier in the life of the landfill [199].

Modeling landfill behavior has been attempted, but the complexity of the process means these simulations have difficulty replicating actual observed outputs at a site. There are physical, chemical, and biological reactions occurring in heterogeneous liquid, gas, and solid phases. Some attempts to capture this very complicated environment include Wall and Zeiss [198], Zacharof and Butler [201], Hanson et al. [202], Lobo et al. [203], McDougal [204], Gourc et al. [205], and Robeck et al. [206].

5.2 Anaerobic Digestion (AD)

Anaerobic digestion (AD) is similar to the processes that occur from Phase II to Phase IV in landfills. A consortium of microbes working in concert degrade complex organic molecules to CH_4 (and either CO_2 or water) [94]. There are a number of distinct stages to methanogenesis. In the first, the complex and solid organic matter is hydrolyzed into soluble molecules. In the second, these molecules are converted by acid forming bacteria to VFA, CO_2, and H_2. In the last stage, CH_4 is formed by methanogenic bacteria, either by breaking down the principal acids, or by reducing CO_2. The entirety of the process includes hydrolysis of biopolymers, fermentation of amino acids and sugars, anaerobic oxidation of long chain fatty acids and alcohols, anaerobic oxidation of intermediary products such as volatile acids (with the exception of acetate), conversion of acetate to CH_4, and conversion of H_2 to CH_4 [207]. One way of considering AD is to classify it into three end stage reactions (Equations 17-18):

(1) Acetotrophic (degradation of acids)

$4\ CH_3COOH \rightarrow 4\ CO_2 + 4\ CH_4$ (Eq. 16)

(2) Hydrogenotrophic (using H2 to reduce CO2):

(3) $CO_2 + 4\ H_2 \rightarrow CH_4 + H_2O$ (Eq. 17)

(4) Methylotrophic (compounds containing a methyl group; methanol used as an example) [94]:

$$4\ CH_3OH + 6\ H_2 \rightarrow 3\ CH_4 + 2\ H_2O \qquad \text{(Eq. 18)}$$

The Buswell formula (Eq. 15) is also applied to calculate the maximum amount of methane may be generated during AD process. Because excess produced H_2 is available to reduce CO_2, the “theoretical” 50:50 ratio of CH_4 to CO_2 is rarely observed; CH_4 content in produced biogas is usually greater than CO_2 and ranges from 40-70% [94]. Anaerobic digestion is not very efficient, however, and typically only 20-30% of infeed organic matter is mineralized, because of the large amount of lignin in typical AD feedstocks [208]. Lignin itself is recalcitrant, and also inhibits the digestion of more degradable cellulose compounds [188].

Various inhibitory or toxic substances are the primary cause of AD reactor upset; many are common elements of MSW and other wastes. The most common inhibitors include ammonia, sulfide, light metal ions, heavy metals, and organics (chlorophenols, halogenated aliphatics, N-substituted aromatics, long chain fatty acids, and lignin-related compounds); ammonia is the most common cause of problems [209] [210]. Unlike a landfill, where wastes are rarely completely saturated, an AD is saturated, and so the entire process can be upset whereas inhibition of methanogenesis in a landfill is likely to remain relatively isolated. Because AD occurs in a microorganism ecosystem that can vary in composition, and wastes are rarely similar, and process methods and conditions vary, reports on AD inhibition due to specific toxicants are not consistent [210]. Inhibition can also occur when essential nutrients are not present, or are not present in ratios that support microbial growth. Carbon and nitrogen are considered the essential nutrients, and optimal growth is achieved under differing C/N ratio, depending on process feedstocks [94]. Competition between sulfur reducing bacteria and methanogens can also occur; this can result in biogas contamination with H_2S [210]; typical H_2S concentrations from manures and sewage sludges are 200-1500 ppm, with some reports of concentrations as much as 10,000 ppm [88].

Anaerobic digesters are continuous feed or batch feed, “wet” (low solids content, generally <15%) or “dry” (higher solids content, generally 10-20% although sometimes as high as 40%), one stage or two stage processes, and mesophilic (~35 °C) or thermophilic (~55 °C). A special case is the “anaerobic filter,” where fermentable wastewaters flow upwards past solid media, where the microbes are intended to be attached to prevent washout (this is a short retention, high flow rate system). Batch feeds enable sequential completion of the multi-step digestion process, and have greater gas production, but require storage of feedstocks. Microbial populations can also become unstable. Wet processors allow for homogenization of the slurry. This can present process issues with some feedstocks, as when scum layers form or inhibitory compounds are produced. Dry systems allow for removal of scums by promoting segregation of different elements in the vessel, and can prevent total system shocks and process upsets, limiting effects to smaller areas of the vessel – and the process may be able to mitigate the production of process toxins with time. However, in dry systems solids may discharge prior to complete treatment, and larger solid materials tend to be more recalcitrant. Plug flows may slow or even prevent inoculation of input wastes. Although loadings are greater to dry systems, retention times tend to be longer. Two stage (sequential vessel) systems typically separate acidogenetic from methanogenetic phases, minimizing opportunities for process upsets, but other elements of the process can be separated depending on system needs. Such an installation obviously requires shifting materials from vessel to vessel. Thermophilic systems require heat additions, and may promote production of inhibitory ammonia, although the breakdown of matter may be faster; economics dictates that most sewage sludge digestion is mesophilic. In Europe, most installed capacity is dry, single stage digesters, with various configurations of the other factors [94] [93] [208].

Various combinations of substrates are recommended; the mixtures depend on what is considered to be the primary waste to be managed, and what is the additional material or materials to be added. Feedstocks for AD include sewage sludges (”biosolids”), animal wastes, crop residues, aquatic and marine biomass, MSW, food wastes, and various industrial effluents (wood and paper pulp, food processing wastes, even textile effluents and petrochemical plant residues) [94] [93] [210]. More AD plants are in use in the EU, partly because of the EU Landfill Directive requiring landfilled organic matter to be pre-treated (see Section 7), and partly because of tariffs and generally higher electricity prices which make biogas-to-electricity plants more profitable [94]. The solid digestate from AD is often composted, and used as a soil amendment [96].

In Asia (especially India and China), there has been a history of small, household- to neighborhood-sized AD plants [211]. Expanded use of these plants began in the 1970s in China when 7 million plants were constructed. In the 2000s, another 20 million plants were installed. In India, over 7 million plants have been installed or are planned for. They manage animal manures primarily, but also can be connected so as to treat domestic wastewater and other organic wastes. Although decentralized production of biogas, especially to replace the use of biomass for cooking, but also for household heating and illumination, and even electricity generation, is very attractive in rural areas otherwise devoid of modern infrastructure, the technology has not flourished. Owners and presumed operators of the plants were not adequately trained to run these plants, nor were any mechanisms for maintenance (spare parts, etc.) ever provided. Costs for plants are enormous compared to household cash incomes in rural, undeveloped areas, and so subsidies are a necessity for construction, and financing for system maintenance, even if the know-how had been transferred, is also difficult to accommodate. At least 50% of installed plants from the first wave of China construction are inoperable, and data from other Asia locales are not very different (unless only recently constructed plants are included in the assessments) [212].

5.3 Methanotropes in Cover Soils

Microbes in a variety of environments oxidize CH_4 to CO_2. There is great such activity in deep-sea sediments (70 Tg CH_4 yr^{-1}), where methane oxidizing organisms appear to be symbiotic with sulfate reducing bacteria. The marine sediment oxidizers appear to be Archaea, with strong genetic links to methanogens [55]. This metabolic activity appears to be close to the lower limit of beneficial energy recovery [213]; this low level of activity may be supported because some methanotropes may link to manganese and iron reducers which are energetically more favorable [214]. In terrestrial environments, methane oxidizers occur primarily in upland, forested settings and take up CH_4 from the atmosphere, apparently without any microbial symbiosis. They oxidize considerable amounts of atmospheric CH_4: 30 Tg yr^{-1} (2-3% of released CH_4) [12], which, given the smaller terrestrial area compared to oceanic areas, indicates a similar overall activity level. Terrestrial methane oxidizers are inhibited by ammonium, which is present in fertilizers, so applications of fertilizers decrease CH_4 removals, a growing concern with the increase in worldwide agriculture [12].

Uptake at landfills appears to be different in certain ways. Organisms in cover soils consume CH_4 in much higher CH_4 concentration environments [135]. These organisms primarily oxidize CH_4 to CO_2 to support metabolism and use some of the CH_4 for assimilation, as well. They appear to primarily be obligate aerobes. Differences among landfill specific organism groups include the ability to co-metabolize other non-CH_4 organic compounds, CH_4 consumption rates, O_2 requirements, the CH_4 concentration that triggers oxidation, temperature and moisture change resiliency, and the release of various extracellular chemicals (at least partially to address internal production of formaldehyde) [215]. These extracellular chemicals can clog soil pores and prevent organisms from accessing gas [189]. In general, methanotropes transform more CH_4 in summer than winter

[135]. Although they represent a variety of organisms with different abilities and traits (for instance, not all oxidize CH_4, and some additionally transform NMOCs in landfill gas), this set of soil organisms that are involved in transforming CH_4 and reducing releases to the atmosphere are lumped together as "methanotropes" [215].

Oxidation of CH_4 requires methane mono-oxygenases [176], and follows the following pathway: CH_4 to methanol to formaldehyde to formic acid to CO_2 [68]. There are two ways to assimilate CH_4. Type I methanotropes (eight genera in Methylococcaceae) assimilate formaldehyde via the ribulose monophosphate pathway, but Type II methanotropes (four genera in Methylocystacecae) assimilate formaldehyde through the serine pathway [189]. Approximately 50% of CH_4 affected by these microbes is assimilated, and the remainder is oxidized, providing metabolic energy [176]. Methanotropes are very similar to ammonia-oxidizing chemoautotrophs [68]. In cover soils, some oxidation of CH_4 may proceed chemically, as the atmosphere mixes diffusively and through soil pumping with landfill gases in the top soil layers of the landfill [216]. Then, OH· reactions, just as in the open atmosphere, will oxidize CH_4 to CO_2, as discussed in Section 1.

Coarse sandy soils support substantial CH_4 oxidation [217], although higher carbon content is preferential: the salient feature of sands is its good structure, so silty or sandy loams are probably the best soil types overall for methanotropes. Low and high moisture levels impede gas production [189]. The presence of plants appears to enhance methanotropism. This may be because many organisms establish symbiotic relationships with rhizosomes, and also because the rhizosphere generally appears to be a favorable environment for bacteria [189]. Additionally, it may be that methanotropism is generally N-limited [176], and root zones are often prime locations for nitrogen fixation. The establishment of plants on a landfill surface enhances reduction of CH_4 releases and decreases associated soil concentrations; it may also be that decreases in soil CH_4 concentrations enhance conditions to foster plant growth; in any case, older landfill sections support more plants and have lower soil gas concentrations of CH_4 [159]. Interruption of gas supplies to the surface soils has a small impact on populations of methanotropes. Methanotropism is detected in anoxic soils as well as oxygenated soil, suggesting at least some of the community is facultative, although greatest consumption occurs in more aerated environments [217], and, generally, O_2 is necessary for methanotropes. Gas extraction systems can increase the depth of methanotropism by drawing atmospheric gases deeper into the fill than they might naturally diffuse to. Maximum CH_4 oxidation rates by methanotropes appear to be 250 g m^{-2} d^{-1} (2-3 mg m^{-2} s^{-1}) [176]; most reports are for much lower oxidation rates [68]. At three French landfills, where gas migrated to the atmosphere (as opposed to being entirely controlled by the gas collection system), between 4% and 50% of the fugitive CH_4 was consumed [101]; a landfill with specially prepared cover material oxidized 55% of fugitive CH_4 [218]. Some data suggest 80% reductions can be achieved [219] with at least one experimental achievement of 90% reductions [220]. In addition to comparisons of modeled gas generation to releases to the atmosphere as a means of determining methanotropism, indirect measurement of CH_4 consumption can be estimated using $\delta^{13}C$ of collected CH_4 in flux chamber experiments. Methanotropes prefer C^{12}, therefore increasing the $\delta^{13}C$ of gas as it passes from the landfill to the atmosphere, so changes in CH_4 $\delta^{13}C$ indicate methanotropism [101]. And, not only will methanotropes reduce CH_4 releases at landfills, they also degrade important NMOC such as aliphatic hydrocarbons (benzene and toluene) and chlorinated solvents (trichloroethylene and 1,1,1-trichoroethane) [68] [216], with significant reductions being measured in the field [218].

Modeling this process is not simple. There are two transport media (gas and liquids), and reactions are multi-component. In porous media, molecule-molecule reactions dominate, and so diffusive processes are often more important than advective processes (which need to account for tortuosity as well) [219]. However, it is also asserted that small pressure gradients within the fill or very coarse soils can drive advection to be the dominant transport process. At the edge of the fill, and where leachate seeps occur, bubbling (ebullition) mechanisms are important [176]. Unequal density of the target gases affects considerations, as well. When modeled, it appears that diffusion is the dominant transport mechanism within the active methanotropic zone. Because the reactions reduce 2.5 moles to gas to 0.5 moles of gas, there is a decrease in pressure which also energizes transport, although CH_4 (a light gas) is transformed to CO_2 (a heavier gas). Moisture reduces reactions by slowing O_2 diffusion into the soils. The model did not show significant effects (over time periods of weeks) from exudations that could clog pore spaces [219]. Models of methanotropism help elucidate process controls, and there was fair agreement between a model and field measurements made when argon gas was used as a tracer, which was interpreted as suggesting these models may capture some of the natural dynamics, as well [176]. Methane generation models typically apply a constant correction factor to account for methanotropism, most often decreasing releases by 10%.

Biosystems (soils or other media that support methanotropes) have been proposed for closed landfills where gas collection and management may not be feasible [218] [170]. Unsuitable conditions for gas management include: startup phases; post-closure times when gas production rates dip; small sites; sites where waste composition issues make gas quality insufficient (too little CH_4) or inappropriate (too much contamination) for use; and, sites where forced aeration is used to reduce labile carbon (so-called MBT sites, almost all in the EU) [215]. They may be useful adjuncts to cover systems, as engineered controls like caps have limited lifespans (perhaps only a few decades) [189]. At landfills with active gas systems, augmenting soils to induce more oxidation of fugitive gases could reduce CH_4 releases by tens to hundreds of Mg yr^{-1} [218].

Biocovers are final caps composed of a gas permeability layer topped by a medium designed to support methanotropes: typically compost. Biofilters are engineered media designed to support methanotropes on packing materials. They are suitable for use over landfill cover systems such as clay liners or geomembranes. Biofilters can be open beds with passive gas feed to the organisms, or closed beds with active gas feed. Composted wood chips can make good media. Biowindows are sections of uncapped fill in an otherwise capped fill. They receive preferential gas flow, and have been used in Europe to remediate old dumps. Biotarps are alternative daily or intermediate covers; the compost (or other media) is a better support system for methanotropes and so improves gas reduction rates [215]. Treated waste can also serve as a biosystem substrate, as shown by an experiment where MBT residuals were used as a biocover that reduced 90% of produced gas from a waste lysimeter [220].

6. Methane utilization options

In the developed world, landfills with capacity > 1 MT yr^{-1} almost all beneficially use produced biogas (as well as most sewage treatment plants > 100 ML d-1, and over 8,200 US dairy and swine operations). Feasibility is a function of revenues versus expenses [221], tempered by regulatory requirements and government support. In the US, LFG has been used to produce electricity (LFGTE), fire industrial boilers, power dryers and kilns, and for greenhouses, infrared heaters, leachate evaporation, glassblowing, potttery, blacksmithing, hydroponics and aquaculture [222].

6.1 Composition of LFG

The composition of LFG (Table 12) is primarily determined by waste components, landfill age, and climatic conditions. Nearly all of LFG is CH_4 and CO_2; there are much smaller concentrations of hydrogen sulfide (H_2S) and ammonia. Usually, the gas is saturated with water vapor, and typically contains dust particles, siloxanes, and part-per-billion concentrations of various volatile organic compounds [223]. Landfill gas is not homogenous, and the age of wastes and the depth of collection affect important constituents [173].

Table 12. Typical LFG composition (adapted from [137])

Constituent	Composition (%, v/v, dry basis)	Mean (%, v/v, dry basis)
CH_4	40-60	50
CO_2	25-50	42
N_2	0-15	7
O_2	0-4	1
H_2S	0-1.0	0.03
H_2	0-1	0.5
NH3	0.01-1	
CO	0-1.0	
Trace gases	0.01-0.6	

As many as 116 NMOC have been measured in LFG; concentrations have been decreasing at US landfills, attributed in part to more aggressive segregation of hazardous materials from the waste streams, and product substitutions by industry. Data from 1000 US landfills suggested mean NMOC concentrations were less than 1000 ppm, with most regions in the US reporting mean concentrations less than 500 ppm. Many of these compounds are acutely or chronically toxic, constitute hazardous air pollutants or form them through atmospheric reactions (especially ozone), and are odorous [173].

6.2 Gas collection systems

In order to collect gas at a landfill, a collection system must be installed. Typically, for a system installed after the landfill has been operating, there are a series of vertical wells drilled into the waste to just above the liner (or bottom of the waste, as the case may be). Screening of the wells may be continuous, at discrete intervals, or only at one point (rarely just at the bottom, as bottom screened wells may become flooded with leachate).. The wells are fitted with valves to allow vacuum control. At the most modern sites, variable speed pumps controlled by a central, computerized monitoring system can optimize collection from individual wells or over sections of the piping network. A network of headers, often with condensate traps to allow for collection of liquids created due to temperature change (LFG is generally saturated, and landfills tend to be warmer than ambient temperatures, so that moisture condenses as the gas cools), is used to transport gas to one or more central locations. There, the gas is either treated and then used, or used as is. Installing a cap on the waste will increase the capture rate, and reduce incorporation of ambient air [224] [137].

A planned gas collection system can be installed as a landfill is built. In these cases, horizontal pipes are generally laid into trenches at regular intervals as the landfill rises. The pipes are extended out the side of the landfill. Flexible connections may be included to account for deformation of the wastes through densification or settlement of the waste mass [137].

Typically, rigid plastic piping is used. Common configurations of the piping network are radial collection systems (a central collection point) or using a main collection pipe connected to each well; it is common to use either the radial pattern or the main collection pipe systems in a sectorial factor, so that the systems are modular (enabling them to be isolated for repairs, and allowing for expansion as the site grows). Blowers and compressors are required to establish vacuum and to move gas. Regular monitoring of each well and network of wells is important to tune gas production optimally, both to maximize withdrawals from areas where gas production is best, and to ensure that not too much atmospheric gas is being captured, as well. When the landfill as a whole, or a particular section ("cell" of the landfill is closed, fitting the cap material (geomembrane or clay, usually) around gas wells is a complicating factor [137].

High leachate levels and perched water in the fill cause gas extraction problems. Clogging of pipes due to condensate pooling is also an issue. Internal fires play havoc with gas systems. Corrosion of parts due to H_2S oxidation causes part failure, as do abrasion due to silicon and siloxanes.

Gas treatment facilities and processes are discussed below.

6.3 Gas capture efficiency

There is some controversy regarding the effectiveness of gas control systems at landfills. One element is the rapidity with which organic matter is converted to CH_4. Some believe it is very rapid: onset within a day or two of materials being covered, to the point where one interpretation of data is that 50% of all available material is converted within the first year of placement in the fill [98]. The other has to do with methods used to estimate CH_4 generation.

The classic model for CH_4 evolution, as presented above, is that wastes take up to several years to enter mature CH_4 generation.

Most estimates for CH_4 generation depend on models. LandGEM is relied on by USEPA. A key input to Land GEM is waste deposition. In the US, there has been controversy regarding the amount of waste generation. The USEPA model is the most relied upon source of data, but this has been criticized as being theoretically unsound [120] and as underestimating waste disposal considerably [225] [121]. Powell et al. [121] used revised estimates of disposal to re-estimate CH_4 emissions, and estimated open landfills have a collection efficiency of 70% and closed landfills slightly exceed 80% efficiency.

Gas collection is a function of the landfill surface type. During operations, a sanitary landfill has a 0.15 m soil cover (or something similar), designed to restrict vector access and absorb odors. When filling operations are expected to stop for a lengthy but not permanent time period, “intermediate” cover is used: 0.3 m of local soils (or equivalent, designed to meet the vector and odor control functions of daily cover, and to be resistant to erosion. Depending on soil types (or the choice of alternative materials), these covers may or may not impede gas release from the fill. Final cover is supposed to seal the fill from the environment (using clay or plastic as the main element of a cap), and should be impermeable to gas [226]. Older developed country dumps and landfills and many developing country landfills only have soil covers of varying thickness as a final cover (c.f., [159]). Therefore, gas capture efficiencies are strongly affected by the cover type. The purpose of gas collection also affects efficiency. In the US, for regulatory compliance, most but not all gas needs to be collected (allowable concentrations are <500 ppm CH_4 measured 15 cm above the fill). Control processes for lateral gas migration or to prevent off-site odors are often greater than needed, so that atmospheric gases are collected as well as LFG. Lateral migration is often enhanced when landfill surface soils are saturated [176], and has also been caused when fills are capped without an active gas control system, and gas venting is absent or insufficient. Maximizing energy output may require allowing some LFG to escape from collection, to avoid any LFG dilution [226]. With all these site specific factors, it is difficult to develop one general LFG collection efficiency value. Barlaz et al. [226] reported on a selection of reports, and found that, using a definition of efficiency that measured collection compared to modeled gas generation, final covers generally resulted in 90%+ collection efficiency, and intermediate and other soil covers resulted in lower collection efficiencies between 50% and 80%. A comprehensive set of tests at three French landfills, where efficiency was determined to range between 41% and 94%, depending on cell parameters, resulted in the French government setting a 35% efficiency value for operating cells, 85% for a cell with a clay cap, and 90% for a cell with a geomembrane cap [101]. In the U.K., data suggested a good cap and a well-operated gas system would be highly effective at controlling emissions, reducing them by at least one (90%+) and often two orders of magnitude (99%+), to as low as 10^{-4} mg m^2 s^{-1} [169]. However, collection rates can never be 100%; there are inevitable leaks at wells and along pipes and other installed equipment [215]. In the US, 90% of large landfills reported gas collection efficiencies; these ranged from 47% to 95%, and the median value was 75% [111].

Operational policies can further limit control efficiency; plants may not operate when collected gas is uneconomical to use, and these times may account for up to 50% of system operations [215]. In the US, limits on O_2 (5%) and N_2 (20%) concentrations in gas treatment systems, established for air quality purposes, limit the intensity of collection by operators by preventing over pumping so as to incorporate significant amounts of atmospheric air [227].

6.4 Gas clean-up

Raw biogas from landfills is usually cleaned and upgraded for further utilization. Water, H_2S, siloxanes, and other impurities are removed in the “cleaning” process to minimize corrosion or other downstream problems which can double maintenance time intervals. Upgrading means removing CO_2 to increase the energy density [164].

6.4.1 Hydrogen sulfide removal

Sulfur compounds are common contaminants in LFG. They are generated both from anaerobic degradation of sulfur-bearing organic molecules (mainly proteins) and through sulfate reduction. In landfills, construction and demolition debris, especially wallboard which is largely composed of gypsum degrade with relatively large releases of H_2S due to sulfate reducing bacteria [228]. Hydrogen sulfide oxidizes to sulfuric acid, and so combusting LFG containing H_2S would cause corrosion to compressors, gas storage tanks and engines, and cause the release of sulfur oxides (“SOx”) that are considered to be harmful air pollutants.

Standard technologies for H_2S removal fall into two categories: physicochemical and biological conversion. Physiochemical treatments can further be divided by media: absorption into a liquid or adsorption on a solid [229].

Marketed in 1890 and modified in 1936, the Claus process is the most popular process employed for H_2S removal on an industrial scale. As a first step, H_2S is partially oxidized to SO_2 with air.

$$\mathrm{H_2}S + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{SO_2} + \mathrm{H_2O} \qquad \text{(Eq. 20)}$$

Then the mixture reacts over a bauxite catalyst yielding elemental S and water.

$$2\mathrm{H_2}S + \mathrm{SO_2} \rightarrow 3\mathrm{S} + 2\mathrm{H_2O} \qquad \text{(Eq. 21)}$$

The main elements of Claus plant unit are a reaction furnace, two or three catalytic reactors, and a tail gas treatment unit depending on H_2S content. Many improvements of the Claus process have been introduced since it was first introduced, and improvements in sulfur recovery efficiency are still being sought [230].

Aside from Modified Claus technologies, many other commercial applications have been developed over last hundred years. At present, adsorption-based technologies are mostly used to reach ultra-low sulfur levels [231]. Biological conversion is considered to be the most economical and environmentally friendly method. Table 13 lists several examples of modern, non-Claus technologies.

Table 13. Comparison of existing sulfur removal technologies for biogas purification

Technologies		Theoretical basis	Representative commercial application	Cost-Loading capacity	Drawbacks
Physico-chemical	Fe-chelated solution	chemical affinity of H_2S for metal cations	Sulferox®; LO-CAT®	Sulferox®: \$0.24-0.30 kg^{-1} H_2S	Large initial investment, small scale system; expensive operation [226] [229]
	metal sulfate solution		Still under development		
	Scrubbing	oxidation and neutralization	Eco-Tec Inc. BgPur™ BioGas Purification System		
	virgin activated carbon (AC)	physiosorption	DARCO®	AC: 0.02 g g^{-1} AC; DARCO® 0.2 g g^{-1}	
	impregnated AC	redox catalysts (sodium hydroxide or bicarbonate & nitrogen compounds) [233]	catalysts with higher capacity are under research	0.15 g/g of AC; up to 2.5 g/g of impregnated carbon aerogels reported [234]	
Biological	chemotrophic bacteria	Sulfide oxidation to S^0 with thiobacteria	Thiopaq®	Operating costs: \$2.20 kg^{-1} S	O_2 and N_2 inhibition following treatment [232]
	phototrophic bacteria		Still in laboratory		

6.4.2 Other contaminants

The standard for acceptable quality depends upon the end use of the gas. Siloxanes, halogenated compounds, other trace VOCs, water, ammonia and sometimes oxygen and nitrogen are all removed from LFG under some conditions. Siloxanes and halogenated compounds are the most harmful of these compounds when energy recovery is the goal, especially when present at higher concentrations [236].

Siloxanes are derived from waste consumer products and are found in almost all LFG. During combustion, siloxanes are oxidized and deposit as silicon dioxide solids, causing abrasion of mechanical moving parts. The deposits can accumulate in layers inhibiting conduction of heat and essential lubrication. Siloxanes are typically removed using one of three technologies: adsorption, absorption, and deep chilling. The most widely used method is adsorption on activated carbon [237]. Bio- and membrane filtration techniques appear promising but are not easily commercialized [238] [239] [237]. Process configurations that minimize deposition surfaces also can limit siloxane impacts [221].

Halogenated compounds volatilize from the waste mass. They will form acids on combustion [221]. Typically, larger molecules are removed by activated carbon adsorption [235]. Many VOCs are also removed when CO_2 is treated; water removal (drying) systems (just below) result in 99% reductions in VOCs [240].

LFG is always saturated. Water must be removed prior to end uses. Water can be condensed by increasing the temperature or decreasing the pressure. Other techniques include adsorption by silica gel, activated carbon, or aluminum oxide, and molecular sieves and absorption in glycol solutions [235].

Ammonia is generated by degradation of nitrogen-containing organics (e.g. proteins) and nitrate reduction. It is a gas contaminant, but its presence in LFG has beneficial aspects. During combustion it reacts with oxidized nitrogen compounds resulting in less NOx production. Ammonia concentrations are often reduced as a secondary byproduct of treating other contaminants, especially water [241].

Oxygen and N_2, indicative of atmospheric gases mixing with the LFG, are contaminants of concern especially for LFG use as pipeline gas or when converted to vehicle fuels. Oxygen and nitrogen can be removed by membranes, low temperature pressure swing adsorption, and at least partially when sulfur compounds are targeted. Even high-powered engines are relatively intolerant of O_2 and N_2, with maximum allowable O_2 being 0.5%, and combined O_2-N_2 being 2.5% [222]. Removing these gases is expensive. Avoiding over pumping the landfill to minimize atmospheric gases in collected LFG can be driven solely by cost considerations.

6.5 LFG Upgrading

The Wobbe index is a common measure of upgraded gas quality, and often is used as a standard for conversion to fuels and for pipeline quality gas. The Wobbe index is proportional to the methane content of LFG. It is measured by the heat produced by combustion of the gas through a defined orifice under standard temperature and pressure conditions. Minimum Wobbe index values tend to be 18 MJ/Nm^3. European standards for pipeline quality often call for more than 40 MJ/Nm^3 [241].

Removing CO_2 is the most expensive part of gas treatment [235]. Costs are defined by the size of the plant and specific selected technology [242]. Pressure swing adsorption (PSA) and water scrubbing have the largest market shares, although since 2009, chemical scrubbers (such as amine scrubber) have increased their share of the market; membrane filtration technologies also hold promise [243].

Pressure swing adsorption causes CO_2 to be adsorbed on materials such as carbon molecular sieves at elevated pressure (300-1000 kPa); the materials are regenerated at lower pressures. Vacuum swing adsorption, similar to PSA, has a supplementary vacuum pump so the desorption takes place under vacuum [244]. Skarstrom-type PSA units have four distinct treatment processes: (1) adsorption, (2) pressurization of the feed stream, (3) more adsorption, and (4) depressurization and desorption. New adsorbents, such as metal-organic frameworks, are being investigated to improve PSA performance [245] [246]. Temperature swing adsorption can also be applied for CO_2 removal.

Water scrubbing is the simplest means of separating CO_2 from LFG. It is based on the different binding forces between more polar CO_2 (and H_2S) and non-polar CH_4. It requires physical absorption in counter-current water at high pressures, usually 700-1000 kPa, and desorption with very little change in pressure or temperature [247]. Complete water recycling is thought to be possible when an effective under-pressure desorption system and water cooler are used, but there are losses in removal efficiencies [240]. Organic solvents, such as polyethylene glycol, can be used in place of water. Because of higher CO_2 solubility in organic solvents, the separation efficiency is greater. The trade-off is increased energy requirements to regenerate the scrubber liquids [241]. Although H_2S can be removed simultaneously in a water scrubbing system, often accumulating elemental sulfur plugs the pipeline.

Amine scrubbing, mainly using mono ethanol amine (MEA) and di-methyl ethanol amine (DMEA), has been used to separate CO_2 from natural gas and H_2 since 1930. Heat is needed to regenerate the amine. It has high efficiency and selectivity [248].

Membrane separation is based on the selective permeability of membranes. Basically there are two types: dry and liquid membranes. Dry membranes are commonly in the form of a hollow fiber with a high pressure (>2000 kPa, or 800-1000 kPa) feed stream inside and low pressure (nearly atmospheric) permeate outside the tube. A compact module composed of many individual fibers is fed biogas. The outlet methane content is controlled via the retentate gas pressure by a proportional valve at the retentate outlet [242]. In liquid membrane systems, a liquid absorbs the CO_2 after it has permeated the membrane. This technology integrates absorption and membrane processes and can be a competitive alternative technology [249]. High selectivity of membranes, appropriate pressure, and recirculation are required to achieve both high CH_4 recovery and high CH_4 levels in the product [247] [250]. The off-gas usually also contains CH_4 and should be burned to avoid emissions.

The cryogenic separation process removes CO_2 by cooling and compressing the mixture based on the difference in boiling points at ambient pressure for CH_4 (-160°C) and CO_2 (-78 °C). It is a developing technology with few commercial applications, but is gaining more attention due to increasing production of liquefied natural gas (LNG), as it can potentially remove impurities and liquefy the CH_4 simultaneously [235] [249] [95].

6.6 Utilization Options

One common end use for LFG is its release to the atmosphere with severe consequences. Many closed landfills in developed countries and most fills in undeveloped countries simply allow gas to escape to the atmosphere. This is due to a lack of collection equipment availability, financial infeasibility for collection, or the inability of collected gas to sustain combustion.

Another exercised option is to flare the gas: combust without energy recovery. The decision to use depends on a combination of factors- a site may be too small to support energy infrastructure, or more acceptable options discussed in the following section are not feasible for a variety of technical and logistic reasons. The USEPA requires landfills that emit a certain amount of NMOCs to control those emissions to the atmosphere, and flaring is generally assessed to destroy 97% or more of NMOC and CH_4. Flaring is a simple and relatively maintenance free technology [172]. In some instances the waste heat can be used for beneficial purposes. One is to evaporate or condense landfill leachate [163]. This way, two environmental hazards are concurrently addressed. A number of landfill sites in the US supplement LFG with natural gas in order to combust collected gas (for odor control or due to regulatory requirements) if gas concentrations are too low ($<20\%$ CH_4) to support good combustion.

IEA [163] identified the major barriers to LFG use. They are as insufficient capital, insufficient awareness of technical options among operators and policy makers who could foster projects, and difficulty establishing utility (electrical and gas) interconnections.

Final applications for purified and upgraded biogas (“biomethane”) are those for natural gas. It can be used to produce electricity, combined heat and power (CHP), injected into the natural gas grid, compressed to be vehicle fuel (CNG), processed to other oxygenated fuels, and used to synthesize general and specialty chemicals. Preferred end uses are generally a function of economics, which depends on regulatory support and hindrances, on the availability of utility infrastructures, willingness of potential users to enter into contracts, etc. On-site gas-fired power generation is still the dominant LFG end use due to its simplicity, and the ability of engines to utilize gas of lower quality [251] [221]. On the other hand, a comprehensive (technical/economic/environmental) analysis of different biogas utilization scenarios in Ireland found that producing fuel with concurrent electricity generation with the process waste heat was the best option [252]. In Italy, a study of GHG reductions associated with various options determined that reforming and conversion in to an alternative fuel had the best result, though the use in molten carbonate fuel cell is most energy efficient [253]. For the US, a cost analysis found that pipeline gas use was always a more profitable option than on-site electricity production, using averaged costs; the report noted specific site factors make the general case too simplistic for more than general guidance [254]. Availability of grid connections for either electricity or gas, the ability of biogas to be compressed and stored, site space restrictions for processing equipment or storage vessels all affect end-use considerations [94], as well as managerial decisions regarding end-use preferences. Other important issues include forecasts of gas production to determine investment risks, settlement of waste that can compromise piping systems, and the need to management condensate that is generated as gases emerging from the hot landfill (60 °C, typically) into ambient environmental conditions [222].

6.6.1 Electricity production

The simplest end use for LFG is to produce electricity. The first such plant in the U.S. was installed in California in 1975 [101]. There were nearly 1000 applications of various LFGTE projects by 2001 (Table 14) [224]. Many other projects have begun since then but there is not a good census of projects. In most places, the number of projects has increased since the mid-2000s: tripling in the U.K. and China, more than doubling in Germany, increasing by two-thirds in the US; the number of plants fell slightly in Sweden, though the reason is no clear. It is difficult to accurately count projects: the LMOP website [255] has a data base that lists ~ 850 operational projects (excluding "self-sponsored" projects), but LMOP reports only 645 LFGTE projects.

Table 14 LFGTE plants in select countries and worldwide

Country	1992 [171]	1995 [107]	2001 [224]	2003 [101]	2004 [98]	2007 [251]	2008	2009 [251]	2010 [251]	2011 [251]	2012 [251]	2013 [222]	2015
US	114	~100	325	350	380							621	645 [255]
Germany			150	180									400 [256]
UK			135	150									442 [257]
The Netherlands			60										
Sweden			70										60 [258]
Italy			40	135									
Canada			25										
Australia			25										
China						15	19 [251] 20 [126]	25	35	46	50		
Worldwide		>400	955	1100									

The most common technology for power generation is an internal combustion engine, sized from 100 kW to 3 MW in the US [222], with production efficiencies of up to 43%, although 30%-40% is more common [259]. Such engines are the cheapest to obtain and operate, are relatively mobile, but have the most emissions, and so can be difficult to permit [223] [222]; they also require relatively frequent overhauls [88]. Smaller systems (<500 kW) became feasible in the US with spiking fuel prices ~2011, although typically small systems have used microturbines [260].

Other options that are used include gas turbine, organic rankine cycle, stirling cycle engine, molten carbonate fuel cell, and solid oxide fuel cell. Larger plants (> 800 kW) tend to use gas turbines [250], which in the US have been sized from 800kW to 10.5 MW [222]. Gas turbines require high pressure gases and so usually need a compressor. At smaller sites, micro-turbines are becoming favored; in the US, installations range from 30 kW to 250 kW [222]. These tend to be simple with few moving parts and so require less maintenance. Efficiency is less, partly because compressors are parasitic loads [88]. Microturbines have been configured not only to use smaller amounts of gas, but gas with lower energy density [261]. The largest turbine project is a 50 MW plant that uses a steam turbine [101]. Stirling engines were developed in the 19th Century, but gasoline and diesel engines were favored over them. Because they work well with fuels with high heat capacity and have external combustion, contaminants do not harm engine parts, they are gaining attention as alternate means of using LFG. Molten carbonate and solid oxide fuel cells have high capital cost; solid oxides require very high operating temperatures (800-1000 ºC), increasing operating costs, and molten carbonate fuel cells are still a developing technology [223]. Solid oxide fuel cells have high conversion efficiencies, but the needed catalysts are sensitive to impurities; this requires gas upgrading, an add-on cost [250]. Electricity pricing also tends to be more stable than other uses, which can make it more attractive, especially if financing is required [262].

An upgrade from simple electricity production is CHP. Waste heat from the electricity production stage can be captured and used to create steam or hot water though its use is restricted to local use [259], though the overall energy efficiency can approach 85% [95].

6.6.2 Natural gas grid

A recent trend has been for governments to provide subsidies to promote biogas upgrading for pipeline injection to avoid wasting energy, such as heat produced by engines, that produce electricity [243]. By injecting biogas directly into the grid, the gas can be transferred to a location where it has a higher value than it does locally. In most regions, there is greater need for gas than there is local production, so there is steady demand for fuels and grid injection [247]. Early adopters of LFG for the natural gas grid include The Netherlands, Sweden, Germany, and Switzerland [250]. Nine EU countries inject biomethane into the natural gas grid [95]. The grid use can be fostered if access is supported by regulations [250]. In order to be accepted into the gas grid, the biogas must meet set limits for sulfur, O_2, particulates, CO_2, water dew point, and, of course CH_4 content [247]. The injected gas must be odorized (to detect leaks), typically with tetrahydrothiophene (THT) or mercaptans [263] to meet the safety guidelines.

6.6.3 CNG vehicles

If LFG meets gas grid standards, it can be compressed and used as a vehicle fuel. Vehicles that can use CNG include buses, trucks of various kinds including waste collection trucks, and even passenger cars [247]. By 2011, over 1 million vehicles used natural gas in Europe, with over 2,800 refueling stations. Italy ranked one in CNG vehicles while Germany had most CNG refueling stations. However, in absolute terms, the numbers represented less than 0.5% cars and trucks, and only about 1% of buses in Europe [95]. As of 2013, there were over 100,000 CNG-powered vehicles in the US [260].

6.6.4 Renewable liquid fuels

Though electricity production dominates LFG use worldwide, it can be transformed into liquid fuels for transportation [247]. One of the advantages of liquid fuels end-product is the avoidance of the forced use of LFG after its extraction, i.e., through convenient storage as a fuel to be used or marketed with a degree of choice to meet the projected needs and not to respond to the availability of the gas.

All methods to convert LFG to liquid fuels go through the synthesis gas (CO and H_2) step. There are four principal technologies to generate synthesis gas from LFG. These are: (1)

steam reforming; (2) dry (CO_2) reforming; (3) partial oxidation; and (4) autothermal reforming [275], though steam and autothermal reforming have been the dominant processing paths [264].

6.6.4.1 Synthesis gas production technologies

The main unit for steam-reforming is the primary reformer, which consists of approximately 10 m long narrow tubes situated in an oven, loaded with catalyst [265]. Steam reforming produces the highest proportion of H_2 with the least amount of CO, but is highly endothermic requiring extensive heat transfer equipment and longer start-up times [266].

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2} \qquad \text{(Eq. 23)}$$

The ratio of synthesis gas constituents (H_2, CO, CO_2, and CH_4) depends on reaction conditions such as temperature and pressure, the feedstock used, reactor characteristics and residence time to reach the equilibrium state [266]. Elevated temperatures favor the forward reaction in Equation 23, and removing products from the reactor can maintain the driving force for the reaction. Some effective removal strategies are H_2 removal by membrane, CO by absorbent, but this is often not economic [267].

Catalysts, based on nickel with supporting materials and promoters, have been used since the 1960s to achieve higher feed conversion and less carbon deposition [266]. Problems associated with nickel catalysts under high temperature and pressure include declining activity, sulfur poisoning, carbon deposition (coking) and sintering [265]. Coking is caused by CH_4 decomposition to solid carbon and H_2 or the Boudouard reaction in which CO disproportionates to carbon and CO_2 [268]. An adiabatic pre-reformer upstream of the primary reformer can reduce the risks of sulfur poisoning and carbon deposition [265], and effective biogas cleanup also reduces risks of sulfur poisoning. Research targets as alternative catalysts include zinc, activated carbon, aluminum, and cerium, which may increase selectivity, stability and activity [267].

Dry reforming [269] can remove both CO_2 and CH_4 from gas streams simultaneously. Dry reforming is also a strongly endothermic reaction and requires operating temperatures of 800–1000 °C to attain high equilibrium conversion of CH_4 and CO_2 to H_2 and CO, and to minimize the thermodynamic driving force for carbon deposition. It produces syngas with a lower H_2/CO ratio than steam reforming. With lower H/C ratios, there is a greater potential for carbon formation, generally the most significant mechanism of catalyst deactivation in dry reforming [266] [268] [270].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \text{(Eq. 24)}$$

Dry reforming works best when the best inflow ratio of CH_4/CO_2 is 1:1. Landfill gas and most AD gases also have approximately equal CH_4 to CO_2 ratios, thus underscoring the feasibility of dry reforming for these gas streams.

Nickel-based catalysts work best in dry reforming [271]. Noble metals like Pt, Rh and Ru are highly active and resistant to carbon formation due to lower operating temperatures. Small amounts of noble metals help in terms of activity, suppression of Ni oxidation, carbon formation, self-activation, and sustainability in the daily startup and shutdown operations [268] [272]. Another effective way of resisting deactivation by carbon formation is to increase pH, which helps activate mildly acidic CO_2 and assists in oxidation of surface carbon [273].

Partial oxidation needs nearly pure oxygen to hinder side reactions between nitrogen and other components [274]:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \text{(Eq. 25)}$$

The reaction is slightly exothermic. Catalytic partial oxidation circumvents the coking problem, and has a greater selectivity to syngas production, but requires the separation of oxygen from air and potential risks of explosion [275].

Autothermal reforming combines endothermic steam reforming with exothermic partial oxidation reactions, separating total oxidation and reforming [276]. A water-gas-shift (WGS) reaction is used to adjust the H_2/CO ratio for the following synthesis:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(Eq. 26)}$$

The WGS and steam reforming are major reactions used for H_2 production. In steam reforming, the WGS reaction departs from its equilibrium position (CO-rich), especially at low methane conversion rates [266].

6.4.4.2 Synthesis gas to liquid fuels

Synthesis of hydrocarbons. Synthesis gas, produced from any one of the methods described in section 6.4.4.1, can be catalytically converted to renewable liquid fuels. Though synthesis gas produced from reforming is ideal to produce the ultimate gaseous carbon-free fuel, H_2, the focus of this section is liquid fuels [267]. The produced synthesis gas can be converted to liquid fuels and chemicals, specifically, drop-in replacement hydrocarbons (diesel, gasoline, jet fuel), methanol, and dimethyl ether (DME) [275] [264] [276] [277].

The Fischer-Tropsch (F-T) synthesis route is long commercially practiced process in which synthesis gas is converted to hydrocarbon liquids over iron (Fe) or cobalt (Co) based catalysts at temperatures and pressures of 200-350°C and up to 1500 kPa [278] [279]. The hydrocarbons, produced via the F-T route, are superior than conventional gasoline and diesel, since these are free of sulfur and aromatics [280]. In terms of mechanism, the F-T reaction is akin to polymerization, and goes through a set reaction sequence: adsorption, chain initiation, propagation and chain growth termination. The overall F-T route to hydrocarbons are represented in equations 27 and 28.

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad \text{(Eq. 27)}$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \qquad \text{(Eq. 28)}$$

The F-T reaction is accompanied by the WGS reaction. Side reactions include production of oxygenates, carbide formation, and Boudouard reaction, the latter two negatively affects catalyst activity over time. Both Co and Fe catalysts are very effective to yield high per pass conversion (up to 90%) of synthesis gas. However, the reaction is constrained in two ways: 1) the gaseous product is high in CO_2 indicating wasted carbon and 2) the overall product slate contains a mixture of hydrocarbons that requires further upgrading to yield gasoline, diesel, jet fuel and waxes and affects process economics. Promoters such as alkali metals and supports to anchor Fe or Co catalysts are added to enhance performance [281].

The F-T processes can be classified either by operating temperature (high temperature F-T, 300-350 °C, low temperature F-T 200-240 °C) or reactor type (fixed-bed F-T, slurry bubble column F-T, or circulating fluidized bed F-T). Circulating fluidized bed is mostly applied for high temperature F-T using Fe catalyst, while fixed-bed and slurry bubble column are usually used for low temperature F-T using both Fe- and Co-based catalysts to produce long chain hydrocarbons [281].

The overall F-T processing scheme consists of reactors, recycling and compression of unconverted syngas, removal of H_2 and CO_2, reforming of produced CH_4, and separation of products [279]. Since the reactions are exothermic, process heat capture can be utilized to produce electricity to offset process cost. High molecular weight hydrocarbon products can be cracked to obtain liquid fuel in the C6 - C18 range [282].

Synthesis of Oxygenates. Conversion of synthesis gas to oxygenates such as methanol (methyl alcohol), dimethyl ether (DME) and higher alcohols (typically C1-C6) is another route to synthesis gas utilization. This class of products is gaining interest due to their clean burning properties. Methanol, a common solvent, is a versatile feedstock for production of formaldehyde, ethylene, propylene and fuels such as DME. Methanol synthesis is well developed since 1960s' when a lower pressure process (less than 10,000 kPa) based on commercial $Cu/ZnO/Al_2O_3$ catalyst was introduced [275]. Other oxides such as ZnO/Cr_2O_3, V_2O_5, V_2O_3, and ThO_2, are also effective supports or promoters of Cu-based low-pressure methanol synthesis catalysts [283]. As for methanol, the reaction:

$$2H_2 + CO \rightarrow CH_3OH \qquad \text{(Eq. 29)}$$

is exothermic and is carried out in two-phase reactors with synthesis gas and products in the vapor phase and the catalyst in the solid phase. Optimal reaction temperatures are limited by the inherent low heat capacity of vapor and large reaction heat. A liquid-phase methanol synthesis process based on CO_2 hydrogenation reaction and the forward WGS reaction was first developed by Chem Systems in the late 1970s [284].

DME (CH_3OCH_3) is a volatile organic compound (VOC) but is considered environmentally benign when used as a fuel. Because it has very low particulate emissions when combusted and contains no sulfur compounds, it is viewed as a potential fuel for the 21st century [276] [285], and can be used as an efficient H_2 carrier for fuel cells and other applications [286]. It has physical properties that are similar to liquefied natural gas (LNG), and so DME could use the existing land-based and ocean-based LNG infrastructure with minor modification, which decreases investment requirements for its transportation and storage [276]. The first presentation of neat DME as a diesel fuel appeared in 1995. Compared with traditional diesel, DME fueled engines generate less noise, and emit fewer pollutants (particulates, NO_x, hydrocarbons, and CO). However, it has a lower energy density than diesel, so a double-sized tank is needed to maintain similar travel range [287]. DME engines have certain special requirements: a vapor pressure of 510 kPa at 25°C, low viscosity and lubricity, with compressibility rising near full load conditions. These require improved seals and the lubrication, issues that are not as significant in stationary engine applications [288].

DME is usually produced in a two-step process: syngas to methanol, and methanol dehydration to dimethyl ether [276]. This is a mature technology, commercialized by companies like Haldor Topsøe A/S, Toyo Engineering Ltd., Air Liquide, S.A. and JFE Holding Inc. [289].

The reaction for methanol dehydration is:

$$\mathrm{2CH_3OH \rightarrow CH_3OCH_3 + H_2O} \quad \text{(Eq. 30)}$$

The reverse WGS accompanies this reaction. The yields of CO by reverse WGS reaction should be kept to a minimum to maximize productivity [286].

The conversion of syngas to methanol and to DME in the same reactor frees the process from the thermodynamic equilibrium constraint of methanol synthesis alone. The best syngas composition for methanol synthesis is a H_2/CO ratio of 2:1, but methanol dehydration should be CO-rich. In a single reactor, synergy can be obtained among methanol synthesis, methanol dehydration, and WGS. By recycling methanol and water along with the unconverted syngas, the overall reaction can be achieved as follows:

$$\mathrm{3H_2 + 3CO \rightarrow CH_3OCH_3 + CO_2} \quad \text{(Eq. 31)}$$

The productivity and material utilization in a one-step syngas-to-DME reactor with recycle depends strongly on the feed gas composition [277]. This reaction has low carbon utilization, due to one-third of the carbon in the syngas lost to CO_2.

The one-step reactor requires a bifunctional hybrid DME synthesis catalyst, consisting of a methanol synthesis catalyst (such as CuO–ZnO, CuO–ZnO–Al_2O_3, CuO–ZnO–CrO_3, or CuO–TiO_2–ZrO_2)), and a methanol dehydration catalyst (such as γ-Alumina and ZSM-5 zeolite). Preventing the aggregation of Cu active sites and preserving catalyst structure are key factors to obtain higher activity and DME selectivity with hybrid catalysts [286].

Higher Alcohol Synthesis (HAS), is another option to utilize synthesis gas. The use of high octane higher alcohols or mixed alcohols (C_1–C_4 alcohols) as a fuel or fuel-additive continues to attract attention [290] [291] [292] [293]. In early twentieth century, non-selective

ZnO/Cr_2O_3 catalysts promoted by alkali were used for higher alcohol synthesis, producing large amounts of hydrocarbons. In 1980s, much more active and selective Cu/ZnO catalysts promoted by heavy alkali were developed [293]. The alkali-promoted transition metal sulfide catalysts, particularly disulfide molybdenum (MoS_2), have been extensively studied, but are associated with low space–time–yield and poor selectivity at high temperatures where these catalysts are active [290] [292]. Studies continue to increase productivity and selectivity to match those needed for commercial operation [290] [292] [294].

So far, this section briefly described pathways to utilize purified landfill gas for renewable electricity and fuels production. However, the challenge is "economy of scale" and all known routes, F-T., Methanol, HAS, DME, discussed herein, face formidable challenge for implementation when LFG is considered as feedstocks at available scales (less than 300 cubic meters). The challenge to use small gas sources has spawned new niche industry, namely mini-gas-to-liquids (GTL) plants. The World Bank Group has been actively sponsoring studies in this area but with a focus on flared gas that normally mirrors LFG range. It is interesting to note that 400 cubic meter natural gas is annually flared during oil and gas operations- this gas is equivalent to 750 billion kWhr or 500 million barrels per year of oil with a value of $35 billion. A recent report provides a comprehensive review of upcoming mini-GTL projects [295); these technologies could be considered for implementation at select landfill sites.

7. Policy considerations associated with landfill gas use

Shindell et al. [296] screened over 400 existing pollution control measures to determine potential worldwide emissions reductions of particulate and gaseous species, and selected measures that reduced climate change and improved human health. The CH_4 mitigation measures have large climate change impacts, greater than controls on black carbon emissions, but little effect on human health. They note that many other policies can reduce CH_4 emissions other than those selected by their criteria, and that CH_4 reductions provide strong short-term mitigation of climate change, but much have much smaller effects on long-term climate change (which is controlled more by CO_2 releases). van der Berg et al. [297] appeared to agree on CH_4 abatements' greater short-term impact (compared to CO_2), as their analysis of changes in IPCC GWP factors showed 25 year horizon computations had greater relative benefits for CH_4 emission controls compared to CO_2 mitigation, but a 500 yr horizon showed more benefits accruing to CO_2 control.

In the last decade, new sources of natural gas have been exploited with the availability of fracking technologies. A comparison of five different models of demand effects, assuming estimates of extractable reservoirs are accurate, found that increased use of natural gas had no discernable impact of overall CO_2 (and CO_2e) releases through 2050. Gas will replace coal for electricity production, but was forecast to have little to no impact on transportation. The effect is seen because natural gas will also displace demand for renewable energy sources, and abundant gas will accelerate the global economy [82]. The impact could be negative if assessments that find fracking cause more CO_2 releases than it prevents are accurate [20]. Still, because of the short atmospheric residence time for CH_4 (especially relative to CO_2), many assessments assert that changes in fugitive CH_4 quantities can have more immediate effects than other GHG reductions [59].

If there is a technology change, and CH_4 is used to replace other GHG-releasing technologies -- for instance, to power vehicles -- the impact may be negative at first before benefits over current conditions are realized. This is due to increases in leakage from the natural gas pipeline network, so that radiative forcing would be increased for 80 years (replacing gasoline vehicles) or 280 years (replacing diesel vehicles) before the greater efficiency of natural gas use leading to lower CO_2 emissions would offset the short-term impact of greater CH_4 releases [86].

Murray et al. [254] point out that increasing end uses and the potential to continue increasing gas supplies through fracking or other technological changes makes accurate price predictions difficult. Good understanding of future markets for recovered gas is important to make sound decisions regarding technology choices and end markets. Higher air pollution control requirements make natural gas a much better choice than other fossil fuels, due to greater efficiencies, lower particulate generation, and generally lower acid gas formation rates, and could also boost demand.

Emissions allowances and carbon trading have been identified as a means of monetizing GHG reductions. These markets have not had great success to date. California has had an emission trading program, with prices varying from \$10-\$16 T^{-1} CO_2e, but towards the lower end of that range as of 2013; the floor price is \$10 T^{-1} CO_2e. In the EU, prices reached \$40 T^{-1} CO_2e in 2008, but the market collapsed with a drop in demand due to the global recession, and did not recover [254].

Given difficulties in assessing current landfill emissions of CH_4 with great accuracy, it is perhaps more difficult to create a credible forecast of future releases. One estimate suggests they will double by 2030. This estimate used forecasts of energy consumption to estimate MSW generation (assuming energy use is a proxy for materials use and general economic activity), and, based on trends from the early 2000s, estimated the amounts of waste that might be diverted from landfilling by recycling and waste-to-energy incineration, and also tried to forecast the future capture of CH_4 at landfills [99]. The forecast is obviously speculative.

A British cost-benefit analysis found that the greatest impact on national LFG release rates comes from capping and installing gas control system at the largest CH_4 sources. Depth of waste rather than landfill surface area is a better indicator of CH_4 production capability. Installing a flare cost only 10% the cost of a cap, and for most small sites a cap was not cost-effective considering the potential reduction in CH_4 emissions, and that the UK could meet its short-term CH_4 reduction goals without controlling gas from these sites [169]. In addition, some have called landfill gas control "technically difficult and costly" [189]. However, there can be synergies when LFGTE projects are considered. One Thailand landfill forecast capturing only 10% of generated gas through a collection system, but displacing fossil fuel electricity by LFG electricity increased the value of captured gas four times, to the equivalent of achieving a 40% capture rate [298].

Currently there is no means to account for "social" costs associated with GHG emissions in general, and LFG impacts in particular. Jaramillo and Matthews [299] assessed effects such as offsets to primary air pollutants and determined there could be substantial benefits, if these could be monetized. In addition, many risk assessments of pollution decreases find that human health benefits are often substantial, and these considerations are included in risk-benefit assessments of proposed regulations (e.g., [300]); but that is not monetizing them for the benefit of project developers.

The sum effect of these and similar reports appear to make the twin goals of greater exploitation of renewable sources of CH_4 and reductions in easily stopped fugitive CH_4 necessary. van Foreest [95] forecast slow increases in biomethane production in Europe, but thought it could comprise as much as 10-20% of current natural gas use there, potentially by 2030. And economic analyses by the Global Methane Initiative [301] find that landfill emission reductions of 30% are feasible and relatively affordable, and reductions as great as 72% are achievable with current technologies and represent the most economical fugitive gas reductions available.

However, for India, IEA [130] assumes that because so much waste is food waste which rapidly decays, that only the largest landfills will be able to support gas projects. The small waste generation rate generally reported for India means that only the ten largest cities can support landfills of an appropriate size. However, it is not clear that anything approaching accurate waste generation data are collected in India, or that food waste necessarily decays as swiftly in India landfills as is assumed by IEA. In addition, growing affluence is likely to alter waste generation patterns in India. Thus, it is difficult to place great reliance on broad assessments of what should probably be local, situational analyses.

If gas collection and control are not to be utilized for any reason, Huber-Humer et al. [215] recommend that various bio-engineered structures be installed on landfills. These promote the growth of methanotropes and therefore minimize CH_4 emissions. In developing countries and for old landfills, degasification is often too costly to consider [189]. Another control is to limit the input of organic material, through organic material landfilling bans [154] [302], or, as in the

EU, requiring treatment to make carbon-containing compounds less labile (see below). India, for instance, banned organic matter from landfills in 2000, with the intention of reducing fugitive CH_4. This would have required a major restructuring of India's somewhat undeveloped waste management system. No significant support was provided to implement the ban and required changes, and so no noticeable effect was seen in waste management practices [163].

Brandt et al. [62] note that the imprecision and inaccuracy of CH_4 assessments mean that policies targeting certain sectors or sources for overall GHG reduction, economical, or efficiency reasons may be flawed, as the basis for the prescription is unlikely to be well described. Note that the range of credible landfill CH_4 emissions collected by Huber-Humer et al. [215] was 35 Tg yr^{-1} to 70 Tg yr^{-1} (the widest we were able to find). These uncertainties concerning the scope of the problem suggest that better activities addressing fugitive CH_4 will be able to stand on their own rights – that while understanding the context and intended larger impact of actions is important to set broad goals, particular projects should be set in the realities of local economics, needs, and purposes.

IEA [163] identifies a lack of capital, ignorance of opportunities by decision-makers, and some technical issues, such as interconnections to utilities, as being the primary barriers to LFG projects worldwide. Capital shortcomings can be partially addressed through financial policies, such as feed-in tariffs, tax incentives and relief, power purchase requirements and incentives that reduce costs or enhance revenues for site operators. Interconnection issues can be addressed through policies that require renewable energy connections, or that may standardize regulations that may favor one provider over another. Net metering at one site or across an owner's multiple sites can provide fiscal relief, too. And government direction and education can foster behaviors by providing information that is useful and pertinent to potential project developers. This can include sponsoring demonstration projects.

For those purposes, we now review existing government policies that address reductions in landfill gas emissions, and support the use of captured gas in the US and China, and also discuss other notable initiatives from the EU.

7.1 US Policies

Methane emissions in the United States have declined by 11% since 1990. However without further action, these levels are estimated to increase to ~25 Tg yr^{-1} by 2030 [303].

The Obama administration announced intent to reduce CH_4 emissions in its 2014 "Climate Action Plan." As part of the implementation of the plan, USEPA proposed in August 2015 to reduce oil and gas sector CH_4 emissions 40-45% by 2025 (from 2012 levels). The plan focuses on leaks, and to reduce and capture gas along the production pathway at pumps and pipelines and at closed facilities. The gas and oil sector plan is to be coupled with existing, voluntary programs: the Methane Challenge Program, the Coalbed Methane Outreach Program (CMOP), the AgSTAR Program, and the Landfill Methane Outreach Program (LMOP). The Methane Challenge program is part of "Natural Gas Star," which encourages, supports, and recognizes companies that are making ambitious improvements in reducing methane emissions. CMOP was formed to address barriers to using coal mine CH_4 (to reduce releases to the atmosphere). The AgSTAR Program in 2014 combined US Department of Agriculture, USEPA, and US Department of Energy efforts to produce a "Biogas Opportunities Roadmap." This outlined government support for research, investments, markets, and communication for the biogas industry, with a focus to reduce methane emissions from the agricultural sector while increasing energy independence, and to supply biogas projects with feedstocks [303].

In 1991, USEPA proposed emissions guidelines for existing landfills and New Source Performance Standards for new landfills under its authority granted under the Clean Air Act. The regulations were promulgated in 1996, and affected sites that released 50 Mg yr^{-1} of NMOC. LFG is the carrier medium for the NMOCs to the atmosphere; NMOC are regulated under the Clean Air Act, but LFG itself is not. However, because LFG control leads to NMOC control, LFG became the target of the regulation. Affected landfills included all sites with capacity of 2.5 million Mg or 2.5 million m^3, and sites under that capacity that modeled emissions of NMOC above the 50 Mg yr^{-1} standard. The regulation required gas collection systems and reduction of NMOC by 98%. Combustion of LFG was the means to meet the standard; sale of gas into pipelines or for other purposes was allowed, as long as gas clean-up did not release NMOC to the atmosphere. Gas had to be collected from active cells within five years of waste placement and from all closed cells [142]. In 2000, USEPA proposed National Emission Standards for Hazardous Air Pollutants (NESHAP) for MSW landfills (65 FR 66672). The rule was finalized in 2003 (66 FR 2227). The rule added monitoring and reporting requirements, and modified regulations regarding process upsets and for bioreactor landfills. It required the emission control devices to be governed by “MACT” – maximum available control technology. This means the landfill emission controls must be as good as if not better than the devices that obtained the highest control of relevant air pollutants. In 2015, USEPA proposed amendments to these rules, which primarily focused on including smaller sites under the rules by dropping the limit of NMOC to 34 Mg yr^{-1}. The new rule also called for increased (quarterly) surface monitoring. Closed landfills that do not produce much CH_4 would be exempted from the requirement to control gas emissions [304].

The US Greenhouse Gas Reporting rule, created in response to requests by IPCC, was set in place in 2009 (Final Rule 74 FR 56260). It required landfills emitting 25,000 T CO2e yr^{-1} to report data annually to USEPA, that affected 1,200 landfills in the US [121].

The US Renewable Fuel Standard (authorized in 2005 and expanded in 2007) requires over 100 billion L of renewable fuels by 2022; biogas from landfills qualifies as cellulosic biofuel (RIN D-code 3 if used as CNG, RIN D-code 7 if converted to a biodiesel) [305]. Renewable fuels, under the standard, must create fewer GHGs as measured by a Life Cycle Analysis (at least 20% less, generally, but more for certain applications). Biodiesel counts 50% more than ethanol and CNG (eCFR Title 40, Chapter I, Subchapter C Part 80 Subpart M). This rule creates a large impetus for LFG-to-fuel conversions [260].

In 2008, the Energy Improvement Act gave public entities (mostly local governments) the ability to issue tax credits in place of paying interest as a financing mechanism for renewable energy projects, including LFG projects. This program was expanded in the American Recovery and Reinvestment Act (2009) [306]. The Renewable Energy Production Incentive is a pricing incentive offered since 1992. It is currently \$0.009 $kWhr^{-1}$ [307]. Various states offer their own production incentives [223].

In 1994, USEPA created the Landfill Methane Outreach Program (LMOP) to expand use of LFG. LMOP not only promotes projects, but assists site managers in complying with US regulations, as they are developed and revised [299]. A total of 580 LFGTE projects have been established in the last 18 years with the assistance of LMOP; the total CH_4 emission reduction is estimated at 8.6 Tg [303]. In 2015, USEPA released proposals to further reduce landfill CH_4 emissions by 440,000 T yr^{-1} by 2025 [304]. LMOP has expanded its program beyond US borders through the Methane to Markets Partnership in 2004 (the Global Methane Initiative). Partly this is a technology transfer activity, promoting US consultants and technology providers, and creating greater energy security and economic growth in the partnership countries, but it is also an effort by the US to create global awareness of the potential to reduce landfilling impacts on the environment [299].

The Global Methane Initiative is a voluntary consortium of 43 countries. Each member is requested to prepare an action plan. Contents of the Action Plan are suggested to be items such as a CH_4 inventory, objectives and planned initiatives, participants in CH_4 generation and abatement, plans to promote reductions, and challenges to achieving any reductions [308]. Table 15 lists participation in some major elements of the MSW portion of the initiative. Projects, which can range from specific machinery at landfill sites to whole landfill gas projects, are listed in a database, which provides inconsistent details regarding the site and the activities, and also links to any project reports. An interactive map is also available for each country, and these maps often show more projects than listed on the data base. The map supports a link to the data base, even if the direct search of the data base disclosed no available information.

Table 15. Global Methane Initiative [301]

	MSW Action Plan	Last Update	LFG Projects (GMI projects)	LFG Projects on Map
Albania				
Argentina	X	2013	14 (7)	X
Australia	X	2006		
Brazil	X	2011	34 (7)	X
Bulgaria		2014	1 (1)	X
Canada		2013		X
Chile		2014	17 (8)	X
China	X	2012	30 (7)	X
Columbia		2013	7 (3)	X
Dominican Republic			2	X
Ecuador		2008	2 (1)	X
Ethiopia		2013		X
European Commission				
Finland		2014		
Georgia			3	X
Germany		2013		
Ghana				X
India			1 (1)	X
Indonesia		2012	3 (2)	X
Italy	X	2005		
Japan	X	2013		
Jordan				X
Kazakhstan			1 (1)	X
Mexico		2014	28 (6)	X
Mongolia				
Nicaragua				X
Nigeria				X
Norway				
Pakistan		2013		
Peru		2012	3 (1)	X
Philippines		2013	3 (2)	X
Poland		2013	10	X
Russia			1 (1)	X
Saudi Arabia				
Serbia			1 (1)	X
South Korea		2006	5 (3)	X
Sri Lanka		2012		X
Thailand			4 (3)	
Turkey			11 (6)	X
Ukraine		2006	8 (7)	X
United Kingdom	X	2006		
United States	X	2014		
Vietnam			3 (1)	X

The IEA [163] attributes the growth of LFG projects in the US to the continuing expansion of the "Landfill Rule." However, the energy opportunity afforded by LFG also has been an important factor.

Individual state policies can be important, such as including LFG use in Renewable Portfolio Standards or renewable Portfolio Goals, and providing loans, incentives, and tax credits [163]. A number of states have established restrictions on inputs to landfills. Yard wastes are mostly commonly banned, but other states are restricting food waste landfilling. Many of these programs are not explicitly designed to reduce CH_4 releases, but rather seek to promote composting and generally increase diversion-recycling rates [302].

7.2 China Policies

China now accounts for 28% of the annual global CO_2 emissions and deserves special attention. The development of heavy industry created environmental problems in China in the 1950s, and social and political instabilities during the Cultural Revolution (1966-1976) exacerbated these issues. Economic reforms that began in the mid-1970s resulted in very fast development and urbanization, creating new kinds of environmental impacts. Laws and regulations to protect the environment were adopted beginning in 1973, and in 1983 environmental protection was identified as a state "fundamental policy." Most regulations in the 1980s were traditional "end-of-pipe" restrictions on pollutant releases. In the 1990s, programs adopted a more flexible approach, based on sustainability principles. In 2005, the major law relating to solid waste management was adopted, as was a major piece of legislation targeting renewable energy [124].

China is a member of the Global Methane Initiative, and as such has been involved in its policy exploration and technical guidance that seek to reduce fugitive CH_4 and increase beneficial use of available CH_4 [123].

China has continued to target CH_4 emissions in the 12th five year plan (2011-2015), primarily through increased research on and utilization of coal bed and coal mine CH_4. Under the policy, China aims to capture an additional 1 trillion m^3 of coal-based CH_4 between 2012-2015, potentially reducing overall GHG emissions by 990 MT CO_2e during the planning period by reducing coal use and capturing and utilizing coal bed CH_4. The plan does recognize that LFGTE projects in western areas should be promoted [251].

A success story to emulate is coal mine emissions. No coal CH_4 was captured prior to the 1990s; currently, China has nearly half of the world's coal mine CH_4 recovery projects, with more than 25% of captured gas being used for electricity production. These projects were strongly supported with assistance from USEPA and the UN, and fostered China participation in the Global Methane Initiative [80] [123].

In 2005, the People's Congress passed the "Renewable Energy Law of the People's Republic of China" (effective in 2006). It stressed the development of wind and solar projects. It was amended in 2009. The law mandates purchase of waste-to-energy electricity by utilities, and funds projects both through the national budget but also through fees destined to be allocated to utilities to cover costs associated with grid connection and other costs of renewable power sources. In 2013, the State grid issued a formal statement recognizing the necessity of incorporating waste-to-energy electricity into the grid [251].

In 2011, the State Council passed the "Opinions on Further Strengthening the Work of MSW Disposal." This requires urban centers to use "safe" facilities (see just below) to manage 80% of wastes by 2015 (with the goal being to approach 100%). "Resource utilization" (recycling and energy recovery) should be 30% by 2015, with a goal of 50%. The 2011 5-year Plan for Environmental Protection also identifies benefits from LFGTE [251].

Federal laws establish principles of management and pollution control. States set standards for pollutant control. Waste management implementation is a function of local government. Disposal sites, collection programs, scope of recycling -- all are determined by and funded by local governments [124].

Because of rapid urbanization and growing affluence, China is experiencing an explosion in the amount of managed MSW. One account is it grew from 31 MT in 1980 to 180 MT in 2011, and could more than double to 480 MT by 2030. The World Bank determined China was the world's largest generator of MSW in 2003 [106]. Additionally, China is facing an energy problem; sufficient coal exists to meet energy needs, but coal has high GHG impacts. Alternative energy sources are therefore attractive, and MSW offers several ways to generate energy. These are primarily waste-to-energy incineration, and LFGTE [251].

Landfills are the primary means of waste disposal in China. Less than 2% of MSW may have been landfilled before 1990, with the remainder going to dumps; urban management rates approached 65% by 1999 with 700 disposal facilities, 200 of them "harmless" treatment plants. The number of "safe" facilities (sanitary landfills, compost sites, and approved incinerators) reached 677 by 2011, accounting for 80% of urban MSW. However, composting is falling out of favor, perceived of as being expensive, difficult to conduct well, and producing a low value product in that soil amendments have much less utility than fertilizers, and the MSW compost is often physically contaminated by glass, metal, and plastic. Incineration has grown by an order of magnitude from 2003 to 2011, with the number of plants doubling to 109, with an astonishing 45 plants coming on line in 2012, but only accounted for 16% of 2011 MSW [251]. There were 498 landfills in China in 2010; many of the new landfills use HDPE liners, compact wastes, and some sites near the larger cities collect and use LFG [124].

The Ministry of Housing and Urban-Rural Construction scores sanitary landfills. A score of 85 or better is Class I, and between 70 and 85 is Class II. Below 70 is Class III, according to the 2005 Standard of Assessment on Non-hazardous Disposal of Municipal Solid Waste (CJJ/T107-2005). The first assessment was completed in 2005, and another in 2008. In 2008, the standard was amended (GB16889-2008) to require CH_4 control at landfills with a capacity >2.5MT, and a depth of waste > 20 m. Collection and flaring of gas will meet the standard [126]. To promote renewable energy, in 2006 the State Commission set subsidies (0.25 Yuan kW^{-1} more than coal electricity) for biomass-based renewable energy such as from LFG. Under the Renewable Energy Law of 2006, electric companies must purchase renewable energy and provide interconnections to the grid. Although LFGTE was pioneered before these laws (the first LFGTE plant was operational in 1998 [164], as of 2008, 28 landfills were collecting gas, with 20 generating electricity or conducting some other kind of beneficial use. There were an additional 29 approved LFG proposals [126] (plants require an environmental assessment, a power use feasibility plan, and local government approvals [162]). By 2012, there were 50 operating plants, more than doubling the number of plants and the electrical capacity since 2007 [251].

China has created a classification of "environmental protection model cities" ("eco-cities"). One standard is that disposal rates for MSW at proper facilities must exceed 85%. This competition has created models for sustainable development, making urban environments "cleaner and tidier" [251].

Cai et al. [125] suggest that because China's MSW has a higher organic fraction than MSW from developed countries, it is important to develop efficient and effective gas controls as new sanitary landfills are constructed. The gas control will not only limit CH_4 emissions, but also reduce complaints about "malodorous" conditions associated with China landfills. Brink et al. [123] also identified addressing growing waste generation and landfilling rates as key to mitigating future CH_4 emissions. Xu [126] however suggested the need for expanding basic waste management services will result in a large number of small landfills (<200 T d^{-1}). The small size of these sites is further affected by the high proportion of food waste. A lot of food waste is believed to limit the duration of gas generation, as the wastes all degrade rapidly. Thus, the feasibility of gas capture and use appears limited. Aerobic bioreactors were identified as a means of limiting CH_4 releases. Other alternatives to LFGTE include using aged MSW as cover material to promote CH_4 oxidation, and also to treat vent pipes with a "wind-heat-bacteria" system that also can promote oxidation. Another proposal is to poison landfills with chlorinated hydrocarbons with the intention of inhibiting methanogenesis [124]. In addition, Zheng et al. [251] believe that, for large east coast cities, there is no land available for landfilling; sites will need to be constructed far from the urban centers, making transportation costs and associated pollution worse, and also requiring transmission of produced electricity. This is recognized in a series of plans issued by the State Council, and the National Energy Council from 2011-2013, which all gave preference to waste-to-energy incineration in eastern cities, and determined LFGTE should be emphasized in the west where large landfills will continue to be used. In addition, while incineration plants benefit from feed-in tariffs and base price supports, LFGTE projects have no such benefits; they do receive an immediate refund of VAT, however [251].

Brink et al. [123] suggest a waste management focus on urban areas. Their analysis suggests that greater reductions in fugitive CH_4 will result there because as more waste is landfilled, waste management generally will become more cost effective (less expense for transportation, more scalable opportunities for infrastructure costs). However, if rural areas gain organized waste management, less sophisticated technology opportunities will probably lead to less CH_4 control. They would also like to see household biogas initiatives re-invigorated for rural areas, which can serve as an alternative to waste disposal. Bond and Templeton [212] have reviewed the promise and poor performance of these systems in India and China.

China joined the CDM process in 2005, and as of 2013 accounted for over 50% of the CDM projects, and over 60% of the CERs. Although most China CDM projects are in wind and hydropower, waste to energy is a focus. The number of LFGTE projects certified by the China NRDC has ranged from 3 to 14 (8 were registered in 2012), with UNFCC registrations ranging from 1 to 11 (11 were registered in 2012). About twice as many incineration plants are registered with both agencies [251]. However, mandating gas control may mean future LFG projects are not eligible for CDM credits, as CERs are only issued if the project was not required -- there must be an element of voluntary adoption of the behavior being rewarded [163].

CDM affects perspectives on potential projects. One analysis compared using LFG as pipeline gas or to produce electricity (at three different collection efficiencies). Greater relative gas utilization (measured as thermal energy) was realized by creating electricity, but the GHG credits were greater to use the gas in the pipeline, making this a better choice. However, electricity and gas grid pricing mean that capture of at least 65% of the landfill's gas is necessary to make the project cost-effective. CDM credits could make either kind of project feasible at lower capture rates [309]. However, in order for CDM credits to be earned by a project, a precise and particular project development process must be followed, and one year of post project monitoring is required to validate the emission reductions [137].

7.3 Policies in the EU

The European Union (EU) and individual member states have a number of policies which target MSW and CH_4 emissions. In Germany, for instance, the Renewable Energy Sources Act of 2004 provided feed in tariffs and a 20 year guaranteed price for renewable sourced electricity. This included CH_4 sources such as biomass digestion, coal mines and LFG. The U.K. was one of the first nations to sign on to the Kyoto Protocol, signaling early and strong support for climate change policy, and the U.K. has strong requirements for renewable energy use. Between 1990 and 2002, CH_4 levels in the U.K. dropped by 43%. One tax policy was to exclude renewable energy sources from a “Climate Change Levy” to provide them with a competitive advantage in the energy markets. The U.K. also provides feed-in tariffs for biomethane. The 2008 Climate Policy Act aims to reduce GHG emissions by 80% from 1990 levels, by 2050. Agricultural practices are addressed, as agricultural CH_4 emissions are the dominant domestic source, but are difficult to reduce. Sweden also provides tax benefits for biomethane use, and has quotas for consumer use [95].

In 2002, an EU regulation was adopted to regularize reporting of MSW. The EU-wide data were first produced in 2007 [94]. The most significant policy affecting solid waste CH_4 emissions is the EU Landfill Directive, adopted in 1999. The directive uses 1995 as a base year. Member nations are required to reduce landfilling of biodegradable wastes. The reductions are 25% by 2004 (to 75% of 1995 levels), 50% by 2007, and 65% by 2016 (to 35% of 1995 levels) [94]. The 65% reduction target date has been reset to 2018, and a "priority project" of zero landfilling of degradable wastes was identified in 2011 (Global Methane Initiative 2013b). Landfilled waste is now required to be treated, except where such treatment is “not technically feasible.” As of 2008, Austria, Belgium, Denmark, Germany, Luxembourg, and The Netherlands were characterized as having exceeded the standard, Finland, France, Italy, Sweden, and the U.K. were in compliance, and Greece, Ireland, Portugal, and Spain were said to be in the process of implementation [94]. In 2011, it was made mandatory for all member states to have gas collection requirements for all landfills receiving biodegradable wastes [310].

The IEA [163] believes its analysis shows individual country's feed-in tariffs were most effective in spurring growth of LFG projects, especially from 2000-2005. Idiosyncratic policies, such as Italy's quota system, were also helpful. The 2009 Renewable Energy Directive and the 2008 Waste Recycling and Recovery directive also support biogas use [95].

The EU requires GHG emission reductions from its member states, with levels of reductions based on each member's relative wealth. The standards are set for the major constituent GHGs, including CH_4, and are further targeted by generating sector. The waste CH_4 targets are driven by the Landfill Directive program, with no specific amounts of CH_4 reductions being specified [310].

8. Conclusions

Methane is the second most potent greenhouse gas; its atmospheric concentrations are rising at a rate of 0.5% yr^{-1}. Although fossil methane is emitted from natural processes and exploitation of petroleum, coal, and natural gas resources, most methane is generated by microbial degradation of organic matter in a variety of anaerobic settings. Landfills already constitute a major source of anthropogenic methane and it is further projected to increase into the foreseeable future. The amount of LFG generated and (more importantly) released to the atmosphere is measured by models and monitoring. The scale of these measurements is from individual measuring points at particular landfills to the entire world, though almost all of these assessments are no more than crude approximations. The materials sent to landfills, even when consistent at one site, are heterogeneous in nature, and the conditions within a landfill are affected by a number of difficult to describe conditions. These include moisture availability, the presence or absence of casings on the degradable matter, the degree of compaction, the presence or absence of internal fires, weather, and climate. This means generalized models or point source measurements may not appropriately detail the actual processes that are occurring. Some more extensive monitoring processes are hampered by reproducibility and quality control issues. Although the processes and conditions that lead to degradation are well tested in laboratory mimics of fills, these experimental data do not appear to translate well to the actual sites where wastes are buried. Broad estimates of LFG releases are hampered by the general inability to count solid wastes well, and by poor descriptions of waste management systems by many countries. Still, although it is not measured well, landfills produce a gas that is approximately equal amounts of methane and carbon dioxide, along with some minor constituents. This product, if released to the atmosphere, can affect human health (due to the carcinogenic and toxic nature of some of the minor constituents), and also has climate change potential. Therefore, most countries are seeking to limit its release. Methanotropes that develop naturally on the surface of landfills will consume a portion of the methane and some of the other constituents of concern, and conditions can be created that favor their growth and enhance their degradative powers. More effective than microbial controls on the landfill surface is to enclose the landfill with some impervious surface, and then to collect the landfill gas within the wastes through a vacuum-driven system. The collected gases will, for many sites, support combustion and the conversion to oxidized forms of much less environmental and human health concern.

Better than flaring the gas is to use it for constructive purposes. Methane is an energy molecule so its stored energy potential can be exploited. For many sites, this means simply burning the gas in an engine and using that energy to produce electricity. However, more complicated and potentially lucrative options are available: the gas can be used in combined heat and power systems, cleaned to meet standards for pipeline use or as a compressed natural gas fuel, or processed in various ways to serve as substrates for specialty chemicals or alternative vehicle fuels (such as drop-in hydrocarbon replacement, methanol, DME, higher alcohols, or hydrogen to run a fuel cell). Many of these options, even the base case of electricity production through an engine, require that the gas be cleaned of impurities and upgraded to increase its energy density. Nonetheless, wastes are produced daily (worldwide waste generation estimates range from 0.5 to 2 kg d^{-1}, or even more for the US), the effort to create a product from this available, renewable energy source may make economic sense. Lately, the biggest challenge is to match the relatively small feedstock and address the "economy of scale"; this has spawned a min-GTL industry for flared gas but is equally applicable to LFG. The vision is to install community-level fuel production units on the landfill sites that have the potential to truly reduce carbon footprint while turning waste into fuels.

Many governments see the sense in using this waste gas for good purposes. Some promote landfill gas use through incentives of various kinds, and policies that foster creative and more widespread exploitation of the gas resource. The US, both at home and through a global organization it sponsors, is the prime player in these kinds of activities. Other governments, however, seek to minimize fugitive methane but cutting it off at the source by limiting the landfilling of organic matter, either by banning particular materials or treating wastes before burial, or by seeking entirely different means of managing wastes other than landfills. The EU countries, especially Germany, have been at the forefront of this strategic approach. China, as the largest waste producer and the largest CO_2 emissions (28% of the global total) in the world, and a nation still establishing an infrastructure for environmentally sound, cost-effective waste management, is a notable example of developing countries, to guide them as they become more prosperous and technologically advanced.

The general understanding is that modern landfills will produce landfill gas for at least twenty years and perhaps fifty years after wastes are first buried. Methane also has a relative short atmospheric half-life, especially compared to carbon dioxide. We, therefore, believe that programs that seek to capture and then beneficially use LFG are needed, and they would be best if they fostered site-specific evaluations and prescriptions, rather than seeking to establish generic approaches based on sometimes poorly-founded conventional wisdom, especially for sites in less developed countries. We think such tailored, nuanced policies and programs could help create sustainable energy projects, often in areas where the need for unconventional, green power is great. Of course, approaches that can process both CH_4 and CO_2 to produce fuels must be at the core of advance technology development. This review attempted to cover these topics to lay the foundation for further study that optimize conditions and allows energy harvest from methane while concomitant reduction of its release into the atmosphere. The recently concluded COP21 agreement in Paris, if fully enacted, could accelerate development of science, technologies and policies that can help contain the set-forth goal of 2^oC rise in earth's temperature by the end of the twenty-first century.

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