Kate Sundeen

Chem 505: Environmental Chemistry

Professor Hermanson

TA: Leslie Anderson

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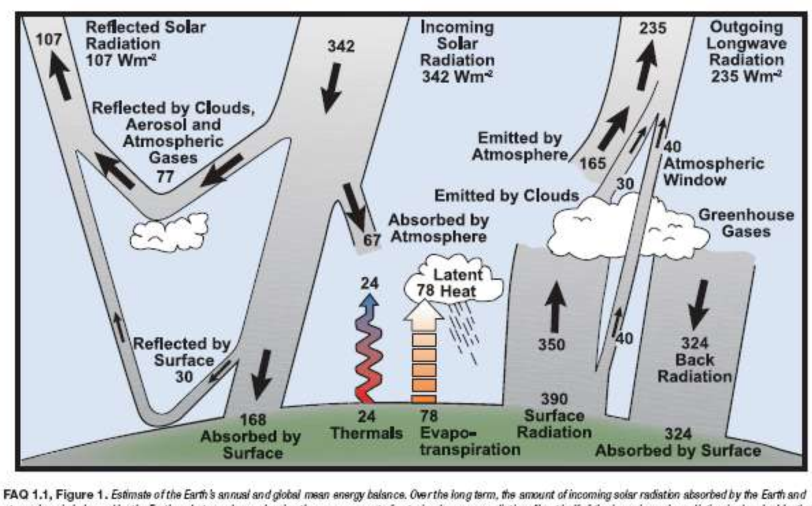
METHANE

A review of methane as a greenhouse gas

Part One: How does it act as a greenhouse gas, and who figured it out?

The Earth absorbs and radiates energy. If the Earth absorbs more energy that it radiates, its temperature increases. Atmospheric gasses may not absorb all of the reflected IR, which is subsequently released into the upper atmosphere, and into space. The IR that does not pass through is absorbed by greenhouse gasses, whose structures cause them to vibrate, subsequently releasing the energy back to Earth (Baird and Cann, 2008). The figure below, shows this necessary process.



FAQ 1.1, Figure 1. *Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming solar radiation is absorbed by the Earth's surface. This energy is transfered to the atmosphere by warming the air in contact with the surface (thermals), by evapotranspiration and by longwave radiation that is absorbed by clouds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kiehl and Trenberth (1997).*

(Le Treut, etal, 2007)

Methane is one of the gasses that contributes to the greenhouse effect. It contributes to the greenhouse effect in two ways. First, methane absorbs IR very easily, as seen in the chart below, acquired from the Institut Carnot de Bourgogne's spectroscopy website, showing 100% and near 100% absorption across the IR range:

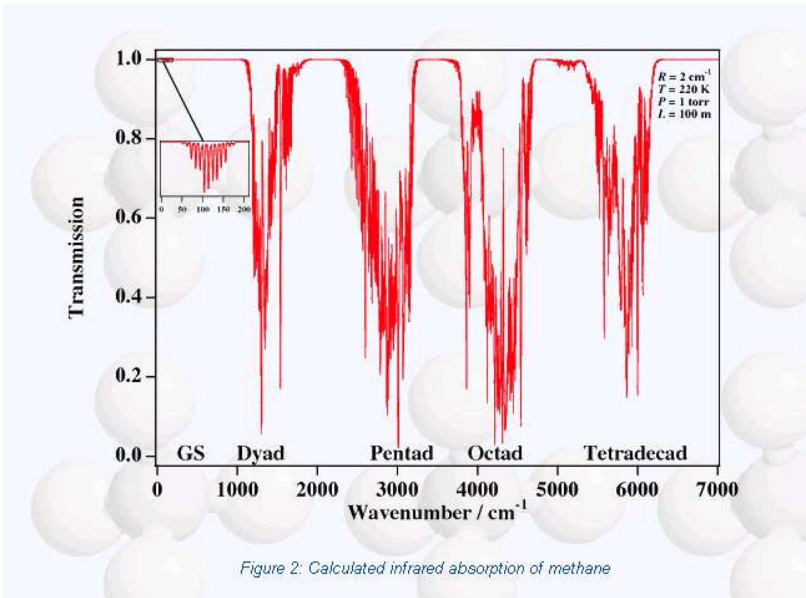


Figure 2: Calculated infrared absorption of methane

(ICdeB, 2008)

However, due to the high symmetry of its structure a considerable amount of torsion, bending and subsequently, vibration can occur. The result is that the IR is then released back towards the Earth's surface as heat.

The second way that methane contributes to the greenhouse effect is the fact that 90% of the methane in the air goes through a reaction with the omnipresent hydroxyl (OH), to create CH_3 and water, which is, itself, a major greenhouse gas. This reaction continues, ending in the creation of carbon monoxide, and carbon dioxide (the other major greenhouse gas). As an ancillary fun benefit, it also results in the destruction of ozone (Baird and Cann, 2008).

This phenomenon was discovered by John Tyndal in 1859, though due to the short lifespan of atmospheric methane, actual methane in the air was not found until 1948 (Weart, 2007). A large amount of work was done in the seventies by Veerabhadran Ramanathan and his colleagues at NASA on CO_2, but it wasn't until the 80s when they started to assert that other gasses, such as methane, could be a major contributing factor, particularly as a result of anthropogenic sources (Weart, 2007). Furthermore, the amount of methane in the atmosphere was increasing and dramatic and alarming rate.

Part Two: The sources and growth of atmospheric methane levels

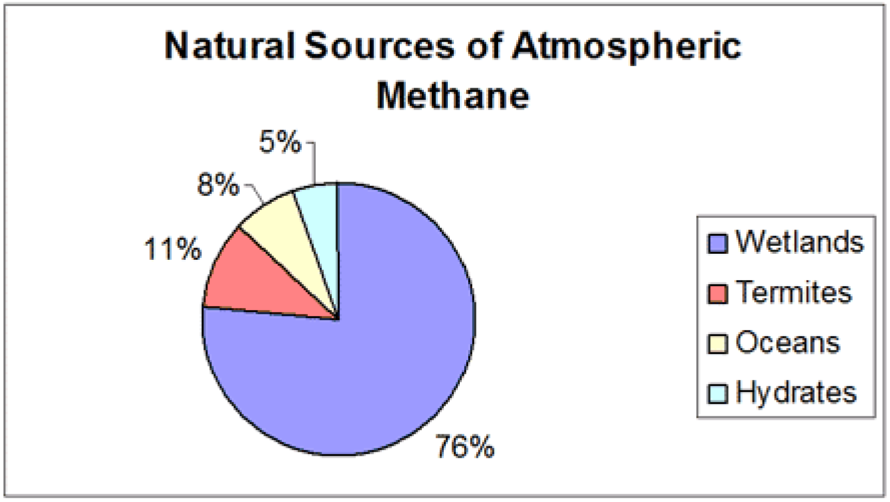
Global warming skeptics like to joke around about the fact that we can't stop cows from farting, so there is little we can do. However, it should be noted that the large number of cattle, particularly in the United States, is entire due to the fact that we consume huge quantities of beef. So, even though the source is "natural" the cause in anthropogenic. In fact, the Intergovermental Panel on Climate Change (IPCC) estimates that 60% of the methane in the atmosphere comes from human-related sources (EPA, 2006). In the United States, the biggest culprit is landfills.

Table 1 U.S. Methane Emissions by Source ($TgCO_2$ Equivalents)

Source Category	1990	1997	1998	1999	2000	2001	2002	2003
Landfills	172.2	147.4	138.5	134.0	130.7	126.2	126.8	131.2
Natural Gas Systems	128.3	133.6	131.8	127.4	132.1	131.8	130.6	125.9
Enteric Fermentation	117.9	118.3	116.7	116.8	115.6	114.5	114.6	115.0
Coal Mining	81.9	62.6	62.8	58.9	56.2	55.6	52.4	53.8
Manure Management	31.2	36.4	38.8	38.8	38.1	38.9	39.3	39.1
Wastewater Treatment	24.8	31.7	32.6	33.6	34.3	34.7	35.8	36.8
Petroleum Systems	20.0	18.8	18.5	17.8	17.6	17.4	17.1	17.1
Rice Cultivation	7.1	7.5	7.9	8.3	7.5	7.6	6.8	6.9
Stationary Sources	7.8	7.4	6.9	7.1	7.3	6.7	6.4	6.7
Abandoned Coal Mines	6.1	8.1	7.2	7.3	7.7	6.9	6.4	6.4
Mobile Sources	4.8	4.0	3.9	3.6	3.4	3.1	2.9	2.7
Petrochemical Production	1.2	1.6	1.7	1.7	1.7	1.4	1.5	1.5
Iron and Steel	1.3	1.3	1.2	1.2	1.2	1.1	1.0	1.0
Agricultural Residue Burning	0.7	0.8	0.8	0.8	0.8	0.8	0.7	0.8
Total for U.S.	**605.3**	**579.5**	**569.3**	**557.3**	**554.2**	**546.7**	**542.3**	**544.9**

Source: US Emissions Inventory 2005: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2003 (EPA, 2006)

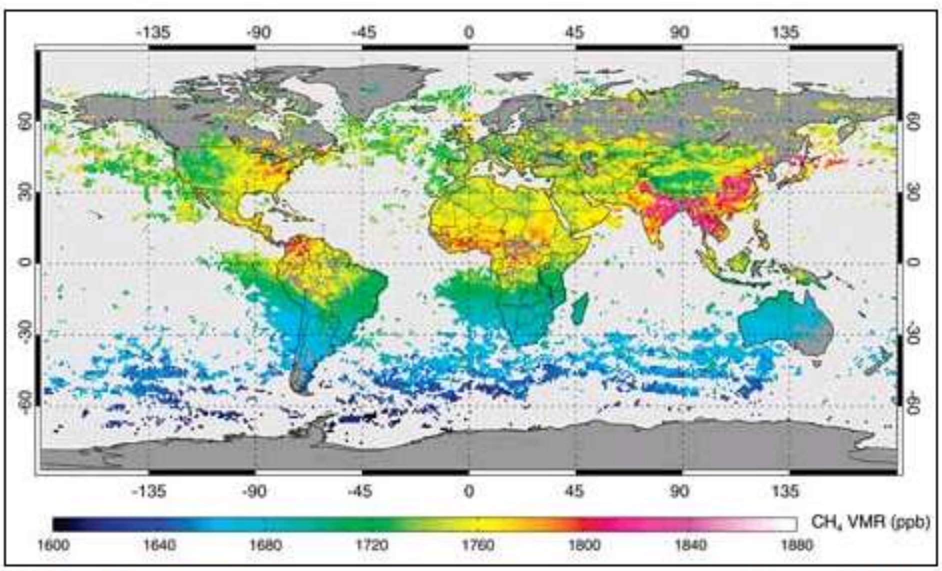
As far as natural sources, the largest producer is wetlands, which corresponds with the production of methane by landfills, as both are full of the chemical reaction that produces methane—rotting organic matter.



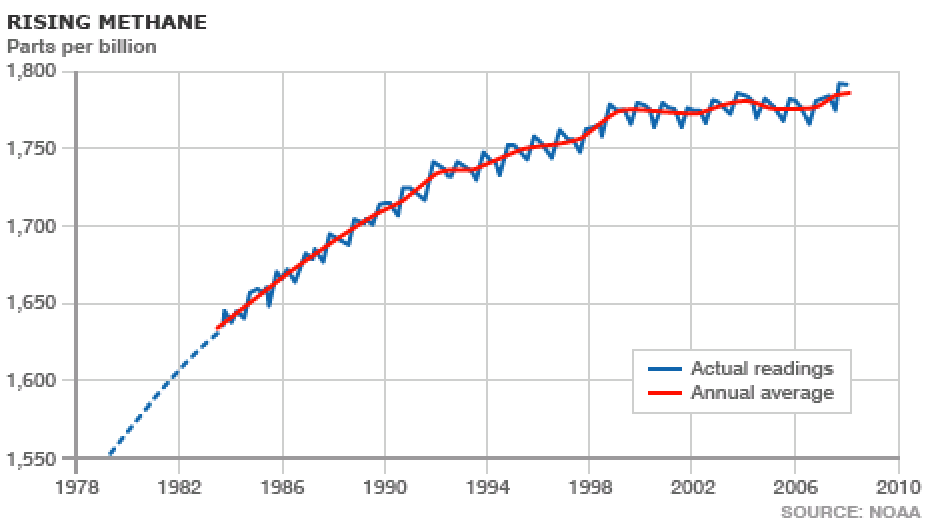
Source: Prepared from data contained in IPCC, 2001c EXIT Disclaimer.

(EPA, 2006)

This is reflected in the geographic concentrations of natural methane, as shown in the figure below:



Currently, methane levels are continuing to rise, even beyond the levels that V. Ramanathan noted, with alarm in the 80s. According to the National Oceanographic and Atmospheric Administration (NOAA), there was a .5% increase in ppm of methane in the atmosphere between 2006 and 2007. Further, there was an average increase of 1.65 ppm between 1979 and 2007 (see figure below). This puts our current concentration of atmospheric methane at 384 ppm, compared to 280 ppm at the start of the industrial revolution. The implication, of course, is that the increase is largely due to industrial causes. However, this is actually fairly difficult to establish clearly (Black, 2008)



However, it should be noted that there is evidence that there have been fluctuations over time (Loulerge, etal).

Part Three: What Next?

There are two major considerations for the years ahead. First, is the reduction of human activity that contributes to the addition of greenhouse gasses to the atmosphere. Since methane is much more efficient as a greenhouse gas than the other greenhouse gasses, and because the trapping of methane is relatively doable, many organizations, including the United Nations (as published in the Kyoto Protocol, suggest that we concentrate particularly on methane remediation (Fogarty, 2007). Encouragingly, the recent G8 summit discussed greenhouse gas reduction, and produced a promise to reduce carbon emissions by 50% by 2050, and to move, in general, towards a complete elimination of carbon emissions. After some discussion, and dissension, this was agreed to, even by the emerging industrial nations (Stolberg, 2008).

This is particularly important, because the greenhouse gas contribution to global warming has caused ocean temperatures to rise and polar ice formations to start to break apart. Why is this a problem? Bubbles of solid methane called clathrates which, if released into the air, due to a decrease of the surrounding pressure or melting of the ice, would result in a catastrophic increase in atmospheric methane levels (Svoboda, 2006).

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