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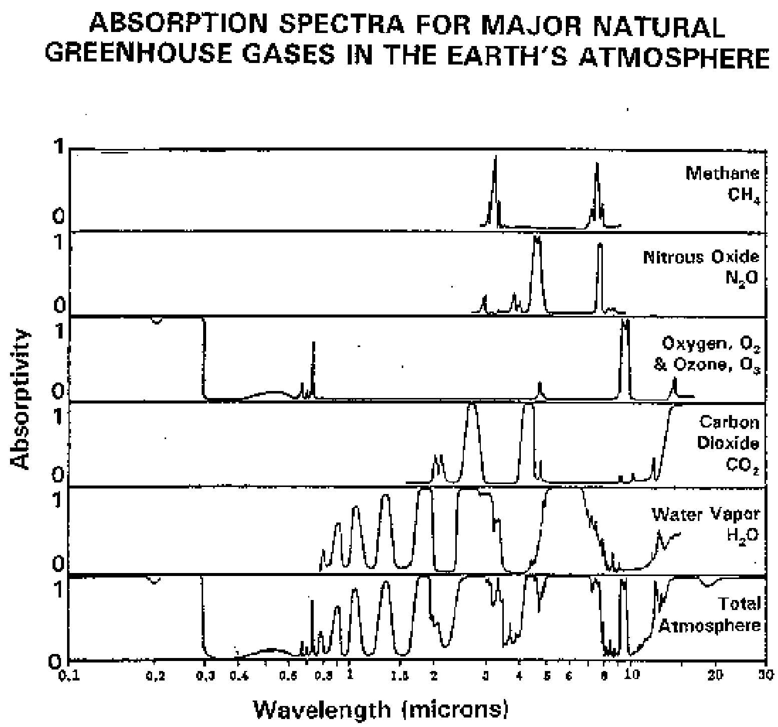
PIM #2—Methane as a contributor to global warming

Absorption (vibrational, rotational energy) in the IR spectra.

Infrared (IR) light is light that has wavelengths of 0.75-1000 microns (1). It is much less energetic than ultraviolet light and the 5-100 micron range is called thermal infrared since the energy is sensed as heat or warmth (1). Methane is a greenhouse gas that contributes to global warming because it absorbs and then can re-radiate IR radiation back to earth. It absorbs IR most strongly around 3 and 7.7 microns (1). Please see figure below (2,3):



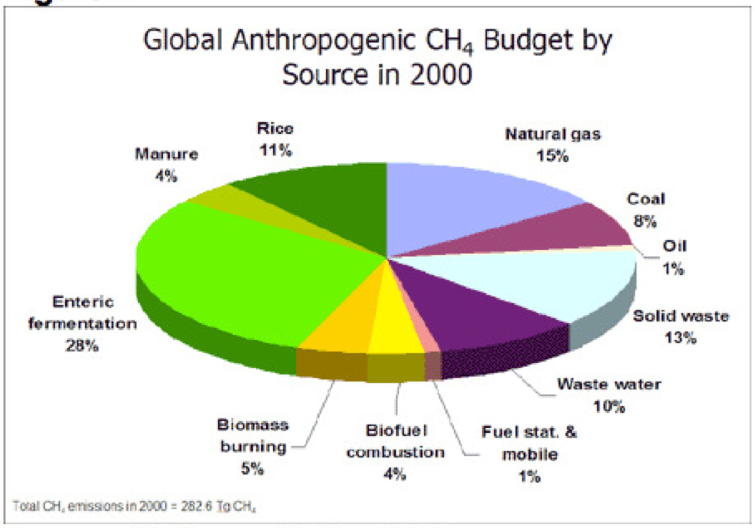
[After J. N. Howard, 1959: *Proc. I.R.E. 47*, 1459; and R. M. Goody and G. D. Robinson, 1951: *Quart. J. Roy. Meteorol. Soc. 77*, 153]

The reason that methane absorbs these particular wavelengths is because the energies corresponding to these wavelengths match the energies (a.k.a. vibrational modes) of molecular bond stretching and bending that is particular to methane (i.e. antisymmetrical bond stretching at $\nu_3 = 3019$ cm^{-1} or about 3 microns and bending at $\nu_4 = 1311$ cm^{-1} or about 7.7 microns(2)). An animation of the molecules movement can be seen by going to the following link: http://icb.u-bourgogne.fr/OMR/SMA/methane/vib_qt.html

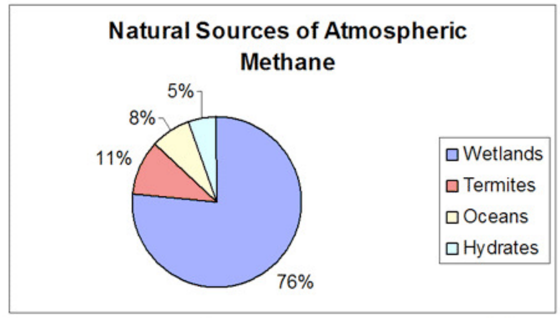
Sources, Sinks, Secondary reactions

70% of current methane emissions are anthropogenic in origin (1), notably agriculture, waste treatment, and fossil fuel use. In contrast, natural sources contribute very little, in large part because methane clathrates store much of the natural methane at high pressure and low temperature. The following figures provides a breakdown of anthropogenic and natural sources (5-7):

Figure 1



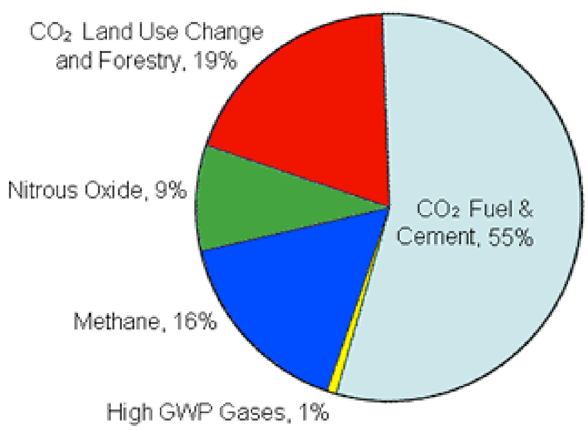
Source: EPA compilation 2002



Source: Prepared from data contained in IPCC, 2001c

It is important to address ways in which we can control the rise of methane emissions. Baird and Cann estimate that methane is "23 times more effective in raising air temperature than the same mass of carbon dioxide (1)." It is the third most important greenhouse gas after carbon dioxide and water because of its higher likelihood of absorbing a thermal IR photon and its role in increasing stratospheric water vapor (1). The following chart shows relative emissions of methane to carbon dioxide (8):

Figure 1: Global Greenhouse Gas Emissions 2000



Methane does get removed from the atmosphere more quickly than carbon dioxide, in large part because it reacts with other molecules quickly. But, even those reactions which remove methane are not completely innocuous. Oxidation by OH radicals removes 507 Tg CH_4/ year, but it produces carbon dioxide (1, 7):

$$CH_4 \rightarrow\rightarrow CH_2O \rightarrow \rightarrow CO \rightarrow\rightarrow CO_2$$

Reactions in the stratosphere with atomic oxygen, chlorine, and hydroxide remove about 40 Tg CH_4/ year (7). The particular reactions with atomic oxygen produce ***stratospheric*** water vapor as a consequence, which is a significant greenhouse gases (1):

$O^* + CH_4 \rightarrow OH + CH_3$
$OH + CH_4 \rightarrow H_2O + CH_3$

Reactions in the soil remove an additional 38 Tg/ year (7).

Uncertainty of Future Amounts

The future of methane emissions is hard to predict. If methane clathrates release large (estimated) concentrations of methane as sea levels change and polar ice caps melt, there is no telling what methane concentrations may rise to (1). Furthermore, a large percentage of methane is generated from agricultural waste and rice-farming. Perhaps as fuel costs rise, we will develop a method to harness the copious amounts of natural gas produced on farms. On the other hand, as the standard of living increases in developing countries, and beef and pork consumption increase, any theoretical methane capture may not be able to keep up with the increasing emission sources. Lastly, since the major method of methane oxidation is reaction with hydroxyl radicals, if the concentration of other competing organic molecules (e.g. pesticides and volatile organics) continues to rise, the concentration of CH_4 may increase if OH radical production does not increase as well (9).

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4. *Spectroscopy of Methane*. http://icb.u-bourgogne.fr/OMR/SMA/methane/ Institut Carnot de Bourgogne. Retrieved on 2008-07-16.
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8. *Methane to Markets Partnership Fact Sheet Brochure*. http://epa.gov/climatechange/emissions/globalghg.html. U.S. EPA. Retrieved on 2008-07-06.
9. Collins, W.J.; Derwent, R.G.; Johnson, C.E.; Stevenson, D.S. *Clim. Change.* **2002**, 52, 453-479