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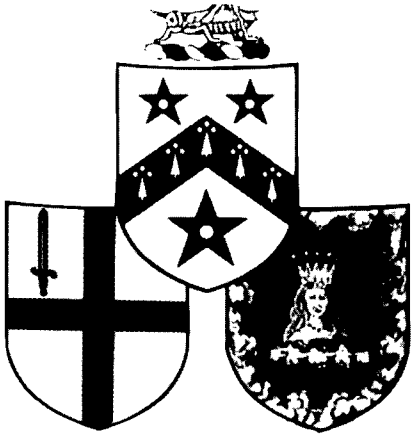

CLIMATE CHANGE

A Lecture by

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Climate Change

An increase in the mean global surface temperature results from altering the energy balance of the Earth-atmosphere system. Radiatively active gases cause the atmosphere to retain heat that would otherwise be lost to space in a natural phenomenon essential for life to exist on Earth, popularly called the *Greenhouse Effect.* Increases in the atmospheric concentrations of some gases result in a more effective greenhouse effect and hence rise in surface temperature. The change in climatic conditions is known as *Global Warming* and is affected by both natural and human factors.

Carbon dioxide has been recognised as an important global warming gas for some time. Extensive efforts have been made to link its atmospheric concentration with global temperature, and to link the post-industrial rise in concentration with human activities. Since this is now reasonably well understood, steps have been made at policy-level to limit future increases of CO_2, or more optimistically to reduce levels in an attempt to halt the rise in temperature which may already be taking place. The atmospheric lifetime of is CO_2 is *ca.*200 years so it will take a great deal of time to undo the harm that has been done.

Up until very recently, other global warming gases in the atmosphere were treated as insignificant because of their relatively small concentrations, but in fact methane, nitrous oxide, the halocarbons and tropospheric ozone, together have a greenhouse effect at least as great as that due to CO_2. By far the most important of these is methane not least because its lifetime in the atmosphere is short therefore steps can be taken to check its influence on global warming on a rapid timescale.

Methane is a naturally occurring trace gas in the atmosphere with a current concentration of 1714 ppbv (parts per billion per volume). It was first discovered by Migeotte in 1948 from absorption features in the solar spectrum. Measurements began to be made during the 1960s and 1970s using gas chromatography with flame ionisation detection (GC-FID) and in 1981 Rasmussen noticed that the concentration of methane was rising. The annual average abundance of methane rose from 1354ppbv in 1962 to 1545 ppbv in 1979, or an average of 13 ppbv/yr. (just under 1%/yr.) over the two decades.

As a result of the above discoveries a global network, co-ordinated by NOAA/CMDL (National Oceanic and Atmospheric Administration and the Climate Modelling and Diagnostics Laboratory, Carbon Cycle Group), was set up to monitor continuously the methane concentration from sites all over the world. There now exists and enormous database so that small perturbations may be detected. In fact, there has been a slowing down of the global accumulation of methane in the latter part of 1980s from 13.5 ppbv/yr. in 1983 to 9.3 ppbv/yr. in 1991.

Air bubbles trapped in ice cores provide a means for investigating the atmosphere of long past climates. As snow was compacted into ice, air was occluded and the rate this occurred was dependent on snow accumulation rates. The only drawback is that the air trapped inside the ice is younger than the surrounding ice by 50 to 100 years. The ice however may be dated using various methods, including oxygen – 18 isotope techniques and matching ash bands with large volcanic eruptions of known date. The concentration of methane in air trapped in ice cores has been measured using wet extractions and gas chromatography with flame ionisation detector (GC-FID). Sections of ice cores from Greenland and Antarctica have been analysed to build up a profile of the concentration of methane over time to show that the global mean concentration has doubled in the last 200 years. The concentration of methane was around 700ppbv throughout the Middle Ages but during the industrial revolution it rose to be 1100 ppbv by 1900 and has continued to rise ever since. This result is even more striking when it is realised that the methane concentration was stable at approximately 700 ppbv for 10,000 years prior to *ca* 1800 AD. A doubling of methane concentration would theoretically cause a 0.3 °C rise in global mean temperature.

The first step is the cleavage of one hydrogen atom from methane by the highly reactive hydoxyl radical:

$$CH_4 + HO\bullet \rightarrow CH_3\bullet + H_2O$$

A sequence of reactions then take place with the resulting production of carbon monoxide, but the mechanism (oxidation pathway) depends on the concentration of catalyst, NO or NO_2. With high N_{ox} concentrations present in urban photochemical smog, tropospheric ozone is produced by the methane cycle, which is also hazardous to health. It should also be noted that

production of ozone will influence the sinks of these gases, by further production of hydroxyl radicals.

Another mechanism for loss of methane is migration to the stratosphere, where it is oxidised by reactions involving photolytically generated radicals including hydroxyl, oxygen O[^{1}D], and chlorine. The stratosphere sink is of minor global importance, 5-10%, compared to the tropospheric chemistry which accounts for 85% of the total annual destruction of atmospheric methane.

Microbial action also removes methane. Methylotrophy, the process by which methane is microbially oxidised in soils is again a minor sink assigned only a 5% share of the total process. It is however of some importance in deriving the global budget of methane since the soil is also a major methane source; it has been estimated that 80% of the gross production of methane from methanogenic micro-organisms is oxidised prior to its introduction to the atmosphere. So a great deal of potential harmful methane is destroyed before it ever does any damage.

The lifetime of methane in the atmosphere is governed by the rates of oxidation reactions. Most important, both as the starting point for all mechanisms and as the rate determining step, is the reaction between hydroxyl radicals and methane which suggests a lifetime in the range 11 to 17 years. The main pathway for destruction of methane in the atmosphere is oxidation by photochemically produced hydroxyl radicals. Hydroxyl (OH) is responsible for destroying air pollutants and trace gases. Without its presence the composition of the atmosphere would be totally different and more hazardous to many forms of life on Earth. For this reason OH is sometimes referred to as the atmospheric policeman.

The main sources of methane are described below. They may be divided into two categories: biogenic and abiogenic. True biogenic methane is that produced directly by microorganisms. Methane production in the Earth is predominantly a product of the breakdown of biologically derived organic material at various temperatures by geologic processes. This is however known as abiogenic methane. There is only one possible real abiogenic methane as will be explained below.

The major production of methane by bacteria is termed *methanogenesis* and the bacteria responsible are known as *methanogens*. All methanogens belong to a group of micro-

organisms within the primitive biological kingdom Archaebacteria. They are strictly anaerobic and flourish in strongly chemical-reducing conditions, so they are commonly found in aquatic sediments, flooded soils, animal gastrointestinal tracts and in sewage. Extreme environments are also tolerated: *themophilic* methanogens (optimum temperature for growth > 45°C) thrive in hot springs, sea floor hot vents and landfill sites; *psychrophilic* methanogens (optimum temperature for growth < 20°C) survive in tundra and cold climates. Some methanogens are able to survive in extreme pH and hypersaline environments. There are many different metabolic subgroups requiring different optimum temperature conditions, but in general soils and sediments, the major methane sources, operate well below their max efficiency for methanogenesis for most, if not all the year. Most methanogens are capable of growth by $CO_2 + H_2$ reduction mechanisms; some use quite exotic energy sources.

Processes which involve the breakdown of organic material at high temperatures, *thermocatalysis,* to produce methane are described as *thermogenesis*. Thermogenesis is the principal source of methane in most subaerial hydrothermal systems. Approximately 80% of commercial natural gas is of thermogenic origin. The main processes for producing natural gas are the cracking of aliphatic structures during the geochemical transformation of kerogen (the intractable macromolecule in sedimentary rocks) and pyrolysis of organic matter.

Truly a biogenic methane i.e. a primordial component could conceivably originate as outgassing from the mantle of juvenile carbon as CH_4 left over from the accretion of the planet. No firm evidence for this exists other than an excess of methane in the water column above the East Pacific Rise. Even this source could be from deep subduction of biological matter.

The reasons for the sudden and significant rise in the atmospheric concentration of methane must be perturbation of the combined effects of changing methane sources and the sinks that remove methane from the cycle. Together the total sources and total sinks describe a *global methane budget* resulting in a measured mean concentration. A snapshot of the current overall methane budget is shown in the table; as can be seen estimates of individual source strengths are quoted as ranges with large (at least two-fold) uncertainties. The rapidity of the rise, and its start contemporaneous with the industrial revolution, leads to the conclusion that the methane budget changes are due to human activities. The two fold errors in methane budget

arise because the models usually derive from some local or laboratory scale experiment extrapolated via a global estimate of the magnitude of the source.

In view of poor constraint of such models, all budgets can be considered at best to be first order approximations, which is hardly appropriate as a basis of governmental or more appropriately an international strategy. With this in mind the Planetary Sciences Research Institute began a programme which could aid in constraining methane budgets via stable isotope measurements.

Methane consists of contributions from four stable isotopes, carbon–12, carbon–13 and hydrogen, deuterium, the rare heavy isotopes are approximately 100 and 6400 times less abundant. The ratio $^{13}C/^{12}C$ and D/H are commonly quoted using the delta notion ($\delta^{13}C$, δD) and values given in parts per thousand ($^{0}/_{00}$).

In an ideal world the double isotope label could be measured for various methane sources, and could be used for monitoring seasonal variations. Such data could be fed into the models and compared to the gross isotopic composition of methane in the atmosphere as a function of time, including a look back into the past via ice cores. The extra parameters would be used to determine the magnitude of various contributions providing methanes from different sources were isotopically different. It is reasonably easy to obtain isotopic data for near source environments but almost impossible to gather sufficient measurements for ambient atmospheric samples. This is because large air samples (20 to 60 litres) have been needed to extract sufficient methane for $\delta^{13}C$ measurements but even these are small compared to the enormous volumes (½ m^3) need for δD. As a result of the sampling requirements stainless steel tanks and pumps were required to collect and compress air samples to several atmospheres. The practicalities of measurements were not easy, and were expensive; definitely not a technique suitable for routine background dual isotopic composition determination of methane around the world. To overcome the problem PSRI has developed a completely new approach based on studying what it calls $\delta^{17}M$ or the integrated study of $\delta^{13}C/D$. We have discovered that $\delta^{17}M$ is diagnostic of various methanes and hence could be of very great assistance in defining the Earth's methane budget in more exact terms.

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Table 1.2 Annual Sources and Sinks of Atmospheric Methane: The Global Budget

Sources and Sinks	Individual Estimate Tg yr^{-1} (IPCC, 1994)	Total Tg yr^{-1}
Natural Sources		
Wetlands	115 (55-150)	
Termites	20 (10-50)	
Oceans	10 (5-20)	
	Sub-Total	160 (110-210)
Anthropogenic Sources (fossil)		
Natural Gas	40 (25-50)	
Coal Mines	30 (15-45)	
Petroleum Industry	15 (5-30)	
Coal Combustion	(130)	
	Sub-Total	100 (70-120)
Anthropogenic Sources (biogenic)		
Enteric Fermentation (animals)	85 (65-100)	
Rice Paddies	60 (20-100)	
Biomass Burning	40 (20-80)	
Landfills	40 (20-70)	
Animal Waste	25 (20-30)	
Domestic Sewage	25 (18-80)	
	Sub-Total	275 (200-350)
Total Identified Sources (natural and anthropogenic)		535 (410-660)
Atmospheric Removal (Sinks)		
Tropospheric hydroxyl radical	445 (360-530)	
Loss to stratosphere	40 (32-48)	
Soil oxidation	30 (15-45)	
	Total Sinks	515 (430-600)
Atmospheric Increase		37 (35-40)
Implied Total Sources (Atmospheric Increase + Total Sinks)		552 (465-640)

The lifetime is 9.4 years for the calculation of total sinks and hence (implied) total source loading.

from Prather, M., R. Derwent, et al., in *IPCC Climate Change 1994, ed. Houghton et al., 1995*

Further Reading:

Books

Stable Isotopes in Ecology and Environmental Science.
K. Lajtha and H. Michener. Blackwell 1994

Science Matters – Changing Climate
K. Warr and S. Smith. Open University Course Book S280 1993

Climate Change 1994 IPCC Report
Houghton etal Cambridge University Press 1995

Papers

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Atmospheric Environment **15** 883-886 (1981)

Craig H. and Chou C. Methane in polar ice cores.
Geophys. Res. Letts **9** 1221-1224 (1982)

Morse A.D. Morgan G.H. Butterworth A.L. Wright I.P. and Pillinger C.T.
Combined isotopic analysis of nanogram quantities of methane.
Rapid Comms in Mass Spect **10** 1743-1746 (1996)

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