SOURCES AND SINKS OF METHANE: FUTURE CONCENTRATIONS AND IMPACT ON GLOBAL WARMING

by

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ABSTRACT

SOURCES AND SINKS OF METHANE: FUTURE CONCENTRATIONS AND IMPACT ON GLOBAL WARMING

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There has been an average increase in the surface temperature of the earth by 0.6 ± 0.2ºC over the 20th century (IPCC, 2001). This increase in the surface temperature of the earth is attributed to the increase in the greenhouse gases in the atmosphere, responsible for trapping outgoing heat radiation. Industrialization and the increase in anthropogenic activities are the causes of increase of these gases.

Methane (CH_4) is the most important greenhouse gas after carbon dioxide (CO_2).The increase in atmospheric CO2 can be attributed due to increase in the use of fossil fuels over the last 150 years. Methane, whose atmospheric concentrations are now nearly 2.5 times of what they were in pre-industrial times, has a variety of anthropogenic and natural sources.

This work is an effort to document the anthropogenic sources of methane since 1960, namely, methane emissions from the use of fossil fuel, rice agriculture, domestic ruminants, biomass burning and waste disposal and handling. A model was created using the sources and sinks of methane and was used to predict the future concentrations of methane up to 2030. considering the atmosphere as a semi-batch reactor. Finally, this predicted concentration of methane was used to determine the surface temperature increase caused due to increase in the atmospheric methane concentrations and was determined to be 0.135 K.

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My parents and my younger sister without whose love and constant support I would not have been able to achieve what I have.

Aunty Tracy, Jan and Shail who made my stay at Pittsburgh an unforgettable one.

Finally, Dr. (Mrs.) Nirmala Srivastava who we affectionately refer to as ‘Shri Mataji’, for dedicating Her life to triggering the spiritual ascent of mankind through Self-Realization and achieve global unity of mankind in the process.

1.0 INTRODUCTION

The fact that there has been an increase in the average surface temperature of the earth is evident by the impact on earth's climate. For example, satellite data shows that the extend of snow cover has declined by about 10% since the 1960's.(EPA Website) There is overwhelming concern as to the impact global warming will have on the biodiversity of the earth. Although, previously there have been bouts of warm and cooler periods but they are not comparable to the drastic rise of the average temperatures of the earth in the past 150 years. This increase in the temperatures is due to the increase in atmospheric trace gases (known as greenhouse gases) such as carbon dioxide (CO_2) and methane (CH_4) whose concentrations have also doubled since pre-industrial times.CO_2 is a well researched greenhouse gas and its sources are well quantified, the major source being the use of fossil fuel. Methane is an equally important greenhouse gas having 21 times the effect of CO_2 on a per molecule basis. This work is an attempt to quantify the sources of sinks of methane and using them to create a model to predict the future concentrations of methane and the impact it will have on the earth's energy balance.

The average flux of solar radiation at the top of the atmosphere, known as solar insolation, is approximately 342 W per square meter. This is approximately one fourth the solar irradiance-the solar power per unit area, which is the ratio of the earth's disc to the surface area. Of the 342 W m^{-2} reaching the earth's surface ,approximately 105 W m^{-2} is reflected back to outer space, the net input of the surface-atmosphere system being 237 W m^{-2}. Applying Stephen Boltzman's law of radiation, the temperature of the surface of the earth should be about 255ºK. The observed temperature of the surface of the earth is 288ºK which is about 33ºK more than what is expected.

The reason for this difference is the presence of greenhouse gases (Hugo et al, 1996). These greenhouse gases cause a global climate forcing, i.e., an imposed perturbation of the Earth's energy balance with space (Hansen et al., 2000, 1997).

According to the report by the Intergovernmenal Panel of Climate Change (IPCC), the average surface temperature of the earth has increased between 0.6 ± 0.2ºC over the 20th century (IPCC 2001, US Greenhouse inventory program). The Third assessment Report attributes the warming over the last fifty years to the "increase in the greenhouse gas concentrations" (IPCC 2001). Thus, it is not the presence of greenhouses gases, but an increase in the concentrations of these greenhouse gases which is a cause of global concern.

Carbon dioxide (CO_2) and methane (CH_4) are the most important greenhouse gases in the atmosphere (IPCC 2001). The concentrations of CO_2 have been steadily on the increase due to the use of fossil fuels and other human related activities and the concentrations of methane today are nearly 2.5 times of what they were during the pre-industrial times. (Wuebbles and Hayhoe., 2002).

Figure 1 below shows the concentrations of carbon dioxide and methane from 1850 till present.

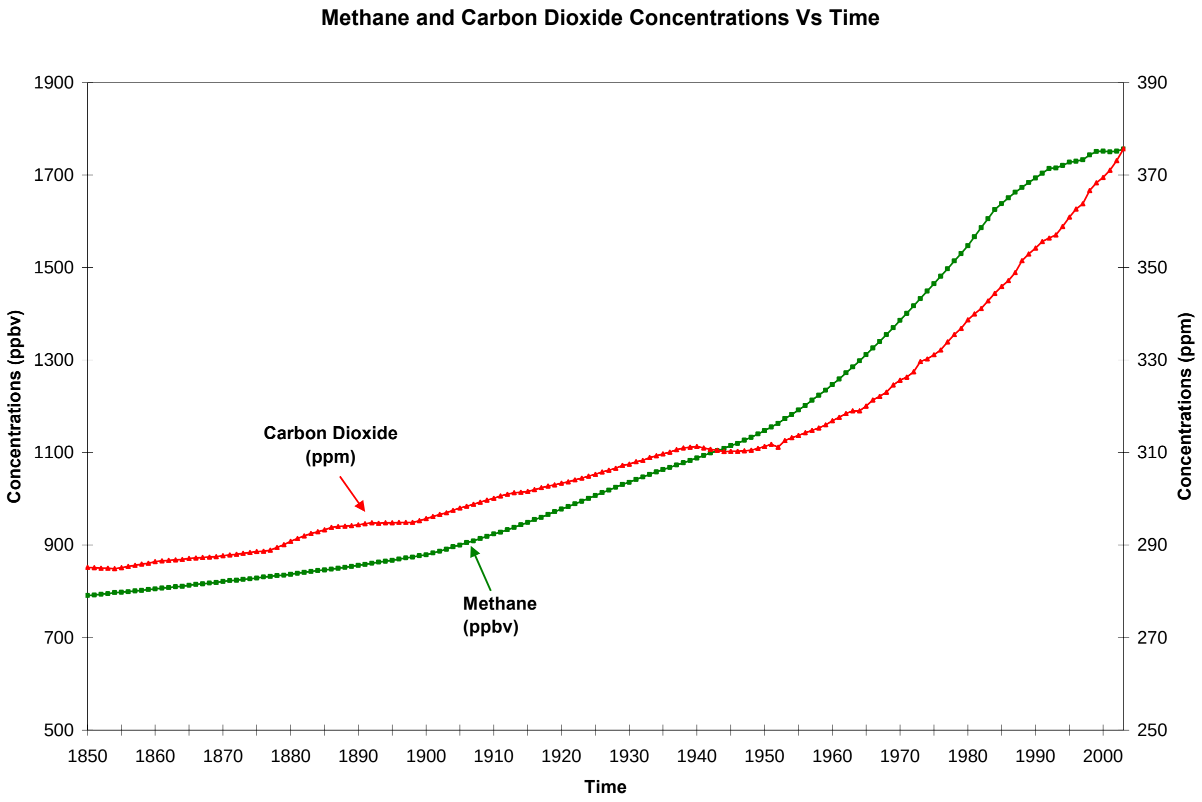

Figure 1: Carbon dioxide and methane concentrations from 1850 till present

It is evident that there has been a sharp increase in the concentrations of both carbon dioxide and methane over the last 150 years. This increase is due to the increase in human activities and from the trends, it is evident that the concentrations of both the gases are on the rise.

An effort to correlate the surface temperature changes along with CO_2 and CH_4 concentrations is presented below.

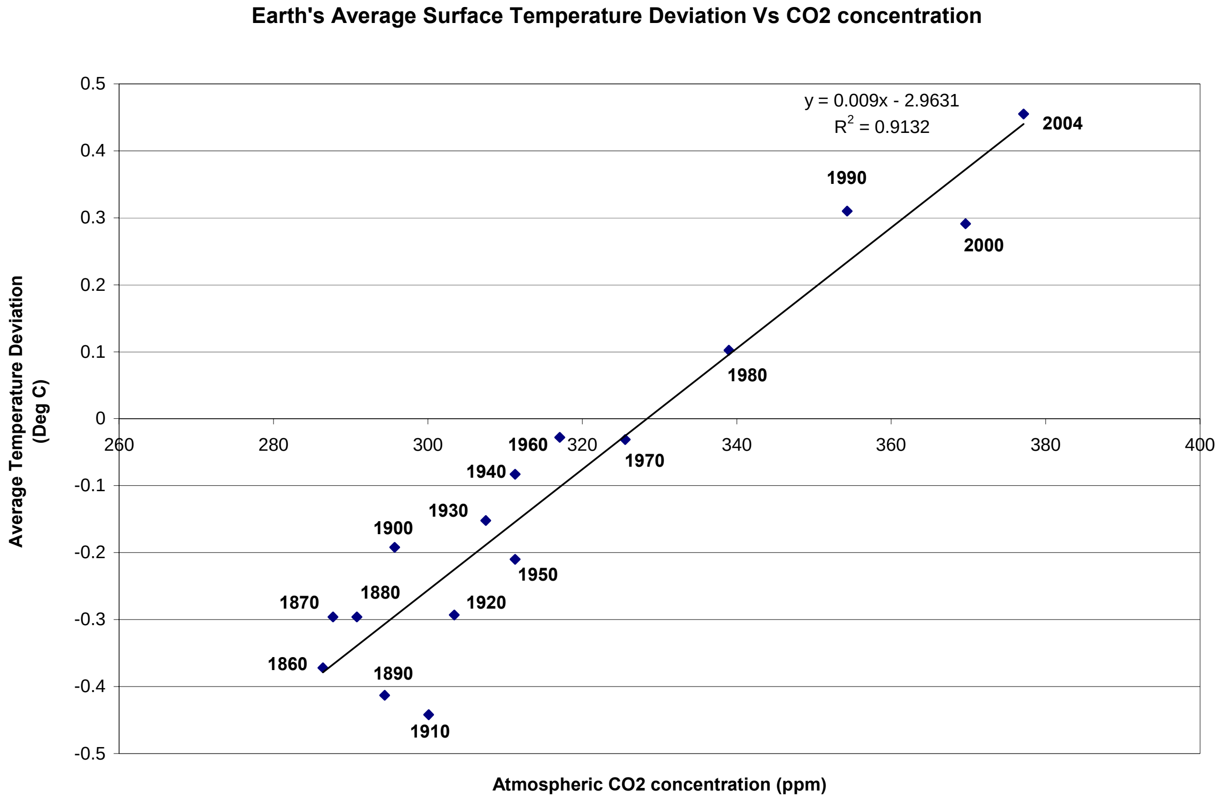

Figure 2: Earth's average surface temperature Vs carbon dioxide concentrations.

Although there is no direct relation between the concentrations of CO_2 and CH_4 and the temperature, it is observed that the temperature of the surface of the earth has increased as have the concentrations of both the species in the atmosphere.

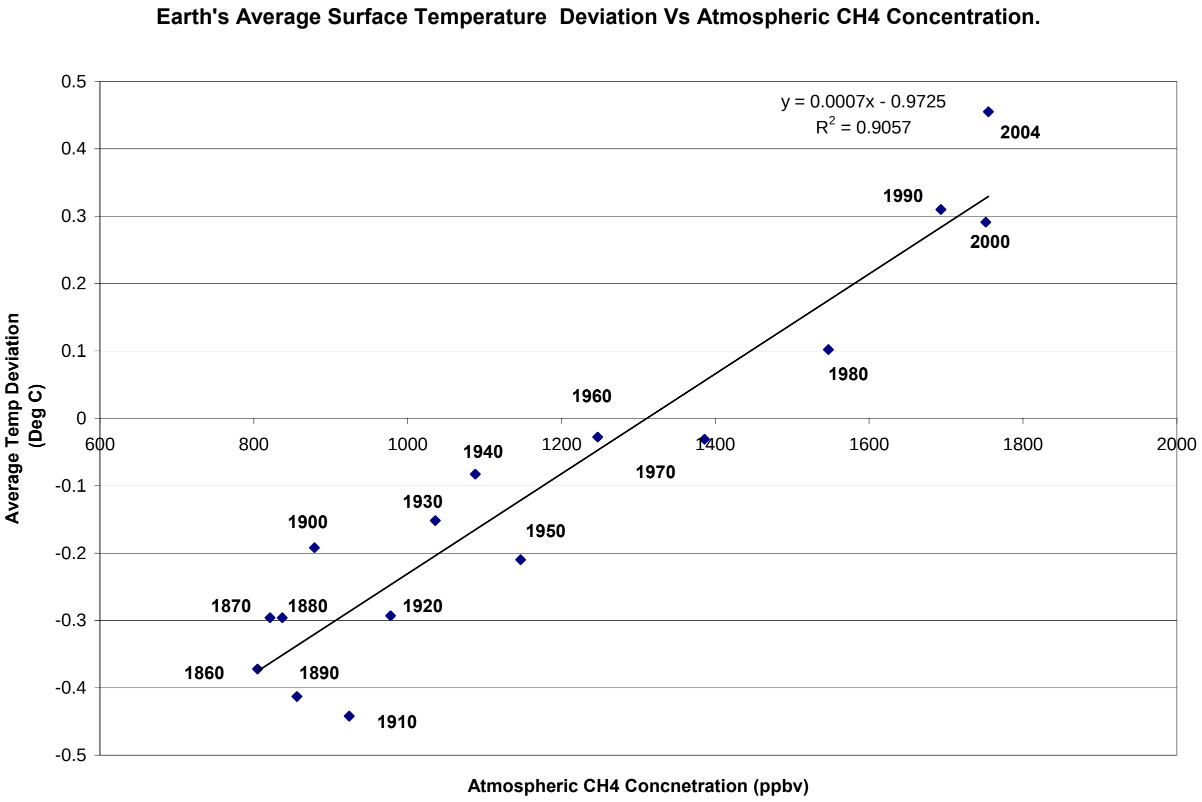

Figure 3: Global average surface temperature Vs methane concentrations

For both of these figures, the concentrations of CO_2 and CH_4 were obtained from NASA's website and the average surface temperature deviation was obtained from the Climatic Research Department of University of East Anglia (UK).From these figures it is also evident that the average surface temperature increase is a combined effect of the increase in both the gases and not merely due to the increase in atmospheric CO_2 concentrations or atmospheric CH_4 concentrations.

2.0 MECHANISM OF THE GREENHOUSE EFFECT

After absorbing heat from the incoming solar radiation, the earth emits energy like any other warm body. For the temperature of the earth to remain constant, the amount of energy emitted by the earth should be equal to the energy absorbed by it. The emitted energy is neither visible light nor UV light but rather it is infrared light having wavelengths from 4 μm to 50 μm ; known as the thermal infrared region since the energy is in the form of heat.

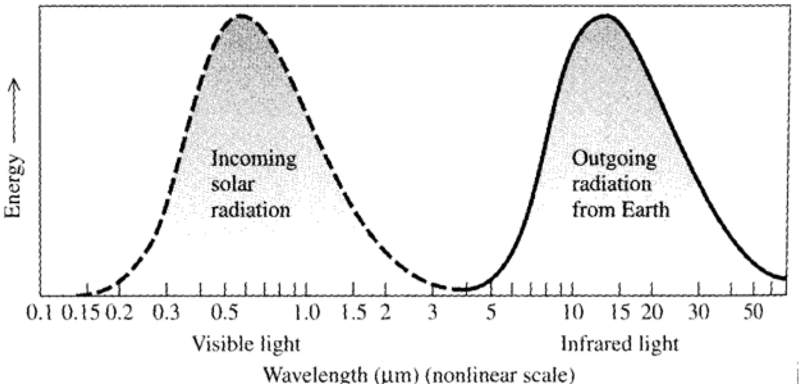

Figure 4:Wavelength distributions for light emitted by the sun (dashed curve) and by the Earth's surface and the troposphere (solid curve). (Source: Baird, Colin, "Environmental Chemistry"2nd Edition, W.H.Freeman Company, NY, 1998.)

Not all of the infrared radiation emitted by the earth's surface and atmosphere escapes directly to space as some gases in air can temporarily absorb thermal infrared light of specific wavelengths emitted by the earth's surface. Shortly after it's absorption by airborne molecules such as H_2O, CO_2, CH_4, this infrared light is re-emitted in all directions in a completely random manner. Thus some of the thermal IR is redirected towards the earth's surface, is reabsorbed and consequently further heats both the surface and the air. This phenomenon is the greenhouse effect and is responsible for the earth's surface temperature being almost 288ºK rather than about 255ºK. The phenomena that is a cause of concern is that the increase in concentration of trace gases will cause a redirection of even more of the outgoing thermal radiation and would this eventually contribute in the increase in the temperature of the earth.

2.1 HOW GREENHOUSE GASES ABSORB ENERGY: MOLECULAR VIBRATIONS

Nitrogen (N_2) and Oxygen (O_2), the principle constituents of the atmosphere, are incapable of absorbing infrared light.

The absorption of light takes place when its frequency matches the frequency of an internal motion within a molecule that it encounters. The vibrations of the molecules atoms relative to each other are relevant for frequencies in the infrared region. The vibrations in molecules for the absorption of light are primarily of the bond stretching type and the bending vibration type. Bond stretching takes place when oscillatory motion takes place between two atoms bonded to each other. Bending vibration are oscillations which take place between two atoms bonded to a common third atom within the molecule.

If infrared light is to be absorbed by a molecule during a vibration, there must be a difference in the position in the molecule between its nucleus (positive charge) and electron cloud (negative charge) at some point during the motion i.e. the molecule must have a dipole moment during some stage of it’s motion. Specifically, there must be change in the magnitude of dipole moment during the vibration. Consequently the molecule can absorb light only during asymmetric stretching. The centers of free charge coincide in free atoms and in homonuclear diatomic molecules like O_2 and N_2 and the molecules have dipole moments of zero during all times of their vibrations.

In the case of methane, a methane molecule contains four C-H bonds. The C-H bond stretching vibrations occur well outside the thermal IR region, but due to the H-C-H bond angle bending vibrations occurring near the edge of the thermal IR spectrum, methane absorbs IR at 7.7μm. Methane absorbs a greater fraction of the thermal IR photons that pass through them than CO_2 and has a greater global warming effect than CO_2. (Baird, 1998)

3.0 PROBLEM DESCRIPTION: METHANE

In December 1997, more than 160 countries met in Kyoto, Japan, to persuade limitations on greenhouse gases for the developed nations, pursuant to the objectives of the Framework Convention on Climate Change of 1992.The Kyoto Protocol was the outcome of the meeting in which the developed nations decided to reduce their greenhouse gas emissions relative to those what were in 1990.

Studies of ice air trapped in ice cores show that CH_4 has sustained a stable atmospheric abundance for centuries prior to the industrial revolution. The concentrations of methane at present are about 2.5 times of what they used to be before the industrial revolution. As shown in figure 6 below, methane levels have increased from around 750 parts per billion by volume (ppbv) to about 1750 ppbv today.

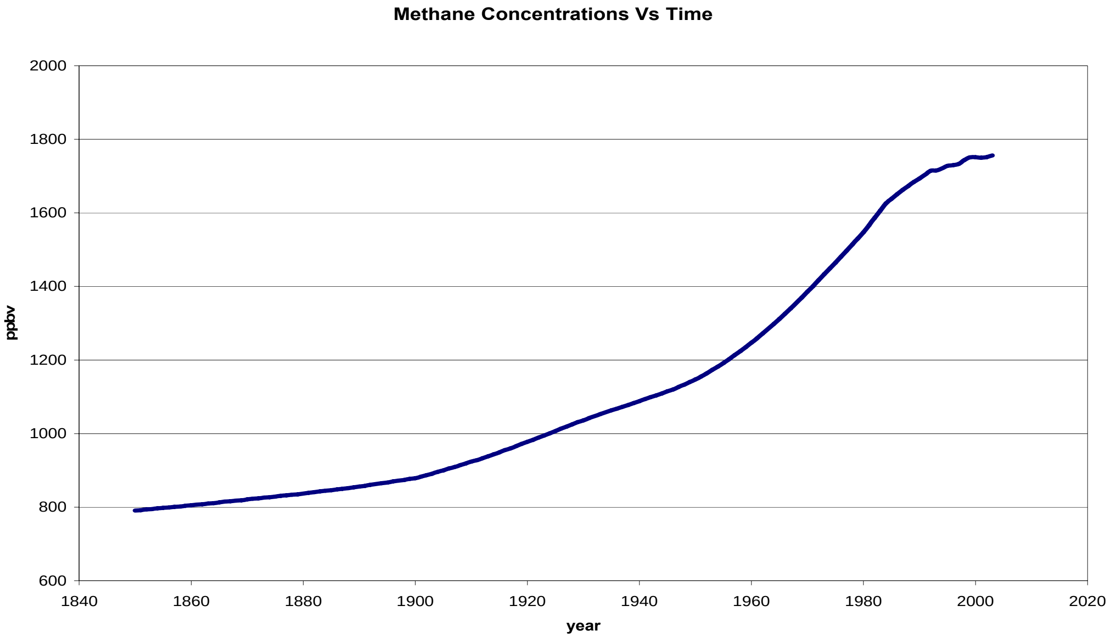

Figure 5: Increase in methane concentrations in the atmosphere from the mid 1800's till present.

One can also attribute the increase in levels of methane to the increasing population as in figure 6.

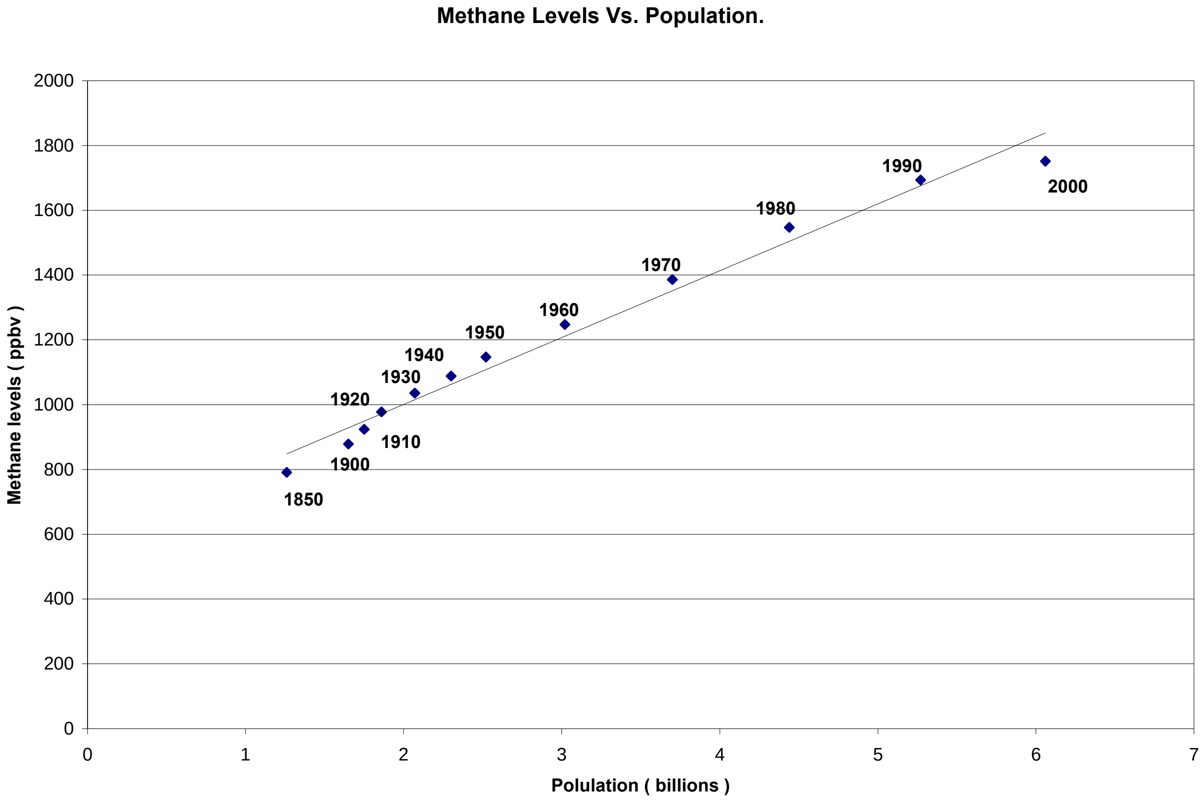

Figure 6: Concentrations of methane Vs world population

(Methane Data Source: NASA; Population Data Source: United Nations).

As seen in the graphs the increase in the concentrations of methane, which had been relatively stable till the early 1800's, can be attributed to the increase in various anthropogenic activities. These activities include the increase in the use of fossil fuels (Figure 8 & 9) along with the increase in rice agriculture to meet the needs of the exponential increase of the world population. With urbanization, there has also been a movement of the rural population into the urban areas increasing the amount of waste generated. Increasing demands for space and for agriculture has also led to an increase in the land burnt. All these are sources of atmospheric methane.

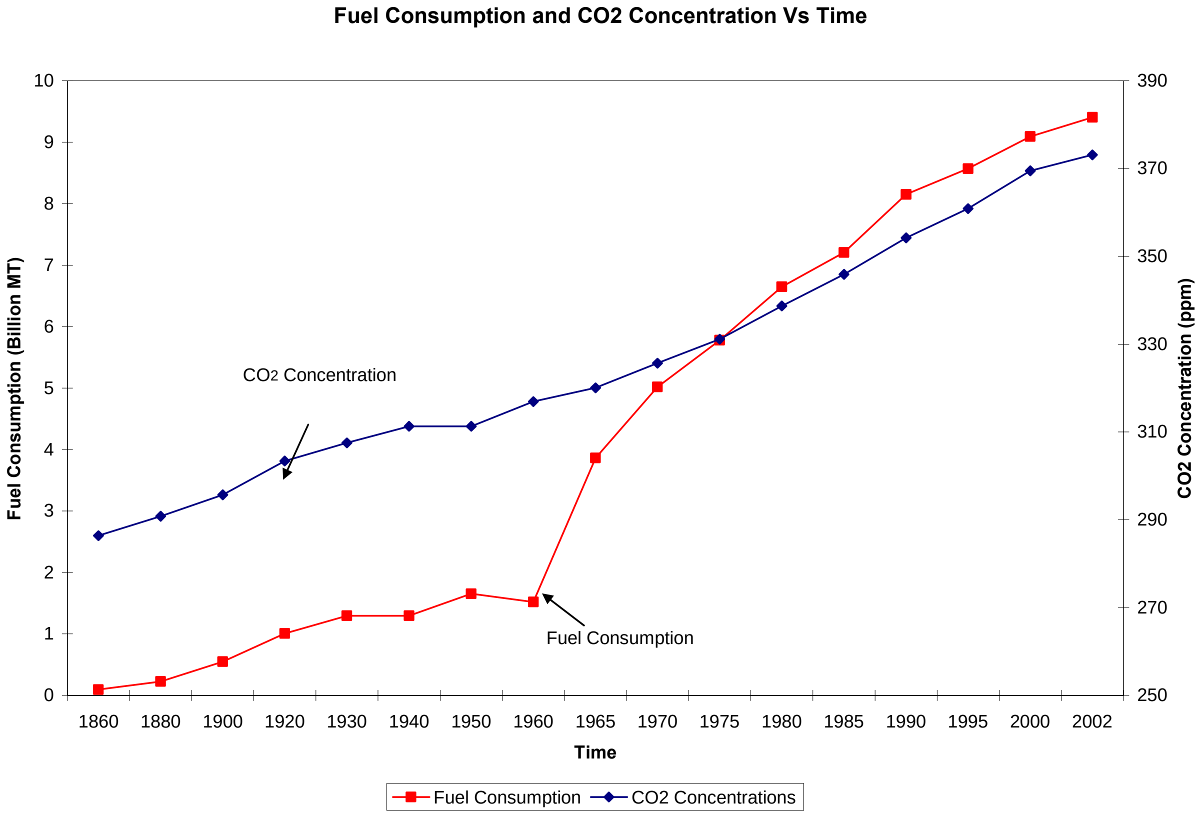

Figure 7: Carbon dioxide concentrations Vs fossil fuel consumption since late 1800's till present.

The historical data for fuel consumption in Figure8 and Figure 9 from 1860-1950 was obtained from Woytinski and Woytinski's "World population and production-Trends and outlook" and the fossil fuel consumption data from 1950 onwards was obtained from British Petroleum's Statistical Energy Review. For the data of the period comprising 1860-1950, the consumption of water power was excluded in our calculations and the coal equivalent was converted to oil equivalent.

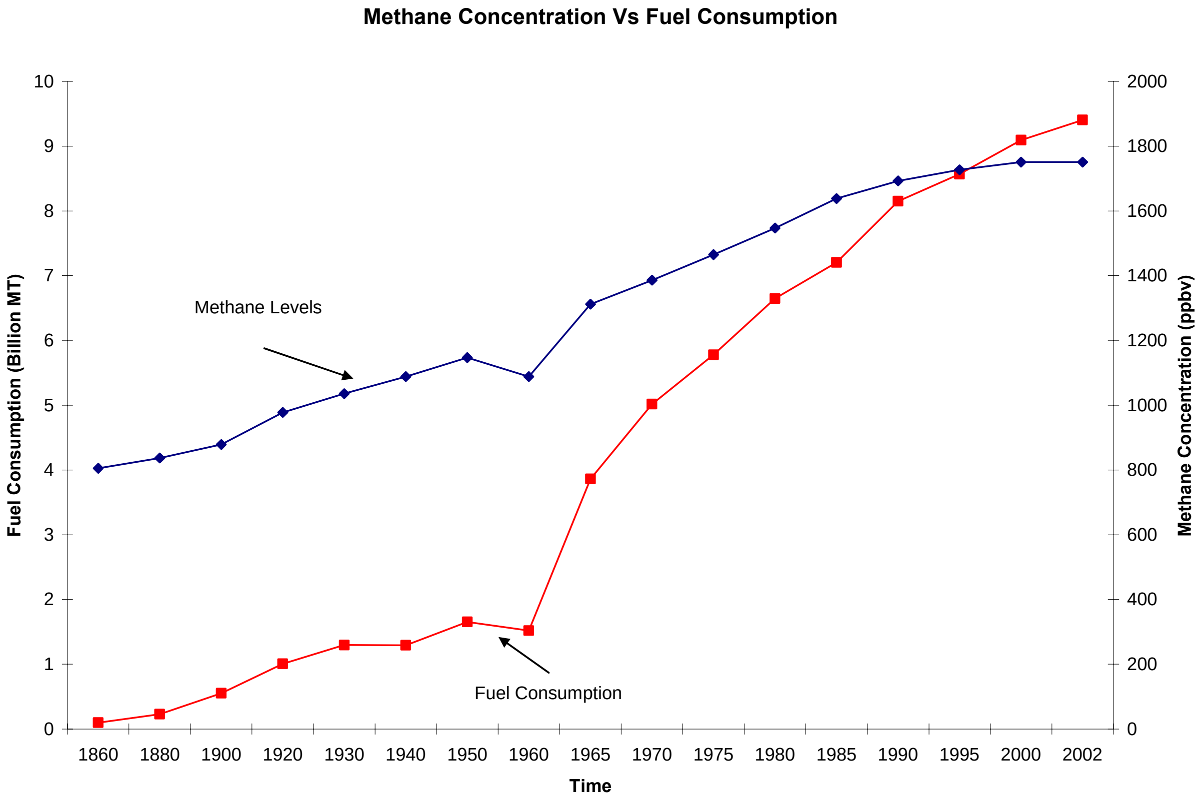

Figure 8: Methane concentrations Vs fossil fuel consumption since late 1800's till present.

Adding each molecule of methane has 21 times more effect on global warming than adding a molecule of carbon dioxide in the atmosphere. The number 21 is the global warming potential (GWP), a type of simplified index based on radiative properties which is used to estimate the potential future impact of emissions of different greenhouse gases in a relative sense. The reference gas is generally taken as CO_2. Moreover methane is also an important trace gas due to the role it plays in tropospheric chemistry.

The purpose of this study is to study the sources and sinks of methane and try to predict its future concentrations taking into account the "business as usual scenario" and the impact methane has on global warming. Understanding the sources and sinks will help us concentrate on the reduction of methane which has more of an impact on global warming than carbon dioxide and to see whether methane is following the same trend as carbon dioxide in the atmosphere. Another object of this study is to determine the change in temperature caused by the projected increase in methane levels over the time period, 2006 to 2030.

4.0 LITERATURE REVIEW

4.1 GLOBAL WARMING

Global warming is caused by the blocking of thermal infrared radiation to escape the earth, which in turn increases global surface temperatures. This has been attributed to the increase of the atmospheric trace gases caused by human activity (Dickenson and Cicerone, 1986) A burst of global warming has taken the global temperature to it's highest level in the past millennium, the average surface temperature having increased by about 0.6±0.2ºC since 1975 (Hansen et al., 2000, Jones et al.1999, Mann et al, 1999, IPCC 2001). Houghton et al state that human influence has been the dominant detectable influence on climate change over the last 50 years (Karl and Trenberth, 2003).

The concern that human activities may be affecting global climate has largely centered on carbon dioxide because of its importance as a greenhouse gas and also because of the rapid rate at which its atmospheric concentration has been increasing. It is being estimated that other greenhouse gases are contributing about half of the overall increase in the greenhouse radiative forcing on the climate (Wuebbles and Tamareis, 1993).

The changes in atmospheric composition take place due to the anthropogenic emissions of greenhouse gases such as carbon dioxide that results from the burning of fossil fuels and methane and nitrous oxide from multiple human activities. According to estimates, the continuous increase in use of fossil energy will lead to an average increase of global temperature by 1.0-3.5 º C in the coming 50-100 years (Kessel, 2000). Highly reflective micron sized aerosols, such as sulfate and strongly absorbing aerosols such as black carbon or soot are emitted into the atmosphere as a result of fuel burning (Karl and Trenberth, 2003).

4.2 METHANE

Methane was determined to be a component of the Earth's atmosphere in 1948 by the analysis of high resolution solar absorption spectra. (Dlugokencky et al,1994.) Methane is only second to CO_2 in its potential for future global warming (Khalil and Rasmussen, 1993). Adding more methane is more effective than adding CO_2 into the atmosphere both on a molecule as well as a mass basis (Wuebbels et al, 2002). Methane has a direct effect on the radiative balance of the troposphere because of its strong IR absorption at 7.66 μm where CO_2 and H_2O absorb only weakly (Dickenson and Ciceraone, 1986).

The concentrations of methane in the troposphere have more than doubled since 1800, the present concentrations of methane in 1998 being about 1745 ppbv and the concentrations of methane before the onslaught of industrialization being about 700 ppbv (Etheridge et al,1992; IPCC,2001). Since direct systematic measurements of it's trends did not begin until 1978, most of the data containing the record of atmospheric CH_4 for earlier times, are obtained by analyzing bubbles of ancient air preserved in polar ice (Khalil and Rasmussen, 1987; Dlugokencky et al, 1994).

Methane is released as a result of both natural as well as human induced activities. Figure 10 shows the break up of individual sources of methane into the atmosphere.

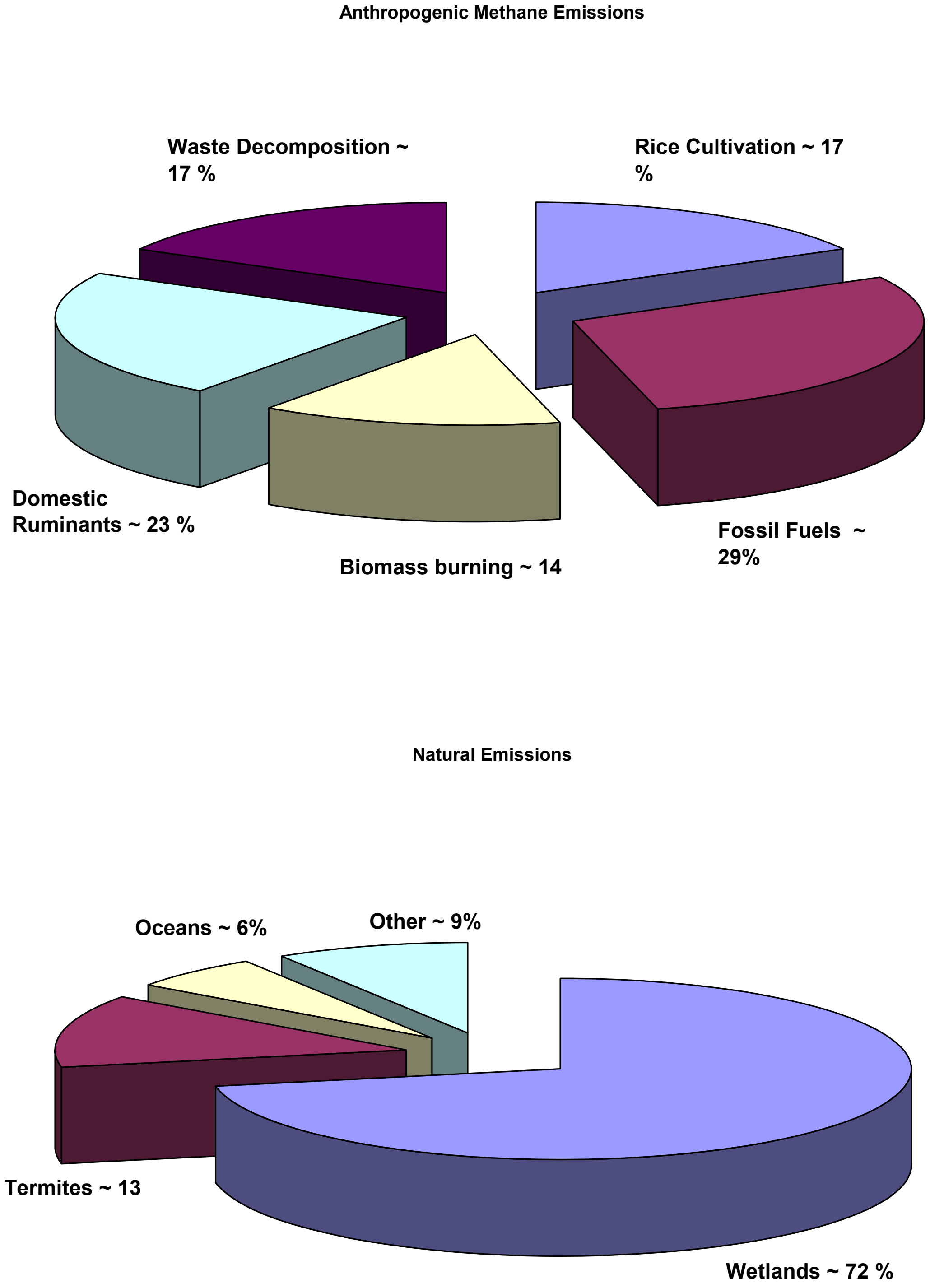

Figure 9: Break up of the anthropogenic and the natural Sources of methane (Source: Wuebbles, 2002 and Khalil, 2000)

4.3 ANTHROPOGENIC SOURCES OF METHANE

Methane from Energy sources

Methane from fossil fuels account to about 29% of the total anthropogenic sources (Khalil, 2000; Wuebbles and Hayhoe, 2002) .Fossil fuels are attractive not only because they are abundant and relatively inexpensive but also because they are used effectively and efficiently (Judkins et al, 1993).Methane is emitted by the extraction of fossil fuels such as natural gas, coal and petroleum (Wuebbles and Hoyoe, 2002).

4.3.1 Natural gas

Methane is released into the atmosphere by the leakage of natural gas during its production, transmission, storage and distribution and also during its venting and flaring.

Gas leakage can occur during extraction at the well head (transport of large quantities under high pressure) and during transmission (which is transfer to the end user under low pressure).The gas leakage rates depend on various factors. These factors may include well head practice, the standard and maintenance of the pipe lines, the pressure of gas inside these pipelines (Watt Committee, 1993).These factors are not easy to determine and not well known in many countries. The leakage rates are very uncertain and vary tremendously from country to country (Law and Nisbet, 1996).Because of the difficulty in estimating the methane emissions from the venting and flaring of natural gas we will assume a constant value of 15 Tg yr^{-1} as done by Law and Nisbet (1996) and estimated by Cicerone and Oremland in 1988.

4.3.2 Coal

Coalification-the process which produces coal also produces methane and other gases. (Revised IPCC Guidelines Workbook, 1996). These gases are stored in the coal bed itself. The excess gas produced in the process migrates into the surrounding rock strata, forming traditional gas deposits mined by the natural gas industry. When the coal seam is exposed to the atmosphere, the methane trapped in the coal seams is released. The methane in the coal seam depends on the coal age, moisture and the depth (Beck, 1993).Methane is released during the mining, crushing or inefficient combustion of coal by the process of desorption (Law and Nisbet, 1996)

4.3.3 Domestic Ruminants

Enteric fermentation is a digestive process by which carbohydrates are broken down into simple molecules for absorption into the blood stream by microorganisms. Methane is a by-product of enteric fermentation in herbivores. Due to the presence of specific microorganisms in their digestive tract, ruminants (e.g. cattle, sheep, etc) and some non-ruminant animals (e.g. pigs , horses), digest cellulose, a type of carbohydrate , and are able to produce methane.(IPCC Guidelines workbook,1996).

The eructation of methane by cattle begins approximately 4 weeks after birth when the solid feeds are retained in the reticulorumen (Anderson et al, 1987; Johnson and Johnson, 1995)

4.3.4 Rice Cultivation

Of the wide variety of sources of atmospheric methane, rice paddies are considered one of the most important. Rice soils are flooded for a large part of the year and usually provide an optimal environment for methane production. By flooding and puddling the soil optimal conditions are created which enhance the fertility of the soils and stabilize the rice eco-system. Flooding provides abundant water, buffer soil pH, enhances nitrogen fixation and carbon supply, increases diffusion rates, mass flow and nutrient availability (Bachelet and Neue, 1993). Methane is produced by the anaerobic decomposition of organic matter in rice fields. The production of methane is the final step in a sequence of anaerobic decomposition of organic matter which is allowed by anoxic conditions in waterlogged soils e.g. paddy rice fields. (Wassmann et al, 1993).

Figure 11 shows the processes involved in methane emissions involve 1) methane production, 2) methane oxidation and 3) methane transportation.

Redox potential is the most important factor for the production of CH_4 in soils. Takai et al.(1956) demonstrated that the redox potential of a soil must be below -200mV in order to have CH_4 production (Minami,1994). The final step of several anaerobic degradation chains is methane. The biochemical pathways which produce methane include fermentation of methylate compounds (e.g. acetate, methanol, trimethylamine, and dimethylsulfide) and CO_2 reduction with molecular hydrogen. Although not as significant as other pathways, methane is also formed by the reduction of CO with formic acid. Thus the methaogenic bacteria can be subdivided into methlyotrophic, obligate chemolithotrophic, and ‘qausi’-chemilithotrophic microorganisms (Wassman et al, 1993). The optimum temperature for these methaogens was found to be between 30ºC and 40ºC.

Methane is oxidized by aerobic methanotrophs in soils and in floodwaters of rice paddies, the immediate product being methanol.

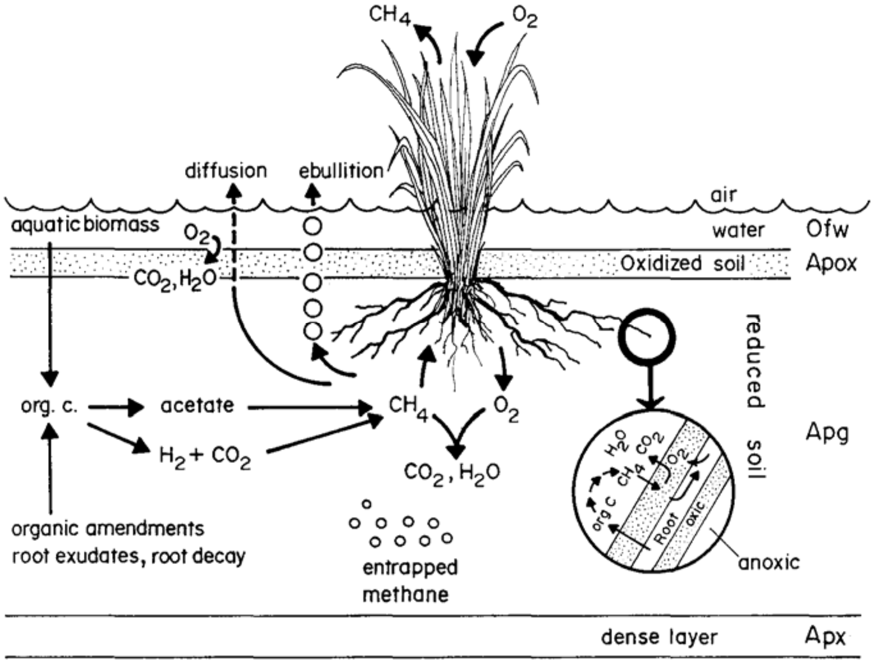

Figure 10: Depiction of production, reoxidation, and emission of CH_4 in a paddy field (Source: Neue and Roger, 1993)

Methane is transferred by three different pathways. They are the diffusion of dissolved methane, the emergence of methane in the form of gas bubbles and plant mediated transport. Plant mediated transport or transport through the aerenchyma is the most important phenomena for CH_4 transport. About 90% of the total CH_4 released from rice paddies is through the aerenchyman system of rice plants. This path of methane through rice plants includes diffusion into the root, the conversion to gaseous methane in the root cortex; diffusion through cortex and aerenchyma and finally release to the atmosphere through micropores in the leaf sheats.

4.3.5 Biomass Burning

Biomass material contains about 40% carbon, 53.3% oxygen and 6.7% hydrogen by weight. Nitrogen accounts for between 0.3 and 3.8% and sulfur for between 0.1 and 0.9%, depending upon the nature of the biomass material (Bowen, 1979).

The estimates of CH_4 emissions from biomass burning are rather uncertain. Methane emissions from the burning of agricultural residues e.g. residues of rice straw, sugarcane and other agricultural disposals are also significant. Other major sources of methane release into the atmosphere are savannah burning, deforestation, shifting cultivation and firewood and agricultural waste burning. (Crutzen and Andrea, 1990).

Biomass burning includes the combustion of living and dead material in the forests, savannahs, agricultural wastes, and the burning of fuel wood. It includes human initiated burning of vegetation for land clearing as well as natural, lightning induced fires, although it is thought that the bulk of biomass burning is human initiated rather than naturally occurring. (Levine et al, 2000.)

Ideally the product of complete combustion of biomass is carbon dioxide and water vapor according to the following reaction:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

Where CH_2O represents the average composition of biomass material. The product of incomplete combustion of biomass produces other carbon species, including Carbon monoxide (CO), methane, nonmethane hydrocarbons (NHMC's), and particulate carbon. This is always the case as complete combustion is not achieved under any conditions. In addition, nitrogen and sulfur species are produced from the combustion of nitrogen and sulfur species in the biomass material. (Khalil,1993).The emissions of methane are dependent upon the stage of combustion reached as well as the carbon content of the biomass burned.(Levine et al.,2000).Bolle et al suggest that the pyrogenic contribution of the increase in CH_4 from 1940 to 1980 has gone up from 10 to 40% (Crutzen and Andrea,1990).

4.3.6 Waste

4.3.6.1 Solid Wastes

Waste landfills have been recognized as a large source of anthropogenic methane and an important contributor to global warming (IPCC 1996, Kumar et al, 2004) Methane is emitted by the biogenic waste in anaerobic environments provided by landfills and waste water pool. A significant amount of carbon that is recycled though the environment consists of domestic and industrial wastes. This carbon is an appreciable source of methane due to the decay of organic carbon due to the anaerobic conditions developed when dumped in landfills.(Sheppard et al, 1982; Bingmer and Crutzen,1987).

Solid wastes disposal sites (SWDS) contains organic matter which is broken down by bacterial action in a series of stages that result in the formation of CH_4 and CO_2 (termed as biogass or landfill gas) and further bacterial biomass. This is done by anaerobic bacteria. Because of the dumping of large amounts of waste, the oxygen availability soon decreases and the decay is taken over by anaerobic microorganism, which is based on the interactions of different kinds of bacteria. Organic matter is first broken down to small soluble molecules which include a variety of sugars. These are further broken down to hydrogen, CO_2, and a range of carboxylic acids. These acids are converted to acetic acid which, together with hydrogen and CO_2, forms the major substrate for growth of methanogenic bacteria. The landfill gas produced contains 50% CO_2 and 50% CH_4 by volume, although landfill gas may contain less CO_2 because part of the CO_2 becomes dissolved in landfill water (Gunerson and Stuckey, 1986)

Bingmer and Crutzen further state that sanitary landfilling near urban centers is the main method in industrialized countries while crude dumping is common in the developing world.

4.3.6.2 Wastewater handling

Waste water can produce CH_4 under anerobic conditions. Anaerobic methods are used to handle wastewater from municipal sewage and from food processing and other industrial facilities, particularly in industrial countries.

Methane is again produced by acetate cleavage or by the reduction of CO_2 with hydrogen. This acetic acid is the result of the conversion of amino acids or sugars. Amino acids along with sugars and higher molecular fatty acids are formed by the hydrolysis of proteins, hydrocarbons and lipids formed by the breakdown of wastewater organic fraction under anaerobic conditions (El-Fadel and Massoud, 2001).Aerobic decomposition processes in wastewater demand more oxygen than can be supplied by surface diffusion (Czepiel,1993)

Degradable organic carbon (DOC) is the main factor which determines the amount of CH_4 produced from wastewater. This DOC is expressed in terms of biological or chemical oxygen demand (BOD) or (COD).Temperature, pH, retention time, degree of wastewater treatment are the environmental factors which influence CH_4 production. Anaerobic systems are very sensitive to the presence of oxygen, which inhibits CH_4 production completely (Casey, 1997; El-Fadel and Massoud, 2001)

4.4 NATURAL SOURCES OF METHANE

Methane Hydrates

Gas hydrates are formed by the physical combination of water and low molecular weight gases. They are solid crystalline molecular complexes formed beneath the earth's surface due to the persistence of low temperatures. These hydrates are a more concentrated form of natural gas which contains 10-15% gas (by weight) and occupy less volume (20% to 80%) than would the same gas in an unhydrated state. (Lee and Holder, 2001; Holder et al, 1984). Methane can be released from hydrates with changes in temperature, pressure, salt concentrations, etc. However, this concentration could be much larger if global temperature increases resulting in massive methane hydrate decomposition (EPA, 2004).

Lelieveld et al (1998) estimate the release of methane from these gas hydrates at the rate of 10 Tg/yr.

Wetlands

Wetlands were the main source of atmospheric methane prior to the industrial era, with other relatively minor contributors (Chappellaz et al, 1993; Methews, 1993). They still are most likely the largest natural source of methane in the atmosphere.

A wide range of environmental parameters influence methane emissions from natural wetlands. These include availability of nutrients and organic carbon, vegetation cover, and most importantly water table depth and soil temperature (Miller et al, 1999; Van Der Nat and Middelburg, 2000).

Lelieveld et al (1998) estimate a source strength of 225 Tg/yr from wetlands, but they included rice agriculture in wetlands. Houweling et al (1999) estimated a source strength of 145 Tg/yr. Fung et al. estimated methane release from wetlands to be about 115 Tg/yr, whereas Cao et al (1998) estimated a release of 92 Tg/yr.

Termites

Termites, although having wide geographical distribution, are particularly abundant in area where biomass is present. Even though a termite produces an credibally amount of methane per day, but when this is multiplied by the world population of termites, the methane emissions from termites are significant (Judd et al, 1993). There is some sort of consensus among authors regarding the emissions from termites. Fung et al (1991), Lelieveld et al and Houweling at al estimate termite emissions to be about 20 Tg/year.

Table 1 sums up the anthropogenic and the natural sources of methane.

Table 1: Anthropogenic and Natural Sources of Methane.

Anthropogenic Sources of Methane	Fossil Fuels (Natural Gas Production, Coal Mining)
	Rice Agriculture
	Domestic Ruminants
	Biomass Burning
	Waste (Solid Wastes, Wastewater Handling)
Natural Sources of Methane	Methane Hydrates
	Wetlands
	Termites

4.5 SINKS OF METHANE

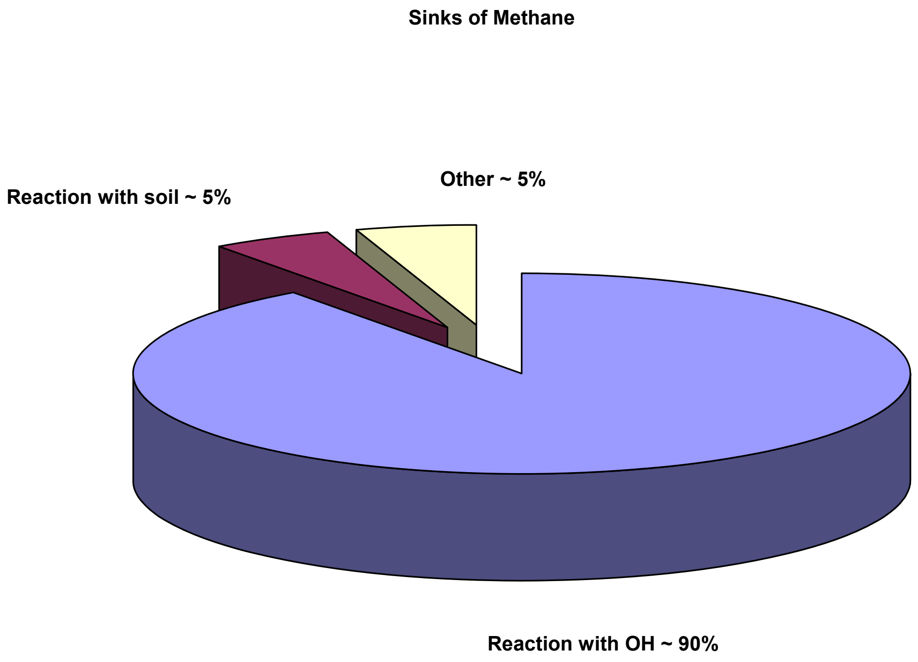

Figure 11: Sinks of methane

Reaction with the hydroxyl [OH] radical is the primary removal method of greenhouse gases containing one or more H atoms. All greenhouse gases except CO_2 and H_2O are removed from the atmosphere primarily by chemical processes (IPCC, 2001). There are only one major and two minor sinks for tropospheric methane.

Methane is removed from the troposphere by the following reaction.

$$CH_4 + [OH] \rightarrow CH_3 + H_2O$$

The majority of methane (90%) is removed from the atmosphere by this reaction. (Wuebbles, 2002).

Ridgewell et al. (1999) estimate that about 5% of the methane is removed through dry soil oxidation and the rest is either consumed by its reaction with [Cl^-] atoms or is transported to the stratosphere as estimated by Gettelman et al. in1997 and Singh et al.1996.

The [OH] radical thus plays a very important role in atmospheric chemistry by reacting with many trace gases and free radicals. In turn the concentration of OH also depends on the atmospheric levels of the species with which OH reacts. Most of the OH is consumed by reaction with either CO or CH_4, which may result in the decrease of OH, resulting in longer atmospheric lifetimes of the gases and free radicals with which OH reacts (Lu and Khalil, 1991).

Modeling studies have shown that the concentrations of OH have decreased since pre-industrial times between 10 and 30% due to increase in the CH_4 and CO concentrations as the concentrations of OH are closely related to CO and CH_4 concentrations. (Wang and Jacob, 1998; Wuebbles 2002). However studies by Karlsdottir and Isaken (2000) show the present OH concentration to be relatively steady or increasing perhaps. The reason might be that the CH_4 and CO increase is balanced by the increases in tropospheric ozone (O_3). OH is formed by the photo-dissociation of O_3 into O (^1D) which in turn combines with water vapor to form two OH radicals. The concentrations of OH are assumed to be constant for the time period concerned for our model.

4.6 MODEL

Objective:

The objective of this work is to predict the concentrations of methane over time by treating the entire atmosphere as a single continuous stirred tank reactor, with the mass balance having being performed on component methane. The reaction feeds are the sources mentioned in table 1.

There is no reactor effluent, or if an effluent is considered, for mass balances purposes, it does not contain methane. The methane is consumed via chemical reaction in the atmosphere via chemical reaction with troposheric OH radicals.

The simplest form of the model is

Accumulation = Sources - Sinks

$$\text{or},\ \frac{d[CH_4]}{dt} = \sum_i F_{CH_4} - k_{OH}[CH_4][OH] - k_{soils}[CH_4][\text{Soil Area}] - k_{other}[CH_4]$$

where $\sum_i F_{CH_4}$ is the summation of the various individual sources of methane

$-k_{OH}[CH_4][OH]$ is the sink of methane via reaction with [OH] in the atmosphere

$-k_{soils}[CH_4][\text{Soil Area}]$ is the consumption of atmospheric CH_4 in the soils

$-k_{other}[CH_4]$ is the removal of CH4 via reaction with Cl- or transport to the stratosphere

Since OH is considered constant and about 90% of the removal of CH_4 is via its reaction with OH , the above equation can be rewritten as :

$$\frac{d[CH_4]}{dt} = \sum_i F_{CH_4} - k_{CH4}[CH_4]$$

Since this is a first order chemical reaction, therefore $k_{CH4} = \frac{1}{\tau}$

The equation for the model can be written as

$$\frac{d[CH_4]}{dt} = \sum_i F_{CH_4} - \frac{[CH_4]}{\tau}$$

where $[CH_4]$ is the number of Tera-grams of Methane (which is the commonly used unit for methane) . 'τ' is the atmospheric lifetime of methane made up of various sinks. It can be given by the equation:

$$\tau = \frac{1}{(1/\tau_{OH} + 1/\tau_{soi}l + 1/\tau_{other})} \quad \text{(Khalil et al, 1996)}$$

The value of $1/\tau_{OH}$ is the same at the product of the rate constant of the reaction between $[CH_4]$ in the atmosphere and [OH] radicals. Therefore, $1/\tau_{OH}$ = k[OH], as [OH] is treated as a constant (Karlsdottir and Isaken ,2000).

Khalil and Rasmussen in 1993, take into account a varied form of the above equation. They introduce a parameter 'λ' which takes into account the rate at which concentrations of [OH] might be changing over time.

Dlugokencky et al. (1998) used the equation above to calculate the source strength in order to figure out the decrease in growth rate of atmospheric methane.

5.0 MODEL FORMULATION

5.1 METHANE EMISSIONS FROM NATURAL GAS PRODUCTION AND TRASMISSION

Methane is released by the venting and flaring of natural gas as well as the transmission and distribution of natural gas.

Since the amount of gas retrieved increases with the age of the installation, the temporal trend of the amount of CH_4 vented and/or flared is not related to production (Law and Nisbet, 1996). Because of the difficulty of estimating a temporal trend for emissions from venting and flaring of natural gas, a constant value of **15 Tg/yr** is assumed for the model in this thesis. This assumes that the increases in methane production are balanced by reductions in venting and flaring.

For the estimate of CH_4 emissions from natural gas production, the world was divided into two groups. The first group comprised of the former Soviet Union (FSU) and the second group comprised of the Rest of the world (ROW).

Natural gas production figures were obtained from the 2003 British Petroleum Statistical Review of World Energy worksheet. Gas leakage rates of 2 % of the entire natural gas production were used for ROW for the entire time period. For the FSU a gas leakage rate of 5% of the entire gas produced was used. These higher leakage rates are attributed to the age of the pipleleines, higher leakage rates from the valves and fittings etc.

It was assumed that 90% of the natural gas is methane for the calculations.

The temporal estimates for methane emissions from natural gas production are presented in the following figure. For the sake of uniformity of the model the 10^{th} year is the time taken as the start of methane emissions as the data for the entire world was available since 1970 onwards.

A value of 717 g/m^3 was taken as the density of methane at 25ºC and 1 atm. to convert the volume of methane released to Tg.

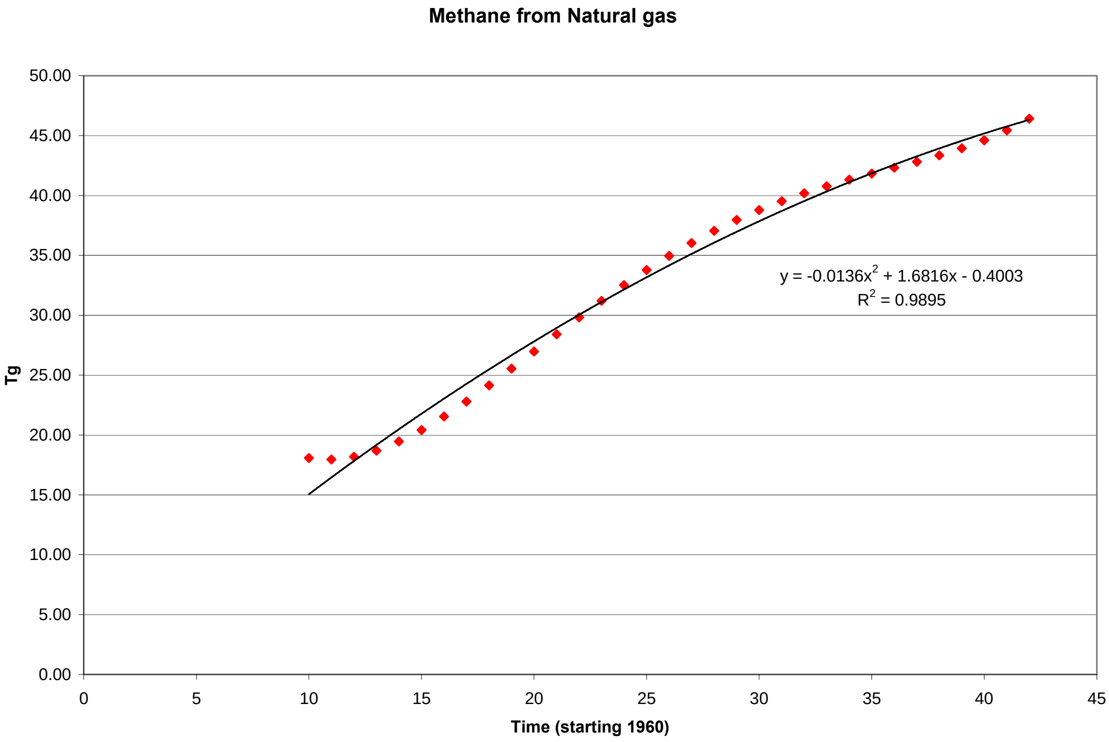

Figure 12: Model of methane production from Natural Gas.

The temporal model for the emissions of methane emissions from natural gas production and transmission was:

$y = -0.0136t^2 + 1.6816t - 0.4003$

The constant value of 15 Tg for venting and flaring will be incorporated in the final simulation of the model.

The temporal estimates of methane emissions lie between 15 and 50 Tg of methane per year. These are close to the IPCC (1996) estimates of 30 to 70 Tg methane per year.

5.2 METHANE EMISSIONS FROM COAL PRODUCTION

The methodology adopted was the same as laid out in the 1996 IPCC Guidelines for the calculation of National Greenhouse gas inventories. The equation for calculating CH_4 emissions from mining activities was:

$$\textbf{CH}_\textbf{4}\ \textbf{Emissions} = \textbf{Coal Production} \times \textbf{Emission Factor} \times \textbf{Conversion Factor}$$

Where CH_4 Emissions are in Tg/yr

Coal Production is in Tonnes/yr

Emission Factor is in m^3/ton

and Conversion factor is in g/m^3

The only difference between the IPCC methodology and the one adopted here was in the Emission factor. The Emission factor in the IPCC guidelines was according to the type of mines (underground or surface) while the emission factor taken in this thesis is according to the type of coal mined (hard or brown).This difference was due to the non-availability of data for the types of mines and the break up of coal mined form each kind of mine for the entire world at different times.

The data for the production of coal was taken from the Energy information and Administration website of the Department of Energy (Govt. of the United States). The data was obtained for lignite (brown) coal and bituminous as well as anthracite (hard) coal. The production of anthracite and bituminous coal exceeded the production of lignite coal throughout the world.

The emission factors was taken from Smith and Sloss' 1992 report which give the emission factors on the basis of the type of coal mined. The estimates for hard coal are between 5 and 20 m^3 of CH_4 per ton of coal produced and between 0.05 and 0.5 m^3 of CH_4 per ton of brown coal mined. For the estimation of methane emissions from coal in this thesis, the emission factors were taken to be an average of 5 and 20 m^3/ton for hard coal and an average of 0.05 and 0.5 m^3/ton for brown coal respectively.

The conversion factor was the density of methane at 25º C and 1 atm., taken to be
717 g/m^3.

The final temporal estimate of CH_4 emissions from coal are presented in the figure below. For the sake of uniformity of the model, the starting period for the estimate of coal emissions was taken to be the 20th year (1980) since the coal production statistics for the entire world was available from this time.

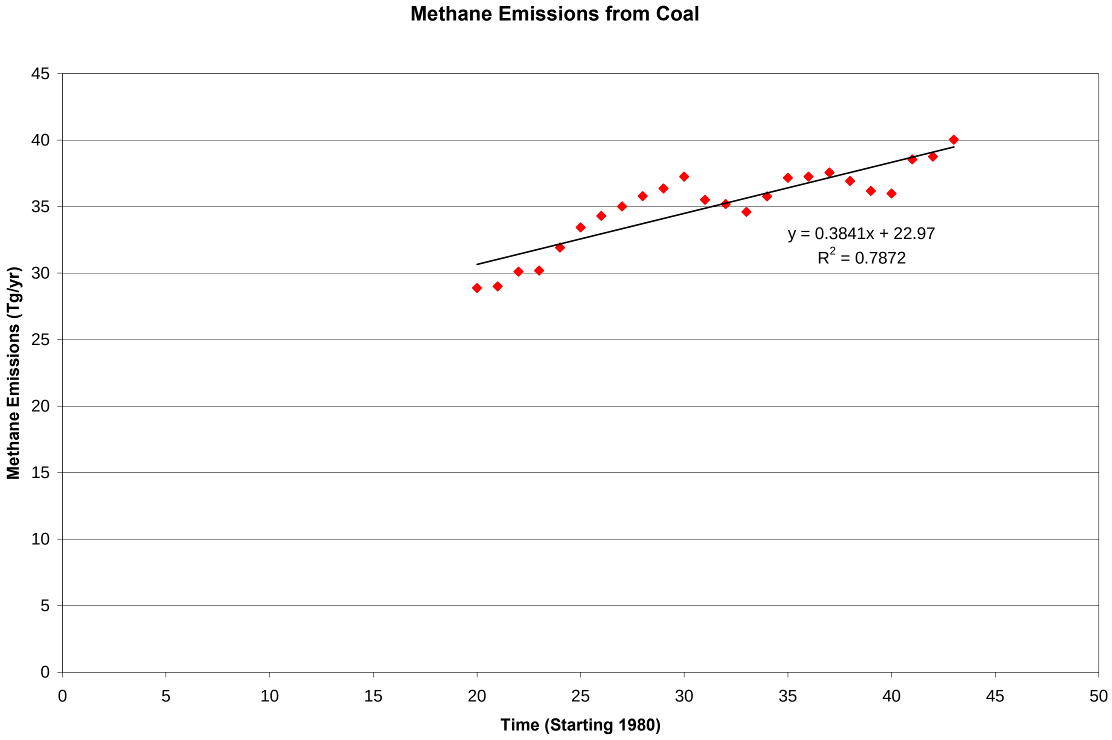

Figure 13: Model of Methane production from Coal.

The model for coal production as a source of Methane was :

y =0.3841t+22.97

with R^2 = 0.7872

Our model estimates coal emissions between 25 and 40 Tg of CH_4 per year with no clear trend. This is due to the variation in coal production throughout the world, with focus now shifting from coal to alternate forms of energy such as natural gas, nuclear energy etc. Estimates from literature are between 20 and 50 Tg of CH_4/yr for coal mining (IPCC, 1995).

5.3 METHANE EMISSIONS FROM RICE AGRICULTURE

Rice paddies are considered to be one of the most important anthropogenic sources because the demand for rice is proportional to the population. Methane is produced by the anaerobic decomposition of organic material in flooded rice fields which escapes to the atmosphere primarily by the diffusive transport through the rice plants during the growing season.

Methane emissions from rice paddies were estimated using the following correlation:

$$\mathbf{CH_4\ Emissions} = \mathbf{Emission\ Factor} \times \mathbf{Rice\ Production}$$

The Emission factor was obtained on a rice production basis. Rice production was obtained from the FAO website. Major rice growing countries were taken into account for the calculations. The countries in question were China, India, Japan, Philippines, Thailand, and USA. Rice production from the rest of the world was considered in the ‘other’ category. The emission factors for the various countries was obtained from table 2

Table 2: Rice emission factors

Country	Total area of rice paddies (Mha)	Total Rice grain yield (Tg/yr)	CH_4 emissions (Tg/yr)	Emission Factor (g CH_4/g rice production)
China	32.2	174.7	13-17	0.0858
India	42.2	92.4	2.4-6	0.0454
Japan	2.3	13.4	0.02-1.04	0.0395
Thailand	11.7	19.2	0.5-8.8	0.2421

Table 2: Continued

Philippines	3.5	8.9	0.3-0.7	0.0561
USA	1.0	6.4	0.04-0.5	0.0421
Other	54.6	158.5	9.2-20	0.0921

Table 2 Source: Sass (1994), Minami and Takata (1997).

The rice emission factors on a rice production basis were obtained by dividing the average emissions from the above table with the total production mentioned. This emission factor was used to obtained the temporal emissions of methane. The rice production statistics were obtained form the FAO website.

The production of rice has dramatically increased, especially since the 1960's. Although the area of rice harvested has not changed by a great extent (The area harvested in 2003 was 1.3 times the area harvested in 1960), the total rice production has changed since 1961 (The total production in 2003 was 2.7 times the production in 2003) to meet the needs of the growing population. This is has been achieved by the use of high yielding rice cultivars, large investments in irrigation schemes and improved soil, water and crop management. These developed irrigation schemes and the sorter growth duration of modern cultivars increased the harvested area by allowing 2 to 3 crops per year. However there has only been a slight increase in the total area harvested due to the expansion of residential and industrial areas as well as diversification of crops (Neue and Roger, 1993)

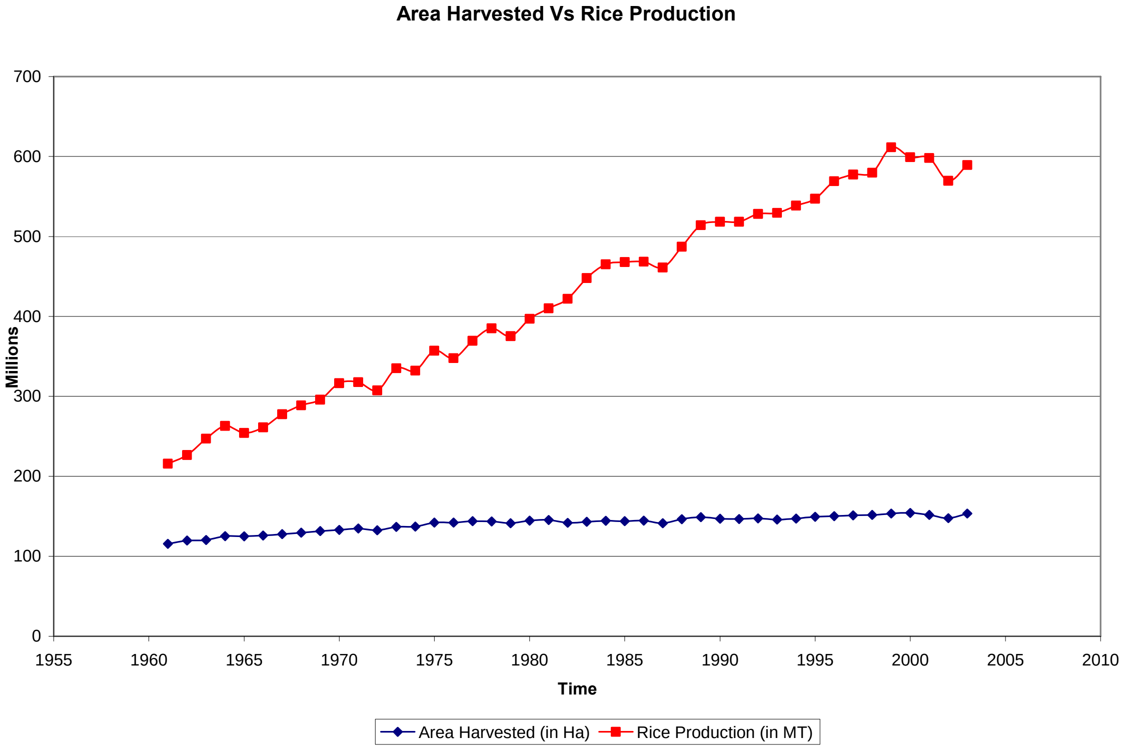

Figure 14: Total rice production vs area harvested for time starting 1960.

The methane emissions from rice paddies are shown in the figure below.

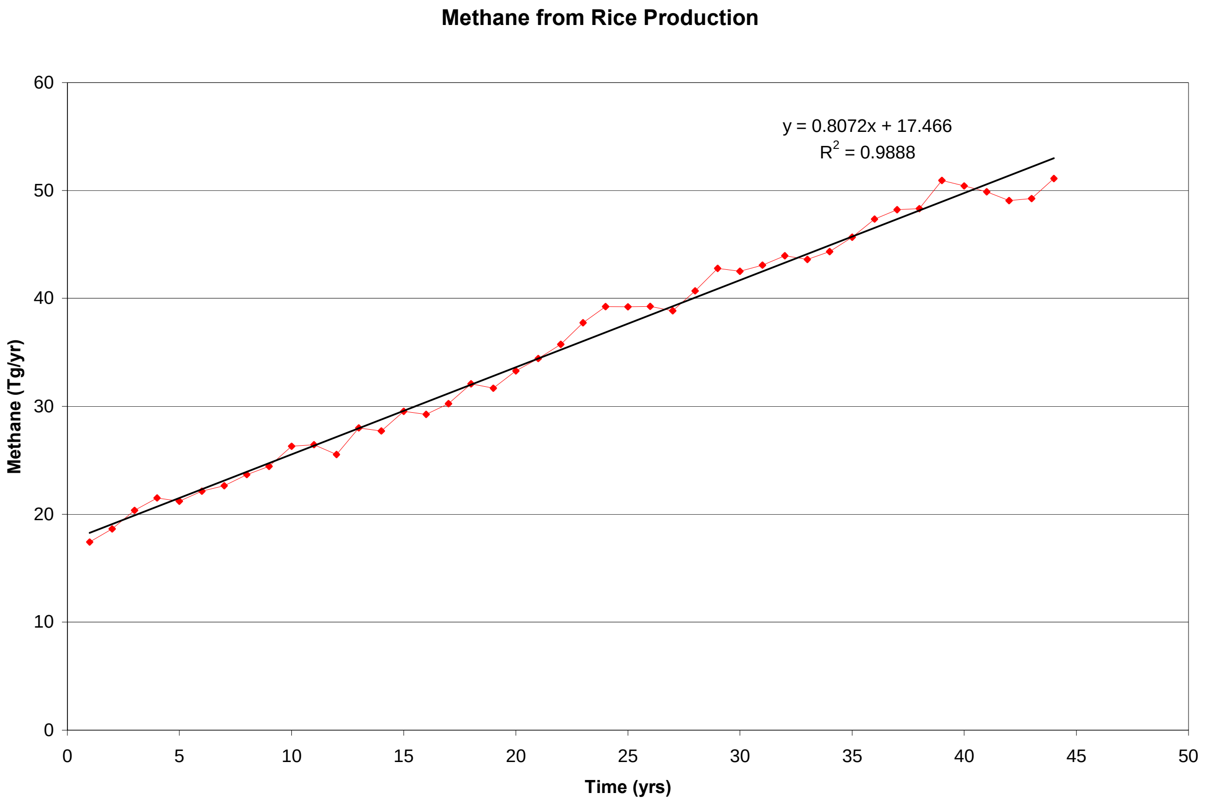

Figure 15:: Model of methane emissions from rice agriculture.

The model for Methane emissions from rice Agriculture is:

$y = 0.8072t + 17.466$

$R^2=0.9888$

Our estimates of methane emissions from rice agriculture are between 15 and 60 Tg for the time period concerned while the IPCC (1996) estimated the global emission rates from paddy fields at 60 Tg/yr, with a range of 20 – 100 Tg/yr.

5.4 METHANE EMISSIONS FROM DOMESTIC RUMINANTS

Enteric fermentation is a process by which carbohydrates are broken down by micro-organisms into simple molecules for absorption into the blood stream. Methane is produced in herbivores as a by-product of enteric fermentation. CH_4 is produced by both ruminant (e.g. cattle, sheep) as well as non ruminant (e.g. pigs, horses) animals, although ruminant animals are the largest source since they are able to digest cellulose, a type of carbohydrate, due to the presence of specific micro-organisms in their digestive tracts.

The Tier-1 approach of the IPCC Guidelines for National Greenhouse gas inventories from agricultural emissions was used to estimate methane emissions from domestic ruminants.

Default emission factors for each group of animals were mentioned in the guidelines and only readily available animal populations were needed to estimate the emissions.

The animal populations were obtained from the Food and Agricultural Organization website of the United Nations.

The emission factors for various groups of animals varied for developed countries and developing countries. The difference in the emission factors are driven by differences in the feed intake and feed characteristic assumptions (IPCC, 1996).

The animals included in the calculations were buffaloes, sheep, goats, camels, horses, mules, swine and dairy cattle.

The total emission was calculated using the following relation:

$$\begin{matrix}\textbf{CH}_4\\\textbf{Emissions}\end{matrix} = \Sigma\left(\begin{matrix}\textbf{Emission factor}\\\textbf{(Kg/head/year)}\end{matrix} \times \begin{matrix}\textbf{Population}\\\textbf{(Head)}\end{matrix}\right)$$

where Σ sums up the methane emissions from different animals.

Table 3: Emission Factors for Domestic Ruminants

LIVESTOCK	DEVELOPED COUNTRIES (Kg per Head per Year)	DEVELOPING COUNTRIES (Kg per Head per Year)
Buffalo	55	55
Sheep	8	5
Goats	5	5
Camels	46	46
Horses	18	18
Mules	10	10
Swine	1.5	1
Poultry	Not estimated	Not Estimated.

Source: IPCC 1996 Reference Manual.

The figure on the next page depicts methane emissions from domestic ruminants.

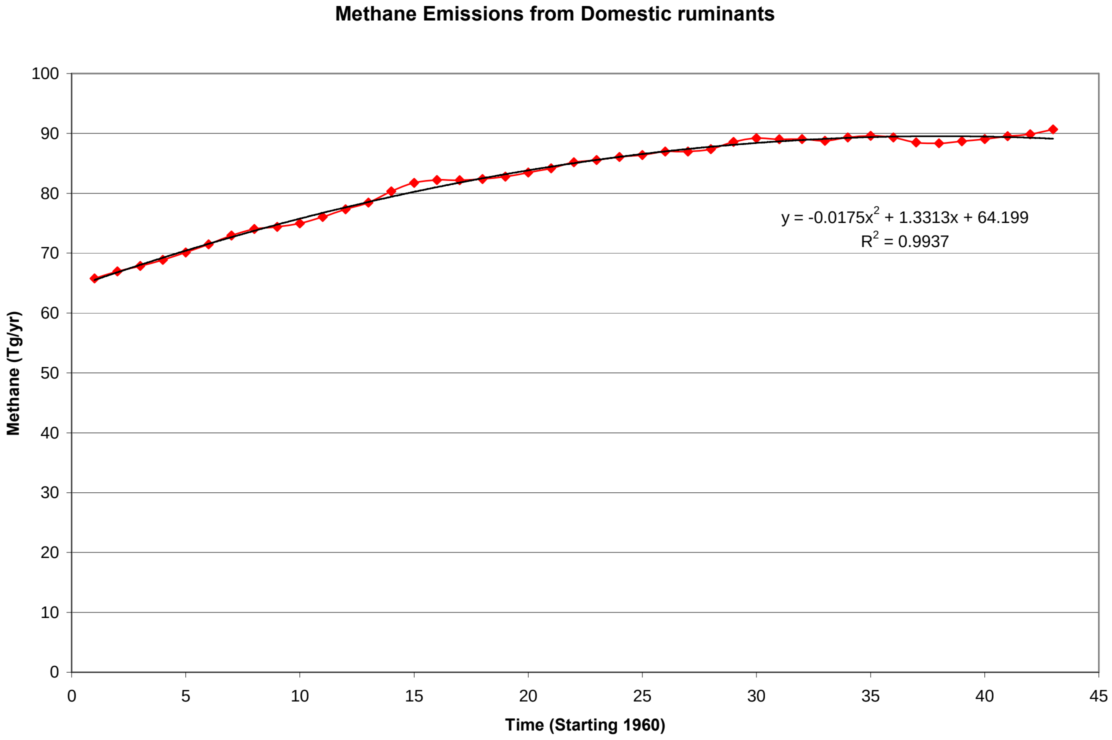

Figure 16: Model of methane emissions from domestic ruminants.

The model for emissions of methane from domestic ruminants is as follows:

$y = -0.0175t^2 + 1.3313t + 64.199$

$R^2 = 0.9937$

Our model estimates methane emissions from domestic ruminants to lies between 60 and 100 Tg/yr.

5.5 METHANE EMISSIONS FROM BIOMASS BURNING

Methane is produced by the incomplete combustion of biomass represented by (CH_2O). Emissions from biomass burning were obtained from two categories. The first category was the burning of forests and wild fires and the second category was the burning of agricultural wastes.

Methane emissions from the burning of forests and wild fires were calculated by first calculating the total mass of biomass fuel burnt. This was done by obtaining the total area burnt and multiplying it by the fuel load and burning efficiency.

Since statistics were not available for the entire time period as were other sources, the data available between 1990 and 2000 was used to create the model. The area of the fuel burnt for various countries was obtained from “Global Forest Fire Assessment 1990-2000”. (Goldammer,2001)

Methane emissions were calculated using the formula:

$$\mathbf{CH_4\ Emissions} = \mathbf{Biomass\ Burnt} \times \mathbf{Carbon\ Mass\ Fraction} \times \mathbf{Emission\ Factor} \times \mathbf{Elemental\ to\ Molecular\ Conversion\ Factor}$$

The biomass burnt was the product of the total area burnt and the biomass load per Ha (137 Mg/ha in this case.) with a burning efficiency of 0.72. 137 Mg/ha was obtained as the average of the biomass fuel load of 208 Mg/ha for closed forests and 67 Mg/ha for open forests. A carbon mass fraction of 0.46 was assumed to be present in the biomass. The elemental to molecular conversion factor was 1.33 for methane and the emission factor was taken to be 0.012 (IPCC, 2001).

For agricultural wastes, methane emissions were calculated form the burning of wastes from coarse grain production, sugarcane production and wheat production.

A similar method to estimating methane emissions form forest and wildfires was adopted. The biomass burnt was calculated by using the following relation:

$$\textbf{Biomass Burnt} = \textbf{Course Grain/Sugarcane/ Wheat Production} \times \textbf{Residue to crop ratio} \times \textbf{Fraction of Residue while burning} \times \textbf{Dry Matter Conten}$$

$$\times\ \textbf{Burning Efficiency} \times \textbf{Fraction Burnt}$$

This method was adopted from the Australian government’s effort to estimate methane emissions from biomass burning.

The production statistics for course grain / wheat / sugar cane production was obtained from the FAO website. The residue to crop ratio for course grain and wheat was taken to be 1.5 and for sugarcane it was taken as 0.25. The fraction of residue at time of burning was 0.5 for course grain and wheat and 1 for sugarcane. The dry matter content was 0.8, 0.2 and 0.9 for coarse grain, sugarcane and wheat respectively. The burning efficiency was assumed to be 0.96 for all the three agricultural residues. It was further assumed that 23% of the coarse grain and wheat burned and 58% of the sugarcane residue burned. A carbon mass fraction of 0.4 was assumed in the agricultural residues and the methane emission factor was taken as 0.012 with an elemental to molecular conversion factor of 1.33.

Methane emissions from biomass burning are presented in the figure below. Although, the estimates are rough, the overall trend is an increasing one.

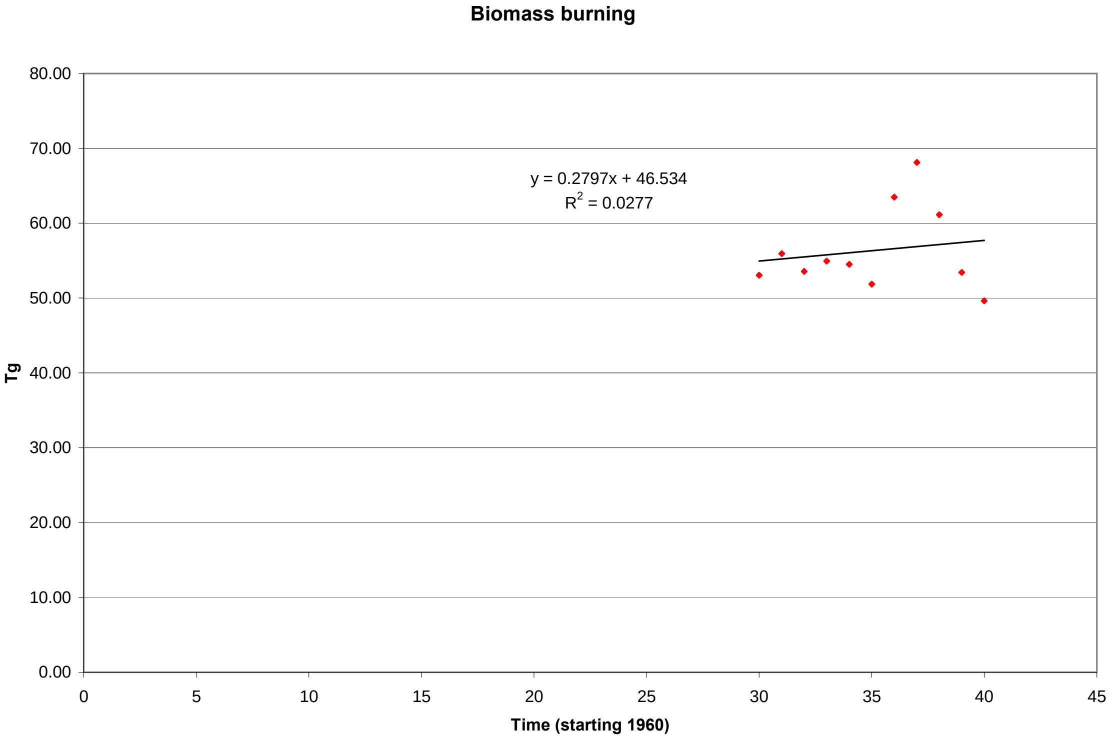

Figure 17: Model of methane emissions from biomass burning.

The model for methane emissions from biomass burning is:

$y = 0.2797t + 46.534$

with $R^2 = 0.0277$.

5.6 METHANE EMISSIONS FROM WASTE DISPOSAL

Most important greenhouse gases are produced by the disposal and treatment of industrial and municipal wastes. Methane is the most important greenhouse gas produced in this source category. The IPCC 1992 estimates approximately 5-20 per cent of the annual global anthropogenic CH_4 produced and released into the atmosphere is a by-product of the anaerobic decomposition of waste.

CH_4 along with CO_2 is formed when organic waste in Solid Waste Disposal Sites (SWDs) is broken down in a series of stages by bacterial action.

The Default Methodology mentioned in the 1996 Guidelines for National greenhouse Gas Inventories was adopted to estimate Methane emissions from MSWs.

The default methodology is a mass balance approach that involves the estimating of degradable organic carbon (DOC) content of the solid waste i.e. the organic carbon that is accessible to biochemical decomposition and using this estimate to calculate the amount of CH_4 which can be generated by the waste (IPCC Guidelines, 1996)

This method does not incorporate any time factors. This method assumes that all the CH_4 is released into the atmosphere the same year that the waste is disposed. It requires the least amount of data to perform calculations and can be modified and reformed as the amount of data for each available country increases.

Bingemer and Crutzen (1987) were the first to formulate this approach, dividng the world into four economic regions and applied different DOC values to the waste generated within these regions.

Methane emissions were estimate using the following equation:

$$\text{Methane Emissions} = (\text{MSW}_T \times \text{MSW}_F \times \text{MCF} \times \text{DOC} \times \text{DOC}_F \times \text{F} \times 16/12 - \text{R}) \times (1 - \text{OX})$$

Where

MSW_T = Total MSW generated

MSW_F = Fraction of MSW disposed to solid waste disposal sites

MCF = Methane Correction Factor

DOC = Degradable Organic Carbon

DOC_F = fraction DOC dissmilated

F = Fraction of CH_4 in landfill gas

R = Recovered CH_4

OX = Oxidation Factor.

The approach followed in this project was slightly different than that followed by Bingemer and Crutzen (1987) in the sense that they had divided the world inot four economic regions and calculated the methane emissions while we have taken the maximum possible countries for which data is available.

The total MSW (MSW_T) can be calculated as the product of the population (thousand persons) and the annual MSW generation rate (Gg/thousand persons/yr).

For countries where no organized waste collections or disposals take place in rural areas, only the urban population was considered. This was particularly true for developing countries. Per capita MSW generation rates are provided for many countries and regions in Table 4.

Table 4: Country waste generation, composition and disposal data

Region/Country	MSW Generation rate (kg/cap/day)	Fraction of MSW disposed to SWDs	Fraction of DOC of MSW	MSW disposal rate (kg/cap/day)
USA	2.0	0.62	0.18-0.21	1.24
Canada	1.81	0.75	0.18-0.21	1.35
Australia	1.26	1.00	0.15	1.26
New Zealand	1.33	1	0.19	1.33
UK/Western Europe			0.08-0.19	
UK	1.9	0.9	0.1	1.7
Ireland	0.85	1		0.85
Austria	0.92	0.4		0.36
Belgium	1.1	0.43		0.47
Denmark	1.26	0.2		0.25
Finland	1.7	0.77		1.3
France	1.29	0.46		0.6
Germany	0.99	0.66		0.65
Greece	0.85	0.93		0.79
Italy	0.94	0.88		0.83
Norway	1.40	0.75		1.05
Portugal	0.90	0.86		0.78

Table 4: Continued

Spain	0.99	0.85		0.83
Sweden	1.01	0.44		0.44
Switzerland	1.10	0.23		0.25
Japan	1.12	0.38		0.43
India	0.33	0.6	0.18	0.2
China			0.09	
South America /Brazil			0.12	1.47
Africa/Egypt			0.21	0.4

* Table Reproduced from IPCC 1996 Guidelines for Greenhouse Gas Inventories.

The population of the world was obtained from the Food and Agricultural Organization website of the United Nations.

The Methane Correction Factor (MCF) reflects the way MSW is managed and the effect of management practices on CH_4 generation. The MCF values for methane estimations for this project were taken according to the following table:

Table 5: SWDs Classification and methane correction factors (MCF)

Type of Site	**Methane Correction factors (MCF) default values**
Managed	1.0
Unmanaged – deep (≥ 5m waste)	0.8
Unmanaged – shallow (< 5m waste)	0.4
Default value – uncategorized SWDs	0.6

* Table Reproduced from IPCC 1996 Guidelines for Greenhouse Gas Inventories.

For the developing countries the value of '1' was taken, for countries in economic transition, the default value of 0.6 was taken.

The DOC values were taken from the table

Recovered CH_4 (R) is the amount of CH_4 that is captured for flaring or use. Except for the United States it was assumed that between 95 to 100 % of the methane generated form MSWs is not captured and is released directly into the atmosphere.

Due to the presence of oxygen in the upper layers of the waste mass, CH_4 is oxidized before it's release into the atmosphere. The Oxidation factor (OX) accounts for the CH_4 that is oxidized in the upper layers. Not much is known about this factor and the OX factor in this estimate has been set equal to 0.

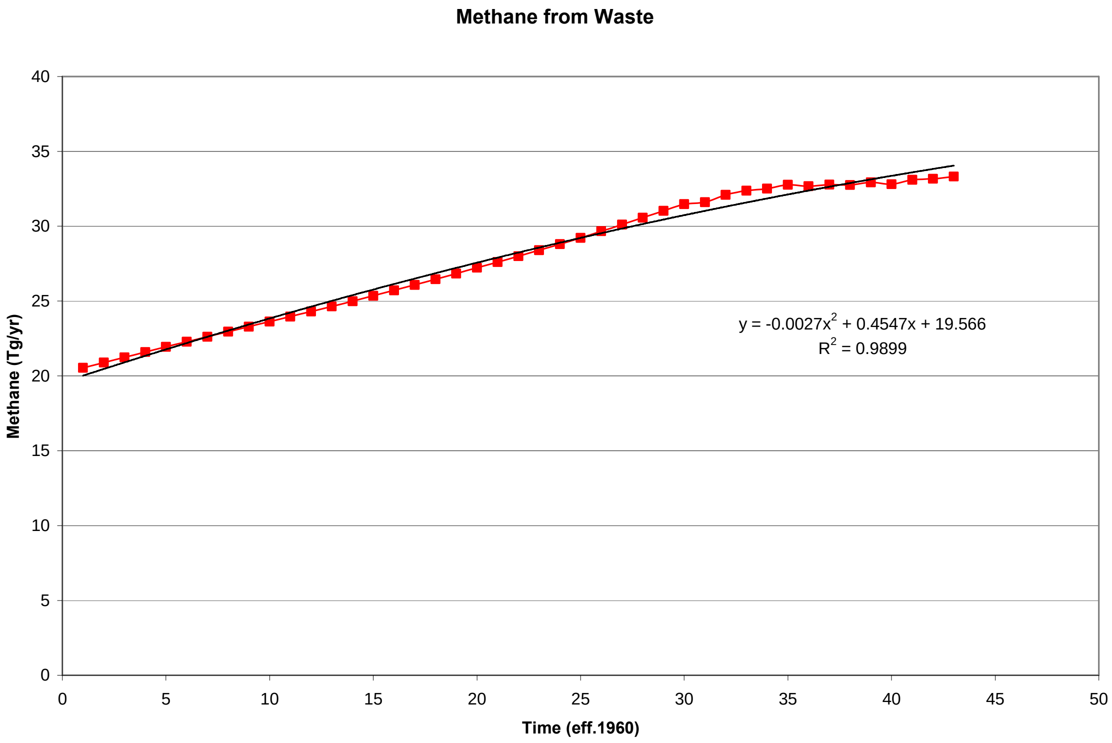

Figure 18: Model of methane emissions from waste.

The model for methane emissions from waste disposal was found to be:

$y = -0.0027t^2 + 0.4547t + 19.595$
$R^2 = 0.9899$

5.7 METHANE EMISSIONS FROM INDUSTRIAL WASTEWATER

Methane is produced from wastewater when treated anaerobically .Industrial wastewater sources are estimated to be major contributors to wastewater emissions. Methane is produced when wastewater from industries like the meat and poultry, paper and pulp, etc are handled anaerobiacally. This is particularly true for developing countries.

The principle factor in determining the CH_4 generation potential of waste water is the amount of degradable organic content of waste water. This is generally determined by the Biological Oxygen Demand (BOD) or the Chemical Oxygen Demand (COD) content of waste water.

The EPA Report by Doorn et al (1997) is the basis of the method adopted for determining the emissions from industrial waste water. The equation below provides the methodology for estimating CH_4 from industrial wastewater:

$$\text{Methane Emissions} = \text{EF} \times 10^{-12} \times \sum_{i} \sum_{c} (\text{P}_{\text{ic}} \times \text{Q}_{\text{i}} \times \text{COD}_{\text{i}} \times \text{TA}_{\text{ic}})(Tg / yr)$$

Where: EF = Emission Factor (g CH_4/COD removed)

P_{ic} = Industry and country specific output (Mg/yr)

Q_i =Industry specific wastewater produced per unit of product (m3/Mg)

COD_i =Organic Loading removed, by industry (g/m3)

TA_i =Industry and country specific fraction of COD in wastewater treated anaerobically

Subscript i = An individual industry; and

Subscript c =An individual country

For this project, the world was divided into six regions, namely Africa, Asia, Europe, North America, Oceana and South America. Emission were estimated for the wastewater emitted from Beverage (Food), Beverage (Non-food), Meat and Poultry, Fish Fruits and Vegetables, Sugar, Paper & Pulp as well as textile industries. Area specific data for the production of these commodities was obtained form the Food and Agricultural Organization (FAO) website of the United Nations.

Q_i, COD_i, and TA_i values for the various regions were taken from Doorn et al (1997). For the regions for which data was not available the data was the neighboring regions were taken for estimation. This is done by taking into account the economic similarities (or differences) between the neighboring regions.

The product of the above mentioned factors that was expected to be treated anaerobically was multiplied by and emission factor of 0.3 CH_4/g COD (Doorn et al, 1997).

Methane emissions from wastewater are represented by the figure below:

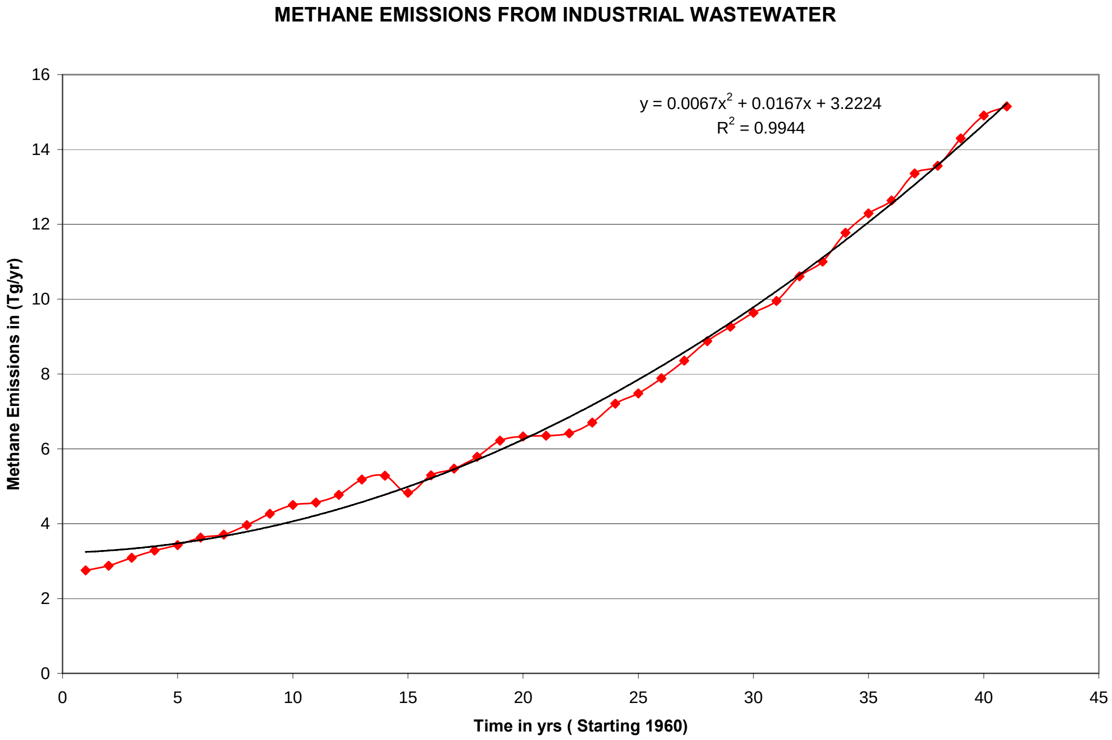

Figure 19: Model of methane emissions from industrial wastewater.

The model is represented by:

$y = 0.0067t^2 + 0.0167t + 3.2224$
$R^2=0.9944$

6.0 MODEL AND RESULTS

The table below presents an example of our estimate of emissions in Tg from various anthropogenic sources.

Table 6: Example of Calculated Anthropogenic Sources

	1985	1990	1995	2000
Energy (Natural Gas Production)	33.8	38.8	41.8	44.6
Energy (Coal Mining)	33.4	37.2	37.2	35.9
Rice Agriculture	39.2	42.51	45.61	50.42
Domestic Ruminants	86.9	89.01	89.3	89.5
Biomass Burning		53.06	51.86	59.61
Waste (SWD's)	29.2	31.5	32.8	32.8
Industrial Wastewater.	7.5	9.6	12.3	14.9

The temporal trends for various anthropogenic sources were obtained. The trends over time for the various sources discussed in the previous chapter. These were the trend lines as the models for various sources.

The equation used for predicting methane emissions was:

$$\frac{d[CH_4]}{dt} = \text{Sources} - \text{Sinks}$$

The sources include all the natural and anthropogenic sources of methane and the sinks include all the processes by which methane is removed from the atmosphere.

The model for anthropogenic sources are time dependent series derived from natural gas production, coal production etc. Since the data for most of the time series was available from 1960, a common time frame of time starting in 1960 was considered for all the anthropogenic emissions. The year 1961 was taken as year 1.Since the sources of methane are additive, the combined methane source was taken as the sum of the individual sources. The coefficients of t^3, t^2, t, t^0 were added to give the combined source.

Along with the anthropogenic sources, emissions estimates of natural sources were taken from Fung et al (1991) were taken as the basis for the model. These are considered to be constant for the time period of the simulation.

The combined sources of methane are presented in table 7. This was for the first 34 years because the trends of methane from domestic ruminants start decreasing after 34 years which is contrary to what is expected. Thus a steady linear increase in emissions from domestic ruminants was assumed after the 34th year for future predictions (Table 8).

Table 7: Combined Sources of Methane for years 1-34

	t^3	t^2	t^1	t^0
Anthropogenic Sources				
Natural Gas		-0.0136	1.6816	-0.4003
Natural Gas (venting and Flaring)				15
Coal Mining			0.3841	22.97
Rice Agriculture			0.8072	17.466
Domestic Ruminants		-0.0175	1.3313	64.199
Waste		-0.0027	0.4547	19.566
Wastewater Handling		0.0067	0.0167	3.2224
Biomass Burning			0.2797	46.534
Natural Sources				
Wetlands				115
Termites				20
Ocean				10
Hydrates				5
TOTAL		-0.0271	4.9553	338.5571

Table 8: Combined sources of methane. Year 34 onwards

	t^3	t^2	t^1	t^0
Anthropogenic Sources				
Natural Gas		-0.0136	1.6816	-0.4003
Natural Gas (venting and Flaring)				15
Coal Mining			0.3841	22.97
Rice Agriculture			0.8072	17.466
Domestic Ruminants			0.0017	67.4262
Waste		-0.0027	0.4547	19.566
Wastewater Handling		0.0067	0.0167	3.2224
Biomass Burning			0.2797	46.534
Natural Sources				
Wetlands				115
Termites				20
Ocean				10
Hydrates				5
TOTAL		-0.0096	3.6257	341.7843

Reaction with OH was taken as the major sink of atmospheric CH_4 with the lifetime (or the atmospheric residence time) accounting for the other sinks (oxidation in soils, reaction with Cl^-) also.

Using IPCC 2001 as the basis and definition of atmospheric residence time from Khalil (1996), the combination of CH_4 loss due to reaction with OH (residence time 9.6 years) with soil as a sink of methane (lifetime-160 years) and stratospheric loss (lifetime-120 years) gave us a lifetime of 8.4 years, which was used in this model.

The equation was thus rewritten as:

$$\frac{d[CH_4]}{dt} = -0.0271t^2 + 4.9553t + 338.5571 - \frac{[CH_4]}{\tau} \quad \text{(Years 1-34)}$$

$$\frac{d[CH_4]}{dt} = -0.0096t^2 + 3.6257t + 341.7843 - \frac{[CH_4]}{\tau} \quad \text{(Year 34 onwards)}$$

with 'τ' taken to be 8.4 years.

Matlab (© 2002) was used for simulation purposes ODE 23 was used for the solution of the differential equation. The initial concentration of methane in the atmosphere was taken to be 2909 Tg (1 Tg = 10^{12} grams) and the time period for which the simulation was run was period 1 to 34 and then period 34 to 70.

The predicted concentrations of methane were as follows:

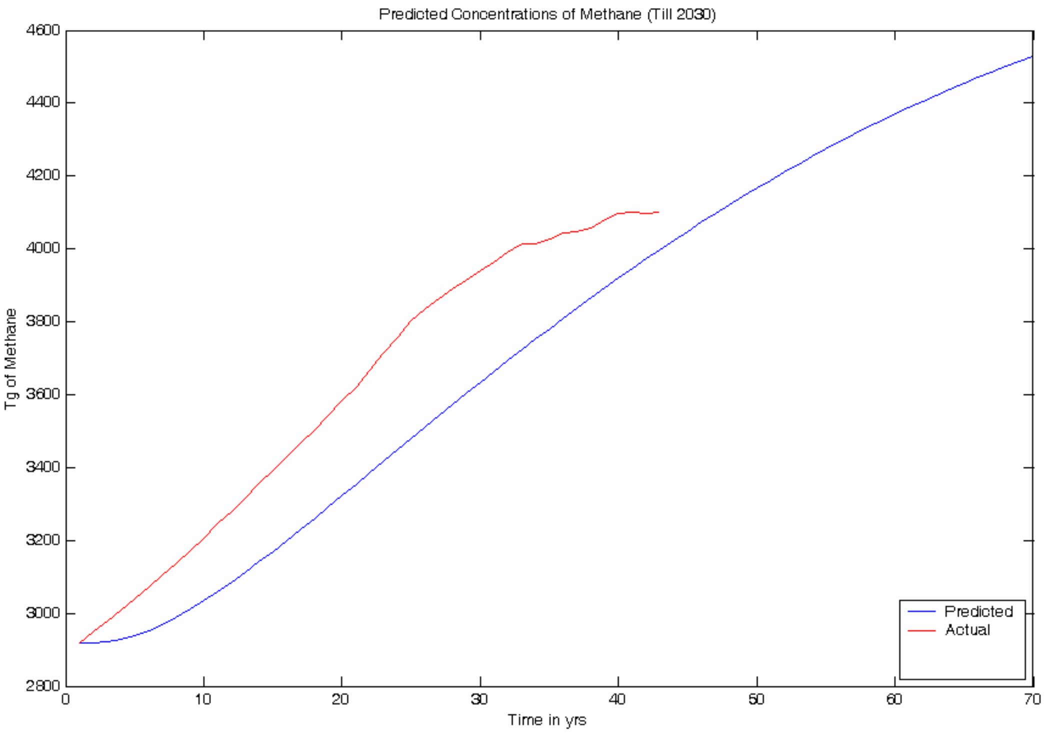

Figure 20: Predicting Methane Concentrations for 70 years

The figure above shows the predicted concentrations of Methane. According to our predictions the atmospheric burden of methane in 2030 should be about 4528.3 Tg which translates into 1934.495 ppb.

An attempt was made to figure out the sources which had the maximum impact on the concentrations of methane. This was done by eliminating each individual source and then running the model:

1. Effect of eliminating natural gas production on atmospheric methane concentrations.

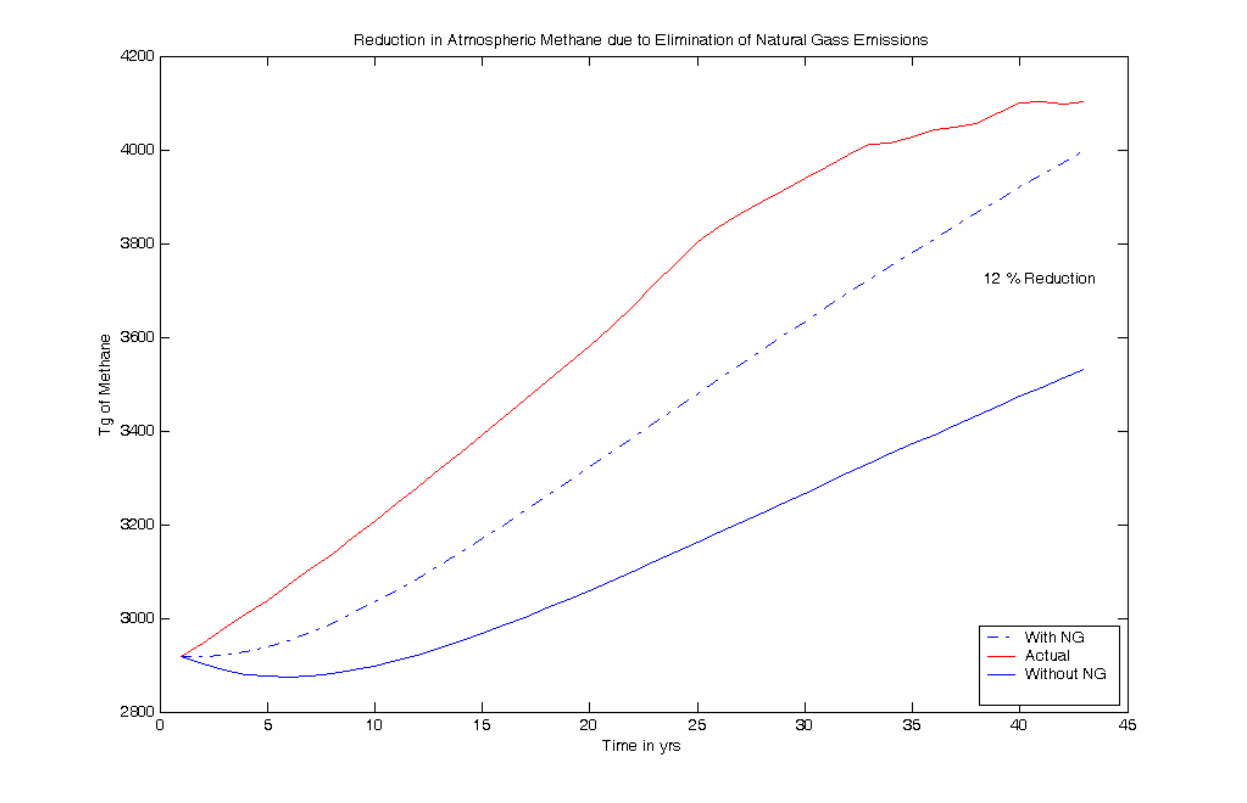

Figure 21: Effect of eliminating natural gas production on atmospheric methane concentrations

Eliminating methane emissions from natural gas production would have ultimately brought about a decrease in the present atmospheric concentrations by about 12%.

2. Effect of eliminating coal mining on atmospheric methane concentrations.

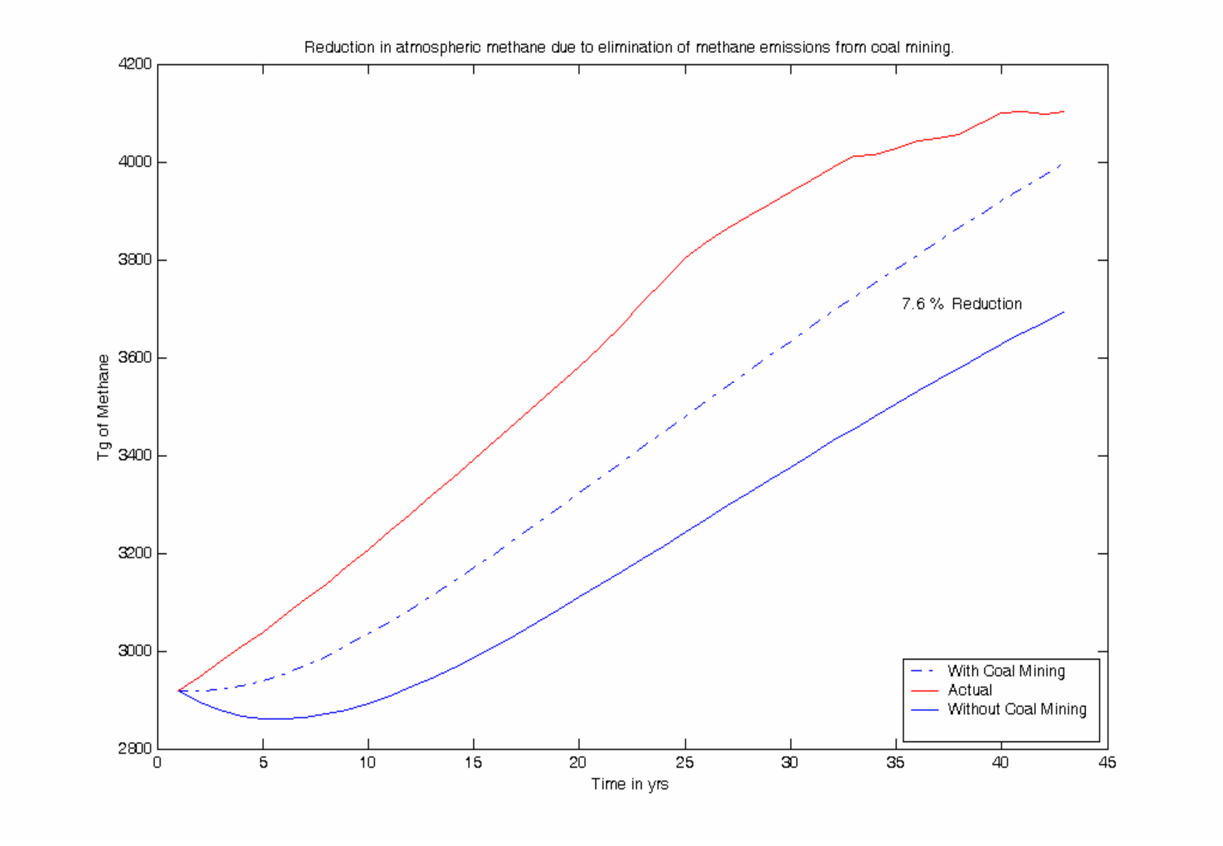

Figure 22: Effect of eliminating coal mining on atmospheric methane concentrations

Eliminating methane emissions from coal mining would have resulted in a decrease of present day atmospheric methane concentrations by about 7.6 %.

If all the emissions from fossil fuel are considered (natural gas and coal mining), the present day atmospheric methane concentrations reduce by approximately 20%.

3. Effect of eliminating methane emissions from rice agriculture on atmospheric methane concentrations.

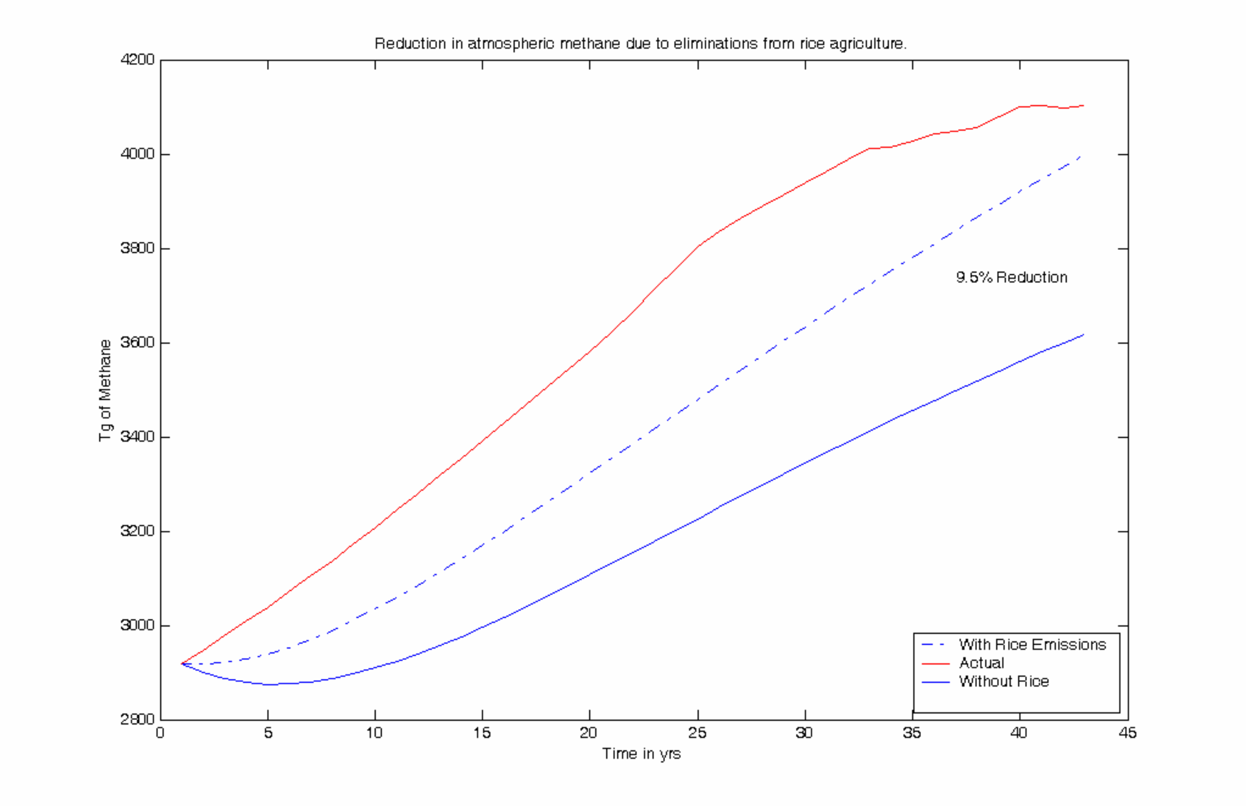

Figure 23: Effect of eliminating methane emissions from rice agriculture on atmospheric methane concentrations.

Eliminating methane emissions from rice agriculture bring down the present day atmospheric methane concentrations by 9.5%.

4. Effect of eliminating methane emissions from domestic ruminants on atmospheric methane concentrations.

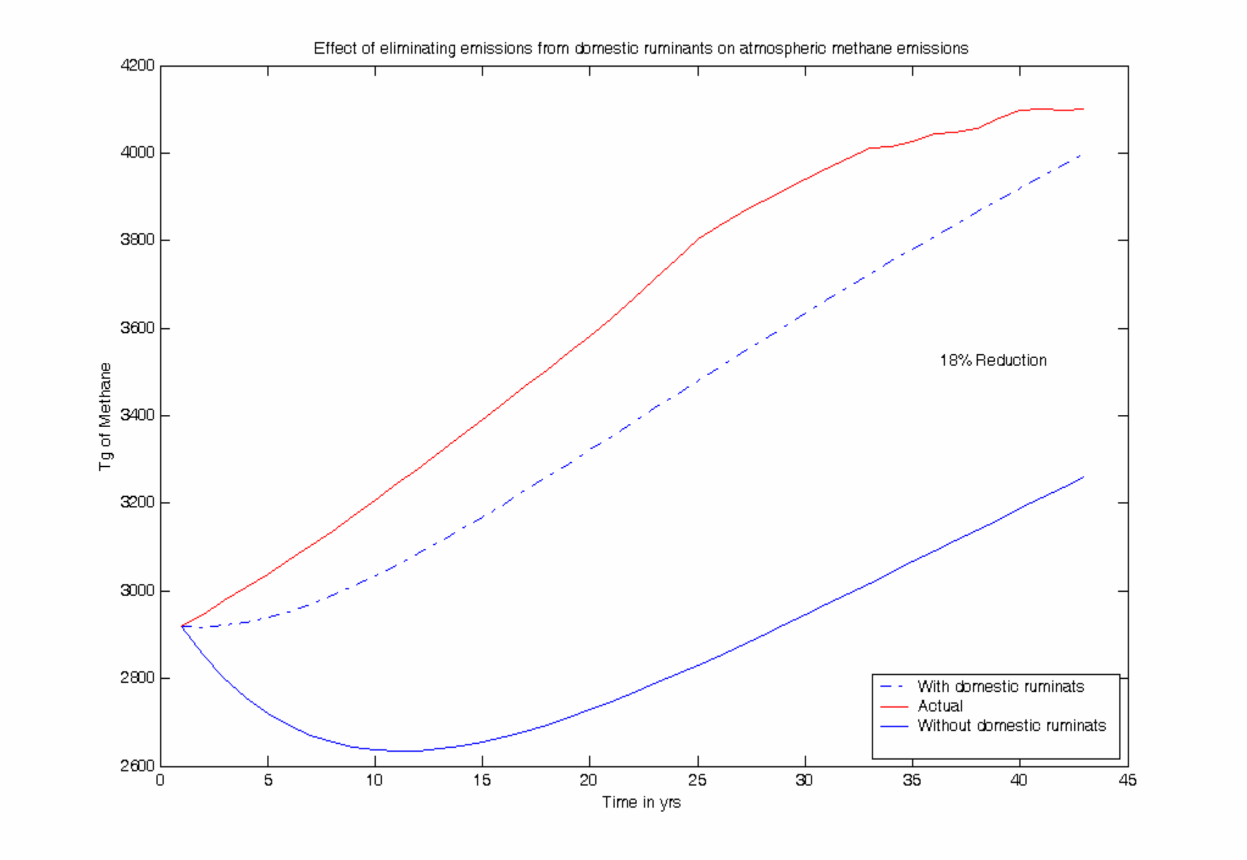

Figure 24: Effect of eliminating methane emissions from domestic ruminants on atmospheric methane concentrations.

Eliminating methane emissions from domestic ruminants reduce the present atmospheric concentrations by about 18%. Clearly individually domestic ruminants are one of the most important sources of atmospheric methane.

5. Effect of eliminating methane emissions from biomass burning on atmospheric methane concentrations.

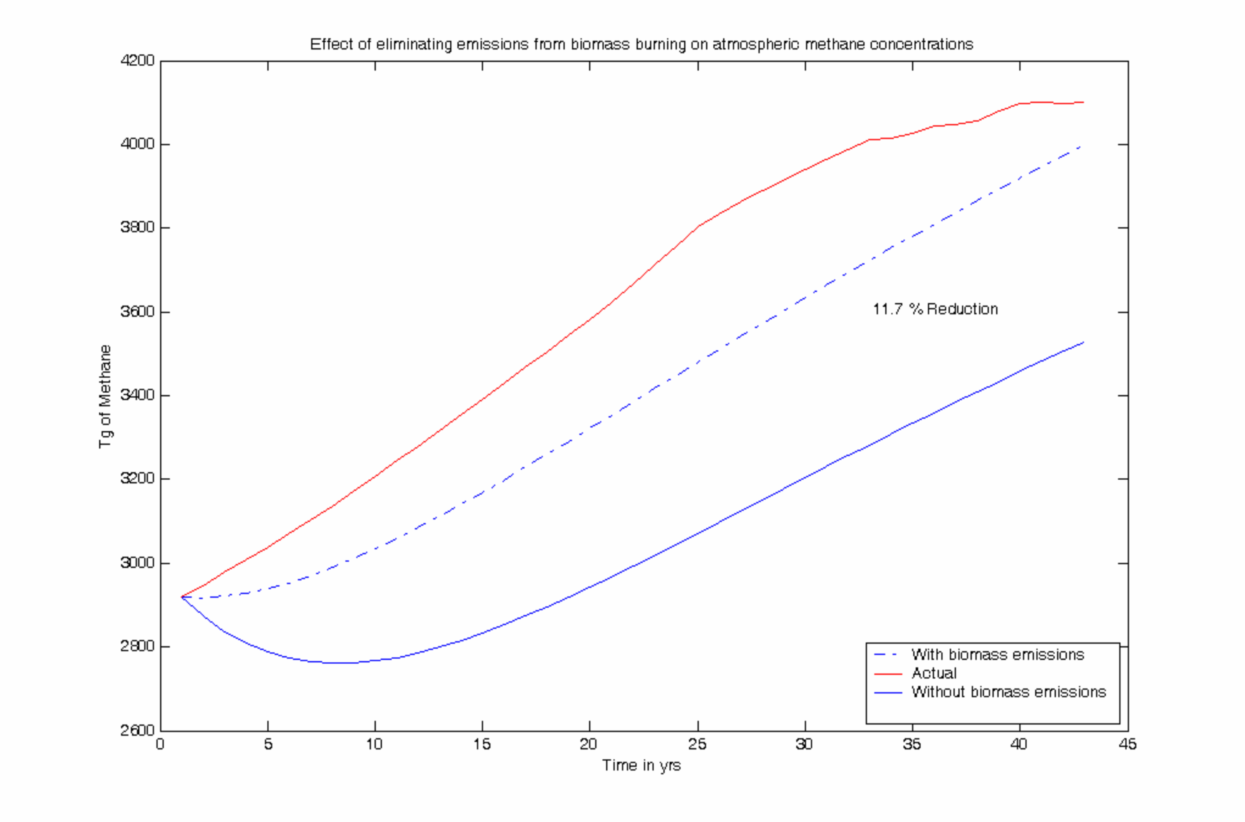

Figure 25: Effect of eliminating methane emissions from biomass burning on atmospheric methane concentrations.

Eliminating methane emissions from biomass reduce the present atmospheric methane concentrations by about 11.7%.

6. Effect of eliminating methane emissions from waste handling on atmospheric methane concentrations.

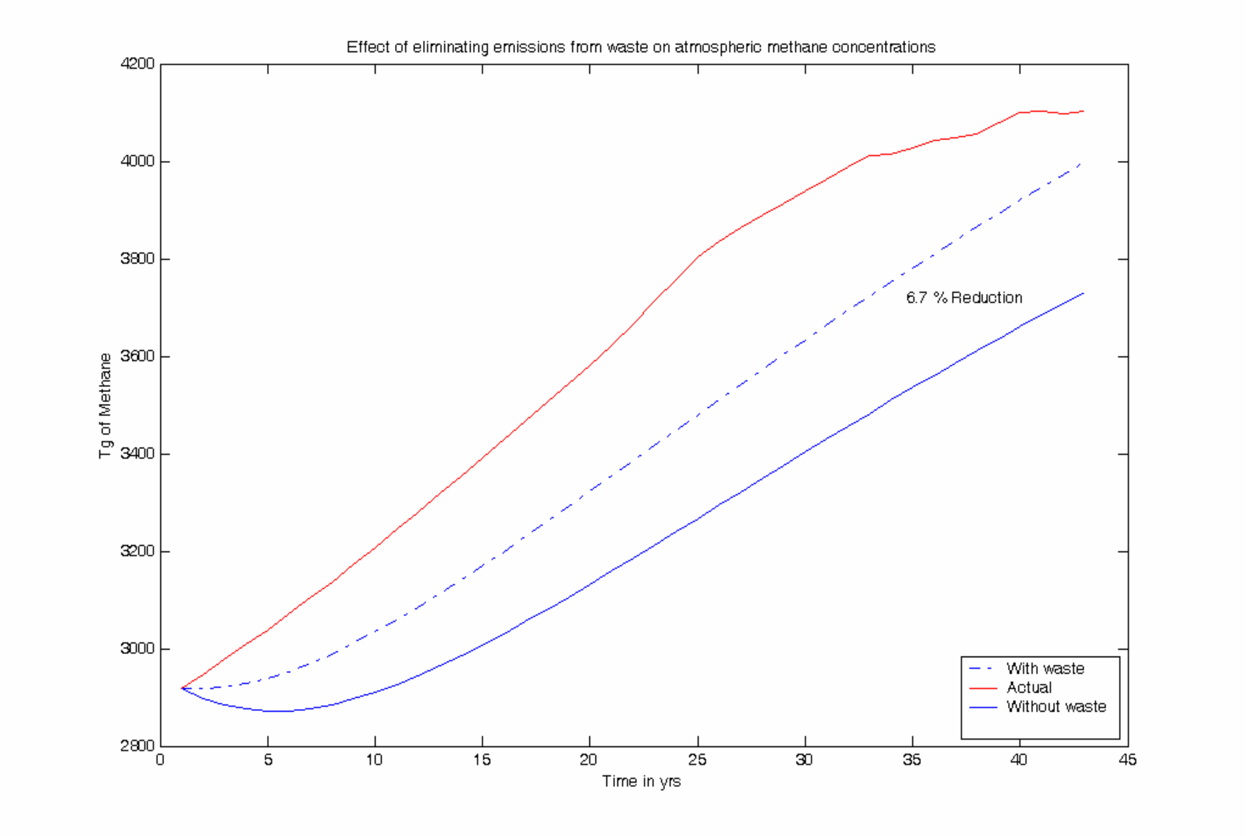

Figure 26: Effect of eliminating methane emissions from waste handling on atmospheric methane concentrations.

Eliminating methane emissions from solid waste decomposition sites reduces the atmospheric methane concentrations by about 6.7%.

7. Effect of eliminating methane emissions from wastewater handling on atmospheric concentrations.

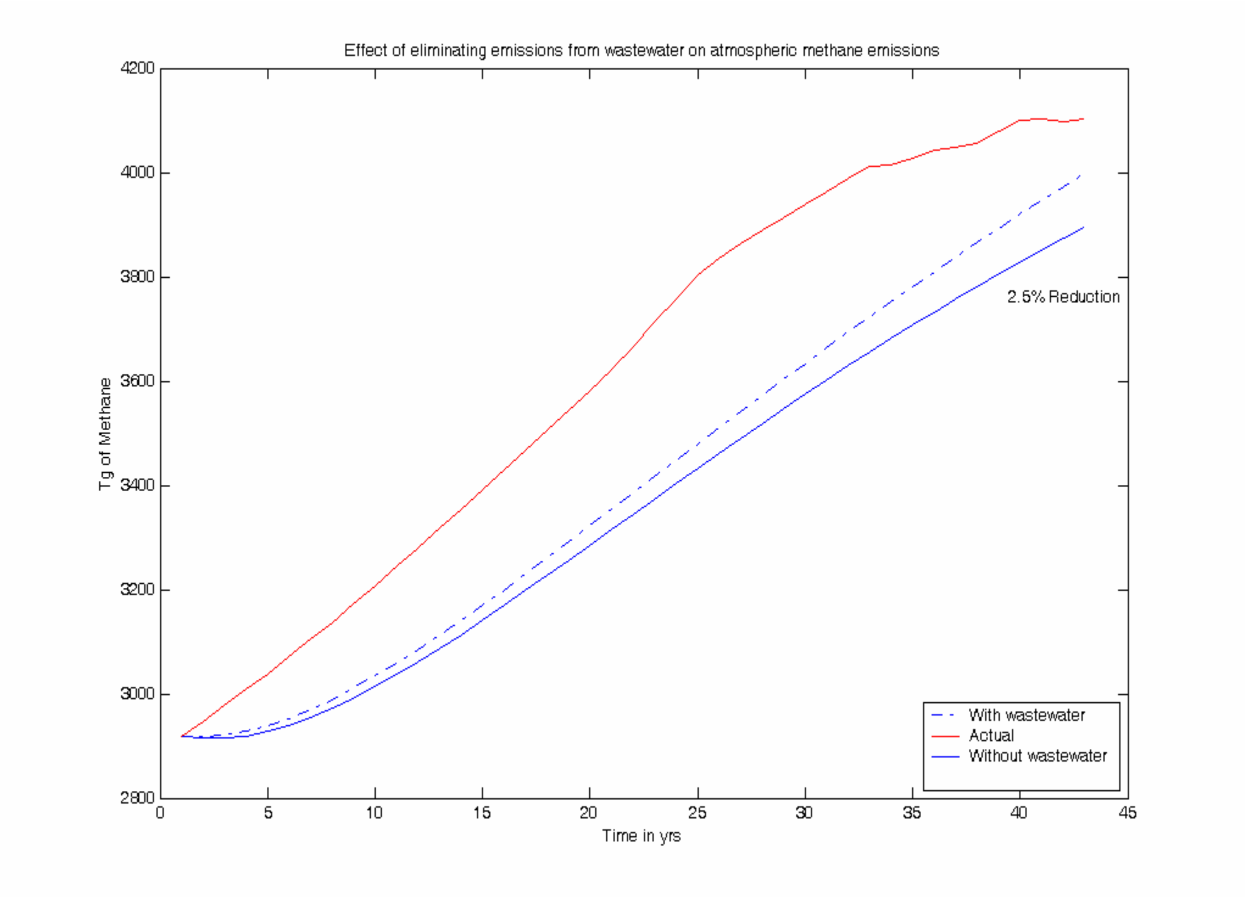

Figure 27: Effect of eliminating methane emissions from wastewater handling on atmospheric concentrations.

Eliminating methane emissions from waste water reduces the atmospheric methane concentrations by about 2.5%.

Although from the above figures it appears that individually domestic ruminants and rice agriculture have the maximum impact on atmospheric methane concentrations, but on a combined basis methane emissions from fossil fuels (natural gas production and coal mining) have had the maximum impact on the atmospheric concentrations of methane. Thus the exponential increase of methane since the start of industrialization can safely be attributed to the increase in the use of fossil fuel over the last century.

It can also be concluded that in order to methane concentrations in the atmosphere, it is important to concentrate upon the reduction of methane emissions from these individual sources.

6.1 SURFACE TEMPERATURE CHANGE DUE TO CHANGE IN METHANE CONCENTRATIONS

Radiative forcing is a term employed in the IPCC Assessments to denote an externally imposed perturbation in the radiative energy budget of the earth's climate system. This change in the radiation budget has the potential to lead to changes in climate parameters and result in new equilibrium state of the climate system. Such an imbalance or change can be brought out by radiatively active species such as CO_2, CH_4 etc.

An attempt was made to determine the temperature change caused by the projected increase in methane concentrations in the atmosphere.

The change in the net irradiance at the tropopause, is to a first order, a good indicator of the equilibrium global mean surface temperature change.

The ratio of the global mean surface temperature response ΔT_s to the radiative forcing ΔF is the climate sensitivity parameter 'λ' and can be written as:

$$\frac{\Delta T_s}{\Delta F} = \lambda$$

(Dickenson, 1982; Cess et al., 1993) and can be defined as the transition of the surface-troposphere climate system from one equilibrium state to another in response to an externally imposed radiative perturbation.

A simplified expression for the calculation of radiative forcing due to change in CH4 concentrations was obtained from Hansen et al (2000) and is given by:

$$\Delta\text{F} = \alpha(\sqrt{M} - \sqrt{M_0}) - (f(M, N_0) - f(M_0, N_0))$$

where, M=concentration of CH_4 in ppb

N=concentration of N_2O in ppb

$\alpha = 0.036$

and $f(M, N) = 0.47\ln[1+2.01\times10^{-5}(MN)^{0.75}+5.31\times10^{-15} M (MN)^{1.52}]$

The time period in question was 70 years i.e. from 1960 to 2030. The concentration of CH_4 in 1960 (M_0) was the measured concentration of 1247 ppbv and the concentration of N_2O in 1960 (N_0) was 291.4 ppbv obtained from NASA's website.

The concentrations of CH_4 in 2030 were obtained from our model and were approx. 1934.49 ppbv.

The climate sensitivity parameter 'λ' was obtained from Ramanathan et al (1985) and was taken to be 0.5 K/ (Wm^{-2}). This parameter, first introduced in one dimensional convective models is a nearly invariant parameter for a variety of radiative forcings, thus introducing the notion of a possible universitality of a relationship between forcing and response (IPCC,2001). Thus radiative forcing has been made an appealing concept in order to measure the global mean surface temperature due to the invariance of 'λ'.

Our predicted methane concentrations of 1934.49 ppbv from 1960 to 2030 induce a radiative forcings of 0.2706 W/m^2.

This calculation using the climate sensitivity parameter leads us to calculate a global mean surface temperature change of 0.135 K due to the increase in methane concentrations over the time period in question. This temperature change is with reference to the temperature in the year 1960.

An attempt to see the overall temperature effect of this increased methane concentration was made using the regression model developed in the early part of this work.

An attempt was made to correlate the change in the surface temperature of the earth with Carbon Dioxide and Methane concentrations. For this a regression analysis was performed using the concentrations of CO_2 and CH_4 and the average change in the temperature of the earth. The result is presented in the figure below.

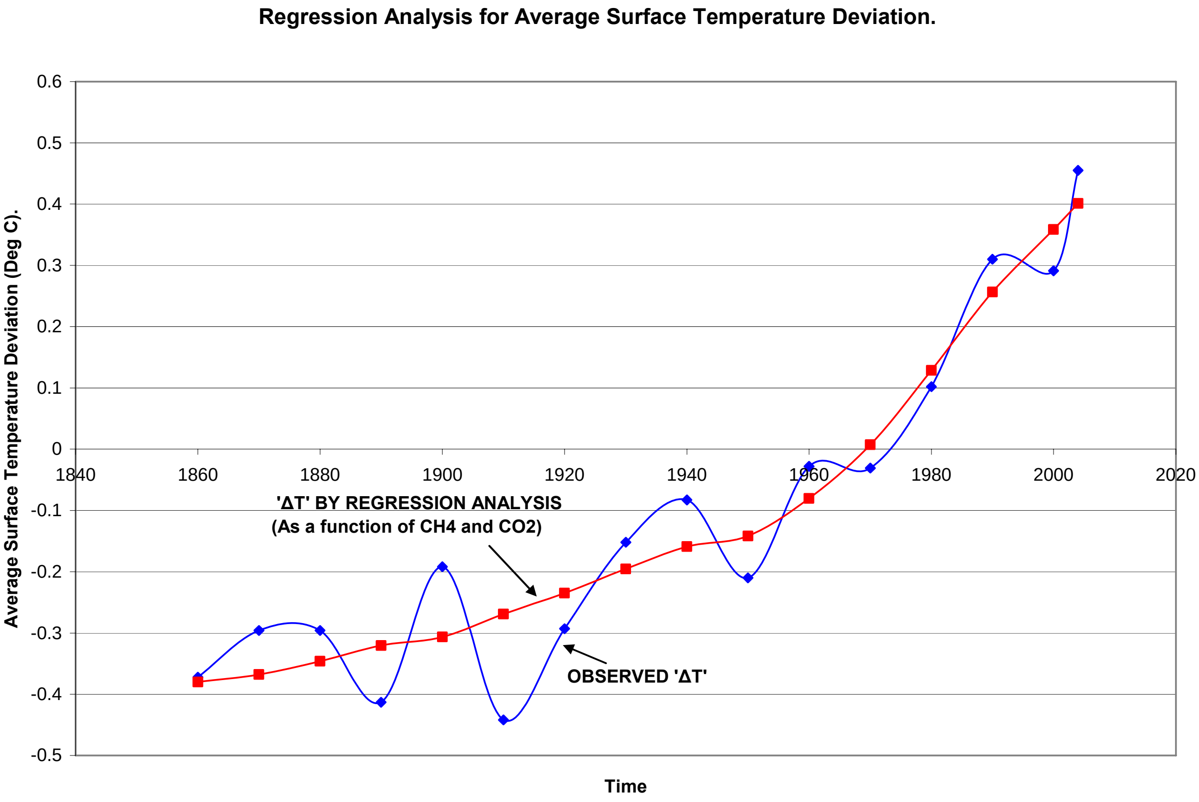

Figure 28:Average Surface Temperature Change as function of concentrations of CH_4 and CO_2

The following relationship was obtained which gave the change in the average surface temperature of the earth as a function of the concentrations of atmospheric CO_2 and CH_4.

$$\Delta T_s = 0.000293\,[CH_4] + 0.005539\,[CO_2] - 2.20224$$

Where ΔT_s = Change in the average Surface Temperature of the Earth

$[CH_4]$ = Atmospheric Methane Concentrations (ppbv)

$[CO_2]$ = Atmospheric Carbon Dioxide Concentrations (ppm)

In order to compare the temperature changes by the radiative forcing method and our mathematical correlation, the concentration of carbon dioxide was kept constant at 1960 levels and the temperature change just due to the increase in methane levels to 1934.4 ppb in 2030 was found to be 0.119 K.

An attempt was also made to see the individual impact of CO_2. These was done by keeping the levels of CH4 constant at 1960 levels and use the predicted concentrations of $CO_{2.}$ The predicted concentration of CO2 in 2030 is 417 ppm. Using this our correlation obtained a temperature change of 0.47 K.

In order to ascertain the entire temperature impact, the predicted concentration of methane in 2030 - 1934.49 ppbv and the predicted concentration of CO_2 in the year 2030 - 417 ppm (NASA, Alternate Scenario) was taken.

The predicted temperature change using these concentrations and the model is 0.674 K. This increase in temperature change is not just due to the increase in methane but also due to the increase in carbon dioxide concentrations as well as the effect of other substances denoted by the constant in the equation. Also, this temperature change is with respect to the reference temperature of 15ºC taken as the average surface temperature of the earth.

We also tried to obtain the contribution of fossil fuel energy in the outgoing radiative budget of the earth. For the entire fossil fuel consumed on for the periods 1965-2002 was obtained from the British Petroleum Statistical Energy Review and the total flux of fossil fuel energy was calculated assuming the surface area of the earth to be 511,200,000 km^2. The average flux obtained was 0.020 W/m^2. This 0.020 W/m^2 when compared to the outgoing radiation of the earth (237 W/m^2) is just 0.0085% of the total energy budget.

CONCLUSION

Methane is undoubtedly the most important greenhouse gas after CO_2.Unlike CO_2 whose increase in atmospheric concentrations are primarily due the increase in the fossil fuel consumption over the last century, methane has a wide variety of anthropogenic sources. These anthropogenic sources can be said to be a function of population. The future concentrations of methane will thus be influenced by the population, the shape of the world economy as well as the ongoing efforts to reduce emissions from the present sources. Examples of these are efforts to reduce leakages through natural gas production lines, improving the quality of feed intake for domestic ruminants to reduce methane emissions, recovery of landfill gas produced on SWD sites etc.

According to our estimates, methane levels will increase by about 100 ppbv over the next 25 years. This increase in methane itself is quite significant as it will cause an increase of the surface temperature of the earth by about 0.135 K, considering the time period concerned.

Thus, concentrating on reducing the emissions of methane will make more of an impact as the impact of methane is 21 times that of CO_2 in the atmosphere.

APPENDIX

Predicted concentrations of methane from 1961 (Time=1) up to 2030 (Time=70)

Time	Methane Concentrations (Tg) × 10^3
1	2.9190
2	2.9176
3	2.9208
4	2.9281
5	2.9391
6	2.9533
7	2.9703
8	2.9896
9	3.0112
10	3.0344
11	3.0593
12	3.0855
13	3.1128
14	3.1410
15	3.1700
16	3.1997
17	3.2299
18	3.2606
19	3.2915
20	3.3227
21	3.3540
22	3.3854
23	3.4168
24	3.4482
25	3.4796
26	3.5108
27	3.5418
28	3.5727
29	3.6033
30	3.6337
31	3.6638
32	3.6936
33	3.7231
34	3.7523
35	3.7811
36	3.8096
37	3.8378
38	3.8655
39	3.8929

40	3.9198
41	3.9464
42	3.9726
43	3.9983
44	4.0237
45	4.0486
46	4.0731
47	4.0972
48	4.1208
49	4.1440
50	4.1667
51	4.1891
52	4.2110
53	4.2324
54	4.2534
55	4.2740
56	4.2941
57	4.3137
58	4.3329
59	4.3517
60	4.3700
61	4.3879
62	4.4053
63	4.4223
64	4.4388
65	4.4548
66	4.4704
67	4.4856
68	4.5003
69	4.5145
70	4.5283

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