METHANE EMISSIONS FROM DIFFERENT BIO-SOURCES UNDER NATURAL ENVIRONMENT

A Thesis

By

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CERTIFICATE

This is to certify that the thesis entitled "Methane emissions from different bio-sources under natural environment" submitted to the Faculty of Post-Graduate School, Indian Agricultural Research Institute, New Delhi, in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Soil Science and Agricultural Chemistry, embodies the results of a piece of bonafide research carried out by Mr. Goutam Debnath under my guidance and supervision. No part of the thesis has been submitted for any other degree or diploma or published in any other form.

The assistance and help received by him during the course of this investigation have been duly acknowledged.

New Delhi
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[M.C. Jain]

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INTRODUCTION

INTRODUCTION

Humanity today is in an unprecedented position. In the span of a single generation, the earth's life sustaining environment is expected to change more rapidly than it has ever been over any comparable period of history. Much of this change will be of our own making. Worldwide economic and technological activities are contributing to rapid potentially stressful changes in our global environment in ways that we are only now beginning to understand. These changes may profoundly affect generations to come. There is now strong consensus amongst atmospheric scientists that global warming during the next few decades is highly probable as a result of the accumulation of greenhouse gases in the global atmosphere (Bolin *et al.* 1986; WMO, 1986). These gases are generally long enough lived in the atmosphere that it does not matter from where these gases are released, soon become widely dispersed in the atmosphere and influence climate globally. The report of the IPCC (Intergovernmental Panel on Climate Change) depicts a scenario that is truly disturbing. According to IPCC estimates, about 300 million people would be severely affected by a one-metre rise in the sea level. Hundreds of millions of people will be rendered environmental refugees.

UNCED (United Nations Conference on

Environment and Development), popularly called 'Earth Summit', held at Rio de Janeiro in June 1992, marked the beginning of a new understanding of cooperation between the rich and poor countries to prevent further degradation of the environment and foster sustainable development. The Climate Change Convention, which came into existence at the Rio Summit, is an umbrella agreement which takes into account the cardinal principles on which actions to mitigate the causes of global warming are to be taken.

Amongst the many significant initiatives taken in the last three years, we are aware of the important work done by UNEP (United Nations Environment Programme), the IPCC, WMO (World Meteorological Organisation), the ICSU (International Council of Scientific Unions), the Toronto Conference on the Changing Atmosphere, the Hague Conference, the G-7 Summit of 1989, the Noordwijk Ministerial Conference on Atmospheric Pollution and Climate Change, the Bergen Ministerial Declaration and the like. In India also, we witnessed a number of organisations and experts, both within the Government and outside, engaging themselves in a major way to grapple with this complex issue. Global warming is indeed being taken in responsible quarters as a *Global Warming*.

Without the presence of water vapour and CO_2 in the atmosphere, the earth's surface temperature would have been 33 °C lower than it is today. They bring

about the greenhouse effect through the property that they absorb electromagnetic radiation strongly in the infrared region. Of the total amount of incoming radiation 31% is reflected by clouds, atmospheric particles and earth's surface while other 69% is absorbed by ozone (O_3) in stratosphere; water vapour, clouds and aerosols in troposphere, and earth's surface. To maintain total energy balance, long-wave radiation, equivalent to the 69% incoming short-wave radiation which is absorbed, needs to be emitted to space. The bulk of this energy comes from the earth's surface which acts as a black-body radiator at about 300 K and emits radiation which falls in infrared region (Wien's law). Greenhouse gases and clouds can intercept this radiation, and re-emit it in all directions, thus redirecting a significant amount back down to earth. As a result of these processes the earth's surface emits black-body radiation at a higher temperature until the correct amount of energy is emitted to space. Hence the temperature in the earth's atmosphere increases which is known as the greenhouse effect (Ramanathan *et al.*, 1989; Dickinson and Cicerone, 1986).

With the rapid development in the field of atmospheric chemistry it was realised that carbon dioxide (CO_2) was not the only infrared absorbing trace constituent which was accumulating in the global atmosphere. Other substances now recognised as

greenhouse gases are methane (CH_4), chloro-fluro-carbons (CFC's), nitrous oxide (N_2O) and tropospheric O_3. Present day observations of these gases (Pearman, 1988), as well as measurements of air trapped in Antarctic ice, which allows CO_2, CH_4 and N_2O concentrations to be traced back for hundreds (Pearman *et al.*, 1986) or even tens of thousand of years (in the case of CH_4 and CO_2) have by now firmly established that the currently observed rising trends are a relatively recent phenomenon (within the last 200 years), closely linked to population growth, land clearing and the industrial revolution. Details are provided in the Table 1.

The changes from pre-industrial times have been significant, with CO_2 increasing by 25%, CH_4 by more than 100%, and the CFCs, being totally manmade, not being present in the atmosphere prior to 1930s. The relative warming effect of the key greenhouse gases on the global basis is shown in the Table 2.

The current and post concentrations of most of the greenhouse gases are now well-known, while research into the sources and sinks of each of these gases is continuing. Although it is currently possible to make rough estimates of the sources, more accurate information is urgently needed in order to enable better estimates of future atmospheric levels to be made, and the impact of possible control strategies to be assessed (Pearman, 1988). Figure 1 shows the relative contribution (%) of different gases to global warming

and estimated percentage annual contribution to global methane emissions from different sources.

A further outcome of a changing atmosphere and global climate change which almost by definition is impossible to predict is the element of surprise. The mechanisms which govern the sources and sinks of the atmospheric trace gases such as CO_2 and CH_4, and the mechanism of ocean/atmospheric dynamics which determine the global climate are sufficiently complex that scientists cannot rule out the possibility of unforeseen sudden changes. Examples of such events are provided by the recent discovery of stratospheric O_3 loss over Antarctica (Fraser, 1989) and the observation from geological evidence that the global ocean circulation has in the past shown sudden and dramatic changes (Broecker, 1987). The most dramatic effect has been the severe depletion of the O_3 layer over Antarctica each austral spring. The total O_3 column is reduced by more than 50% in a layer about 12 cm thick; centered about 17 km altitude, the destruction exceeds 95%. This depletion is usually referred to as **ozone hole**. In the Northern Hemisphere the decrease in column O_3 is less dramatic, but is more widespread (Farman, 1992). In the middle of the next century temperature rise is predicted as 1.5 to 5.5 ^{o}C with a rise of 0.3 ^{o}C per decade (range 0.2 to 0.5 ^{o}C). For a doubling of CO_2 it is estimated that these effects would raise the global sea level by

20 to 50 cm (Van der Veen, 1988). Sea level rise of 6 cm per decade is predicted from the best models currently available (with a range of uncertainty of 3 to 10 cm per decade) (Jenkins, 1992). Sea level will increase 1 to 2 m by year 2100 and 80 to 90% of South Carolina and New Jersey marshes will be destroyed. One metre rise will destroy 50% of the Louisiana wetlands (Titus, 1988). Global warming again means increase in soil acidity which may increase wind erosion and loss of valuable agricultural lands. The destroying feature of acid rain has already been observed in some developed countries. Greenhouse effects always bring about changes in macro and micro climate affecting adversely our established way of agricultural practices.

Methane is of considerable scientific interest because of its relatively rapid growth and the diverse possible causes of this increase. It is an important component of atmospheric photochemistry and the climate system. At the present time atmospheric CH_4 concentration is increasing by 1% per year (Steele *et al.* 1987). Therefore investigation of the causes and sources of the increase in the CH_4 concentration is an extremely important problem. This increase in global CH_4 apparently began in the previous centuries. CH_4 concentrations have been doubled since the eighteenth century, but they were relatively constant for the previous 2000 - 3000 years (Dickinson and Cicerone, 1986). Bush *et al.* (1978) reported 1.63 ± 0.12 ppmV for a

1978 worldwide average while Rasmussen and Khalil (1981) were closer to 1.60 ppmV in clean northern hemisphere air in 1978. Current atmospheric CH_4 concentration, at 1.72 ppmV, is now more than double the pre-industrial (1750-1800) value of about 0.8 ppmV, and is increasing at a rate of about 0.015 ppmV per year. About 12% of the added greenhouse warming forcing during the 1980s is estimated to come from CH_4 (Crutzen, 1991) and 80% of CH_4 is produced biogenically (Cicerone and Shetter, 1981). Average worldwide tropospheric mixing ratio has increased by 11%, 1.52 ppmV to 1.684 ppmV (from 1978 to 1987). At present increase is 1.3% per year (Rasmussen and Khalil, 1984). One gram of CH_4 is 30 times more effective over one gram of CO_2 in greenhouse effect in Global Warming.

Thermal infrared radiation is primarily over the wavelength of (6-16) μm. Water vapour blocks radiation at wavelength <8 μm and >18 μm, CO_2, in turn, dominates the absorption of radiation between 12 and 18 μm. The remaining 8 to 12 μm is known as **window** because of the atmosphere's relative transparency to radiation over these wavelengths. CH_4 being relatively more abundant, increases absorption essentially according to the square root of concentration, whereas CO_2 absorption is proportional to the logarithm of its concentration. CH_4 makes the atmospheric window region opaque. This trapping might be called as **dirty window**.

The steady growth in CH_4 concentration makes an important direct contribution to the atmospheric greenhouse effect (Blake and Rowland, 1988) because each incremental molecule of CH_4 is about 20 times more effective than each additional molecule of CO_2, partially compensating 100-fold larger yearly increase in numbers of atmospheric molecules of CO_2 than for CH_4. The greater effect per molecule of CH_4 is the consequence of its infrared absorption falling into wavelength regions that are not strongly absorbed by the existing atmospheric concentrations of the predominant O_3, H_2O, and CO_2 in contrast to the effects of any additional molecules of CO_2, for which the absorption frequencies must be identical to these strongly absorbed by the 345 ppmV of CO_2 presently in the atmosphere (Dickinson and Cicerone, 1986). An increase in H_2O in the stratosphere also contributes to an enhanced greenhouse trapping of infrared radiation as an indirect consequence of the CH_4 increase. Finally, the mutually self limiting nature of the reactions of CH_4 and CO with OH radical make it plausible that the increase in CH_4 mixing ratio is at least partially the result of a progressively lower steady state OH concentration over recent decades (Thompson and Cicerone, 1986).

The major sink for CH_4, reaction with OH radicals in the troposphere, results in a relatively short atmospheric lifetime of about 10 years. Human activities such as rice cultivation, domestic ruminant

rearing, biomass burning, coal mining, and natural gas venting have increased the input of CH_4 into the atmosphere, which combined with a possible decrease in the concentration of tropospheric OH, yields the observed rise in global CH_4. However, the quantitative importance of each of the factors contributing to observed increase is not well known at present. In order to stabilize concentrations at present day levels, an immediate reduction in global anthropogenic emissions by 15 to 20 percent would be necessary. Prediction of future trends in CH_4 mixing ratios will remain difficult without greatly improved understanding of both its sources and sinks.

It was apparent that the present optimum greenhouse warming of about +30 K will not remain so in future. The very intensive interest in the anomalies of ion composition of the earth's atmosphere shifted partially to the planetary ionospheres and then in the seventies to the stratosphere and now to the troposphere as new results began to emerge on the role and effect of non-CO_2 greenhouse molecules. In the troposphere and stratosphere the reactions are primarily neutral. The troposphere and stratosphere systems are dominated by ozone chemistry and CO_2-CH_4-H_2O-N_2O-CFC greenhouse molecules (Mitra, 1989).

Troposphere is an oxidising region. At these levels only radiations of wavelengths longer than about

300 nm can penetrate and hence direct dissociation of most of the greenhouse molecules does not occur. The only major exception is the photolysis of O_3 by radiations of ≤ 310 nm which produces $O(^1D)$. This process is crucial because $O(^1D)$ generates the catalytic radical OH from H_2O. Concentration of OH depends on the concentration of H_2O (highly variable) and also tropospheric concentration of O_3. Reaction with OH determines the lifetime of many important gases in the troposphere including the greenhouse molecules, and acts as **'chemical filter'** for transport to the stratosphere. OH radicals are a major sink of CO and **CH_4**. An additional source of OH is HO_2 reaction with NO and O_3, and so reactions leading to HO_2 formation adds to OH production. Thus oxidation of CH_4 amplifies primary OH production caused by photolysis of O_3. Another special feature is that more than in stratosphere, heterogeneous chemical reactions are more often encountered here, such as in scavenging of trace gases by aerosols, clouds and precipitation. Oxidation of CH_4 can end up with O_2 or O_3 depending on the concentrations of NO. If NO mixing ratio is less than a few pptV, then there is removal of odd oxygen (O_3) and odd hydrogen (OH, HO_2) but in polluted regions with high NO concentrations (? a few pptV), reactions involving CH_4, CO and NO produces ozone and odd hydrogen. Thus localised production of ozone with local climatic effects can occur.

In the stratosphere, several new aspects

arise : firstly, solar radiations of appropriate wavelengths are now available not only for formation and destruction of O_3, but also for dissociations of CH_4, CCl_4, N_2O, H_2O and others releasing ozone-destroying active species ClO, OH and NO.

We are at a critical juncture of human history, for never before did the concerns of the immediate future cast such gloom on the thinking of the present. The portents are so ominous and imminent that to wait further till every scientific observation could be explained with absolute certainty might be more than unwise. Whether the causal relationships have been understood clearly or not global climate change, essentially resulting from man-made activities, has obviously started itself. So, it is a crying need to identify the sources of global warming as well as their warming potentiality on an emergency basis to save the civilisation through possible mitigation strategies coming out through such type of studies. A considerable amount of work has already been done on CH_4 emissions from paddy as agricultural source of greenhouse gases all over the world, and to some extent in India. But investigations into other possible sources of *in situ* CH_4 production amongst various bio-sources under natural environment is not known in our country. These types of studies have become necessary to work out CH_4 production from various sources and its pollution potentiality on

one hand and on the other hand their scope of possible use as a source of non-conventional energy for our third-world country where energy crisis is very much acute. Present work has been undertaken with the following objectives :

1. To estimate CH_4 flux from different sources such as paddy fields, exposed areas of biogas plants, compost pits, heaps of fruit and vegetable wastes, open drains, distillery effluent lagoons etc.

2. To study the effect of different environmental factors like temperature, pH, redox potential etc. on CH_4 emissions.

Table 1. Important Greenhouse Gases

Gas	Concentration [ppbV] Pre-industrial	1990	2050	Increase [%/yr]	Relative contribution [/kg]
CO_2	275 ppmV	353000	500000	0.5	1
CH_4	750	1720	2100-4000	1.0	30
N_2O	285	310	310-450	0.25	300
CFC-11	nil	0.28	0.7-3.0	4.0	4000
CFC-12	nil	0.48	2-4.8	4.0	8000
O^*_3	15-20	20-30	(15-20)% more	0.5	3

* In the troposphere

Watson *et al.*, 1990

Table 2. Warming effect of Greenhouse Gases

A	B	C	D	E	F	G
CO_2	1.3	1	60[a]	1	59	55
CH_4	0.6	36	10	6	27	20
N_2O	0.05	140	150	350	3	5
CFC-11	0.06	14600	75	18000	3	6
CFC-12	0.12	17000	110	31000	6	12
O_3[b]	0-0.12	430	0.2	1	2	2

[a] The turn over time for atmospheric CO_2 is about 6 years, but the time needed to permanently remove CO_2 to the deep ocean and the long-lived biosphere is about 60 years

[b] In the troposphere

[c] From Dickinson and Cicerone (1986), based on the increase in atmospheric concentrations from pre-industrial times to 1985

A: Greenhouse gas

B: Relative forcing [Wm^{-2}][c]

C: Relative (to CO_2) radiative forcing per ppmV increase[c]

D: Atmospheric lifetime (in years)

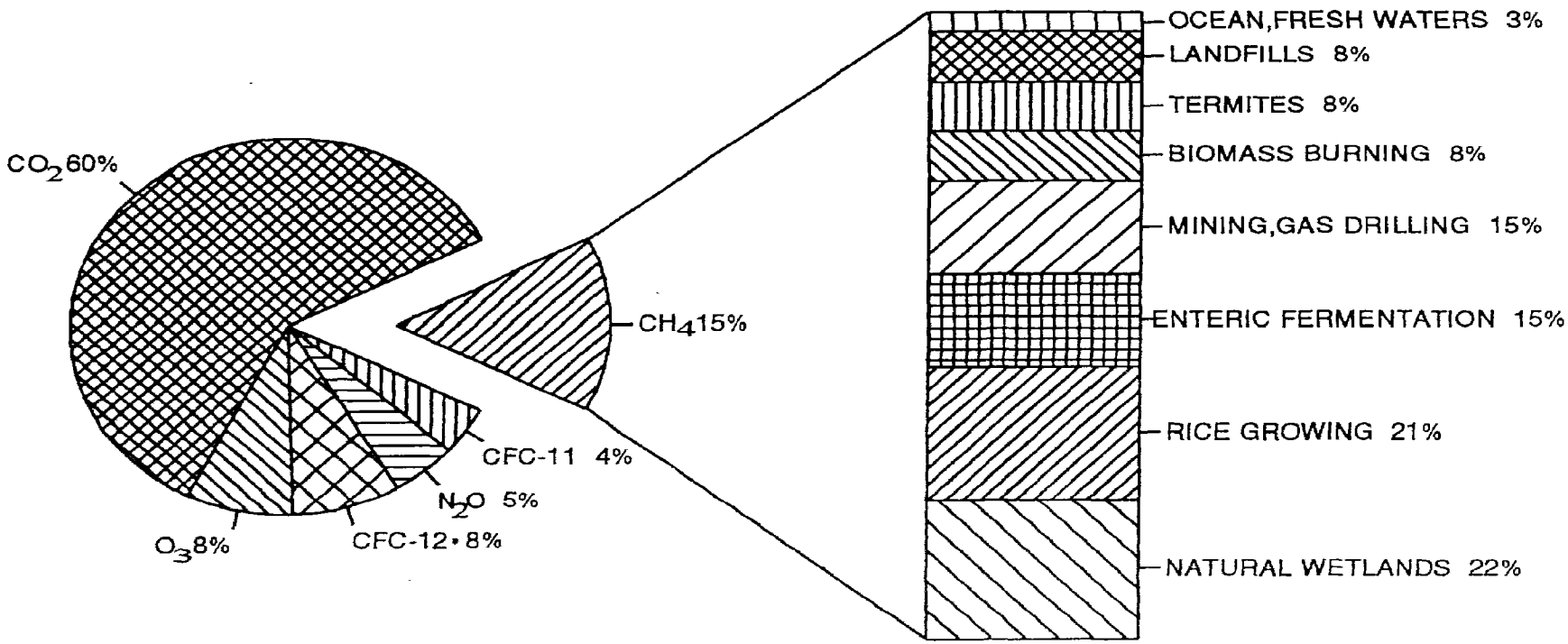
E: Long-term relative (to CO_2) contribution to global warming per molecule emitted

F: Percentage of total radiative forcing to date

G: Percentage of the radiative forcing due to current increases

Pearman, 1986

Fig. 1. Contribution of different gases to Global Warming



Badr *et al.*, 1991

REVIEW OF LITERATURE

REVIEW OF LITERATURE

The review of literature having bearing upon the investigations carried out is presented under the following titles :

2.1 Origins of atmospheric methane

2.2 CH_4 flux from rice paddy fields.

2.3 CH_4 flux from other sources

2.1 ORIGIN OF ATMOSPHERIC METHANE

Methane has been known as a minor constituent of the earth's atmosphere for more than 45 years (Migeotte, 1948). Though it contributes very little to the carbon cycle but is a major participant in the earth's atmospheric chemistry. Photochemical oxidation of methane, mainly in the troposphere, produces CH_2O, H_2, and CO as intermediates and is an important source of stratospheric water. Consequently, there has been continuing interest in sources of methane and their role in atmospheric chemistry (Sheppard *et al.*, 1982). It is generally agreed that CH_4, being such a complicated molecule, it has too high an internal energy to be synthesised within the atmosphere, and so it must be released (into the atmosphere) mainly at the earth's surface (Enhalt and Schmidt, 1978). Most of the atmospheric CH_4 is produced biologically by a group of anaerobic bacteria living in anoxic environments which are rich in organic matter (i.e. by microbial activities during the mineralisation of organic carbon under strictly anaerobic conditions). Such environments occur in water-logged soils, swamps, marshes, freshwater and marine sediments, as well as intestines of animals (Klug, 1985). The principal anthropogenic sources of CH_4 arise from agriculture. Others include the incomplete combustion of biomass, as in tropical deforestation and forest fires as well as in the burning of agricultural residues : gaseous releases from

landfills, and leakages of natural gas from pipelines, venting from gas and oil-wells and its escape from coal in mining and processing (Badr *et al.*, 1991).

Any CH_4 derived from recent organic material has a carbon isotope ^{14}C content very close to that of recently grown wood. By contrast, CH_4 derived from fossil fuels or emitted as a result of volcanic activity contains essentially no ^{14}C. The fuel deposits are also so old that the originally present ^{14}C has decayed. Atmospheric samples collected before the atmosphere was contaminated with ^{14}C (from nuclear explosions and industrial emissions showed that 80% of CH_4 was of recent biogenic origin and 20% was 'dead' CH_4 (Enhalt and Schmidt, 1978). Recent estimates suggest that the known fossil-fuel sources add upto much less than 20% of the biogenic source, so that this old estimate should still represent a reasonable upper limit for 'dead' CH_4 (Hameed & Cess, 1983; Volz *et al.*, 1981). However, measurements by Wahlen (1989) indicated that, at the end of 1987, 21% of the then existing atmospheric CH_4 was derived from fossil carbon. The data also indicated that pressurised light-water reactors are an increasingly important source of CH_4 containing ^{14}C (this emission began around 1960, and is a predominantly Northern Hemisphere source).

The fact that most atmospheric CH_4 is produced biologically by the decay of recent organic

matter simplifies the search for its sources considerably. There is evidence that the rates of emission from known sources increased with growth of the human population (Khalil and Rasmussen, 1983) and that the largest changes of global production of CH_4 are caused by human activities (Khalil and Rasmussen, 1985). Some 200 years ago, the anthropogenic contribution to the global cycle of CH_4 was relatively low as compared with that occurs at present (Khalil and Rasmussen, 1985). About 50% of the present sources of CH_4 are controlled by mankind (Enhalt, 1974). Although the major sources of CH_4 are believed to be known, the accuracy of estimates of emission rates from individual sources is poor (as can be seen from the disparities in Table 3).

Although estimates are uncertain, several CH_4 sources are known to be of increasing output (Table 4). In particular, the area under rice cultivation, ruminant populations, biomass burning and fossil-fuel production have all grown steadily over the past 50 years, simultaneously with the rise in human population. The mean global growth rate for CH_4 release into the atmosphere for the period 1940-1980 was about 3.5 million tonnes per year (i.e. 1% annually). In the 1980s, it is believed that the total CH_4 emission to the atmosphere ranged from 225 to 1210 million tonnes per year . Cicerone and Oremlemd (1988) estimated that the annual CH_4 emission during the late 1980s was 520 ± 120

million tonnes

One percent annual increase in the total rate of CH_4 emissions approximately corresponds to the rises in the emissions from individual sources during the decade 1970-1980. The exceptions are CH_4 fluxes from natural gas and coal deposits which are 4.1% and 2.1%, respectively (Glachenko *et al.*, 1989). If this tendency persists the CH_4 contributions from these sources will be respectively 160 and 70 million tonnes per year by the year AD 2020 (Table 5).

Sheppard *et al.* (1982) on the basis of 17 ecosystems estimated that 9.1×10^{14} g CH_4/yr is emitted into the atmosphere from the biosphere. Enteric fermentation in animals and humans, decomposition of organic wastes and biomass burning contribute an additional 2.0×10^{14} g CH_4/yr. Various fossil sources emit another 1×10^{14} g CH_4/yr. When all sources are considered, they emit 12.1×10^{14} g CH_4 each year. As with earlier inventories, this study indicates that the fossil methane contribution is less than 10% of the total annual production rate.

It is shown that a long lifetime of about 8 years is most consistent with the observed latitudinal variation of atmospheric methane, requiring the current global emissions of CH_4 to be around 550 teragrams per year (Tg = 10^{12} g). On average, there is 25-34 ppbV less CH_4 in the atmosphere of the northern hemisphere during

summer, when compared with the rest of the year. CH_4 concentrations rise rapidly to their yearly maxima in fall. Seasonal cycles of CH_4 concentration in the southern hemisphere include lowest concentrations during the late Australian summer and fall, being about 14 ppbV less than during the rest of the year. The repeating pattern of rapid rise of CH_4 concentrations during fall in the northern hemisphere suggests a large fall source at latitude above 30 ^{o}N. The remaining observed seasonal variations are consistent with the seasonal cycle of OH, which removes CH_4 from the atmosphere. The extensive set of self consistent measurements of CH_4 are reported and analysed showing that methane has increased during the last 3-4 years at rates of 1-1.9% per year all over the world at sites ranging from inside the arctic circle to the south pole (Khalil and Rasmussen, 1983).

Crutzen (1991) estimated that with about 100 Tg yr^{-1} of CH_4 coming from fossil-fuel sector, another 405 Tg Yr^{-1} must come from biogenic sources. The best known among these are emissions from ruminant animals, about 80 Tg yr^{-1}. Landfills may release 50$\pm$20. Oceanic production and production by insects (termites) may contribute 30 Tg yr^{-1}.Consequently, 245$\pm$65 Tg yr^{-1} released, mostly in the tropics, from natural wetlands, rice fields and biomass burning. Biomass burning may release 30$\pm$15 Tg yr^{-1} , leaving an emission of 215$\pm$50 Tg yr^{-1} from natural wetlands and rice fields. IPCC

(1992a) reported on CH_4 sources and sinks (Table 6).

Andronova and Karol (1993) studied the release of CH_4 in the former U.S.S.R. It is shown that the U.S.S.R. CH_4 sources are 11% of the global value of 540 Tg. Thus U.S.S.R. contributes less than 10-13% of the World's CH_4 flux from wetlands. U.S.S.R. contributes up to 43% of the global fossil fuel source of CH_4. The upper limit of the CH_4 flux from U.S.S.R. cattle 12 Tg, which is 15% of the global cattle CH_4 source.

2.2 METHANE EMISSONS FROM RICE FIELDS

Rice is cultivated under a wider variety of climatic, soil and hydrological conditions than any other crop. Rice is grown from the equator to as far as 50 °N and 40 °S, and from sea level to altitudes of more than 2500 m. The temperature may be as low as 4 °C during the seedling stage and as high as 40 °C at flowering. Rice is irrigated in arid areas and is grown in rainfed areas with only 500 mm rain/year. Rice is cultivated like wheat on upland soils and in soils that are submerged more than 1 m.

Parashar *et al.* (1991) studied methane emission from paddy fields in India at four different locations. First order CH_4 budget estimates from the Indian paddy fields indicate a maximum release of 3 to 9 Tg CH_4/yr. which is only 5% of the global CH_4 budget due to paddy cultivation. They found a wide variation in

flux collected from different places at different times. The range of soil temperature was 24 to 33 ^{o}C and the CH_4 flux was 0.07 to 80 mg $m^{-2}hr^{-1}$. Change of CH_4 efflux with temperature varies between 0.01 and 14 mg $m^{-2}hr^{-1}$ $^{o}C^{-1}$ from place to place. The percentage increase in CH_4 efflux per degree rise in soil temperature ranges from 10 to 30.

Saha *et al.* (1989) found that inundated fields with plants other than rice (*Enhydra fluctuans* Lour and *Cynodon dactylon* Pers), with a similar soil and pH value of water (8 to 8.5) gave CH_4 emission rates (5 mg $m^{-2}hr^{-1}$) of the same order as over the rice (2.9 to 8.6 mg $m^{-2}hr^{-1}$) paddy fields.

In calculating total CH_4 budget in China areas were reduced by subtracting the fraction of area in dryland rice from the area planted to mid season rice, and fluxes were reduced by 40% for areas of rainfed rice, also applied to mid season rice (Huke, 1982). In early rice the flux was 8 mg $m^{-2}hr^{-1}$ (Schütz *et al.*, 1990). In late rice it was 27 mg $m^{-2}hr^{-1}$ (Schütz *et al.*, 1990). In the South China in midseason rice the emission rate was 36 (Khalil *et al.*, 1991) and in the North 35 mg $m^{-2}hr^{-1}$ (Chen *et al.*, 1992).

Thom *et al.* (1993) reported CH_4 flux in European rice fields 0.9-2.5 as $g/m^2/hr$.

Bachelet and Neue (1993) used the average rate of 0.5 g $m^{-2}day^{-1}$ (Mathews *et al.*, 1991) to calculate

CH_4 emissions from China and India. Because the greatest areas under rice cultivation are in India and China, their calculated CH_4 emissions are the greatest, 28 and 32 Tg CH_4 yr^{-1} respectively. India with 33% more harvested area, produced 28% more CH_4 than China. Data processing was done with GRASS, a raster base geographic information systems software package (Army Corps of Engineers, 1988). Rice cultivated area in India is 42.86 m ha^{-1} and CH_4 production is 27.6 Tg yr^{-1} (Mathews *et al.*, 1991) or 18.35 Tg yr^{-1} (Taylor *et al.*, 1991) or 18.54 Tg yr^{-1} (Neue *et al.*, 1990). Mean annual temperature in India is 5-10 °C higher than in China and it varies from 20-30 °C. Rice yields in India are 57% lower than in China (IRRI, 1990). Therefore, using Neue *et al.*, (1990) methodology which estimates CH_4 emission from grain production, they calculated that India produced 15% less CH_4 than China.

China is one of the World's largest producers of rice and constitutes a sizable fraction of the Earth's population. Using geographical, agricultural and industrial data along with direct flux measurements, Khalil *et al.* (1993) found that the anthropogenic CH_4 emissions from China are now more than 60 Tg yr^{-1}. In recent decades there has been a decline in the emissions from agricultural sources due mostly to a dramatic decrease in the per capita emissions of CH_4 from rice agriculture. Sources related to energy are on rise so that the reductions from agriculture are offset by

increases from these energy sources. If the present trends continue, the dominating role of rice agriculture on CH_4 emissions in China will be replaced by emissions from energy sources.

Khalil *et al.* (1990) reviewed 11 global CH_4 budgets published between 1978 through 1988. They found that CH_4 emissions from rice paddies ranged from 1 to 280 Tg yr^{-1} which correspond to between 10 and 70% of the total anthropogenic methane emissions. Bachelet and Neue (1993) reviewed and replicated three published techniques to estimate methane emission from rice paddies. They present the results obtained and propose to include soil characteristics to revise these estimates. Since 90% of rice production occurs in Asia, they have only focused their study on rice in Asia. The first technique they replicated, uses the Food and Agriculture Organisation (FAO)'s country statistics and crop calenders to determine the land area under rice cultivation each month. Assuming a constant emission rate, Asian rice fields emit about 82 Tg yr^{-1}. The second methpd they replicated, assumes that CH_4 emissions represent a constant fraction of the net primary production and uses empirical relationships between net primary production and temperature and precipitation records. Asian rice fields then only produce 57 Tg yr^{-1}. The third technique they replicated, relates CH_4 emissions to rice grain

production. It involves the calculation of total organic matter added to rice paddy soils and assumes that a constant fraction is emitted as CH_4. This leads to an estimate of CH_4 emissions from Asian rice fields of about 63 Tg yr^{-1}.

Schütz *et al.* (1990) calculated a global annual emission of 100 ± 50 Tg CH_4 yr^{-1}. This estimate of the source strength of rice cultivation for the emission of CH_4 is consistent with recent calculations by other authors (Table 7). Obviously, the data base available for global calculations of CH_4 emissions from rice cultivation has considerably improved during recent years. Still considerable uncertainties remain, because the data available from Asian rice paddies are only representative for a minor part of this most important rice growing areas.

Neue (1989) subdivided rice lands into wetlands and uplands. Wetland rice soils are submerged for at least the major part of one rice growing season. Wetland ricefields may be without surface water, moist or dry in other seasons and may, therefore, alternately support wetland rice and upland crops. In most cultivated wetlands of the tropics, drainage capacities are insufficient to prevent prolonged soil submergence during rainy season. Irrigated rice has the highest potential to produce CH_4 because flooding and, consequently, anoxic conditions are assured and controlled. The potential for CH_4 production in rainfed

rice should widely vary in time and space since floodwater regimes are primarily controlled by rainfall within the watershed. The potential of upland rice for CH_4 production is not significant since upland rice is never flooded for a significant period of time.

Wetland rice soils :

Flooding in air-dried cultivated soil drastically changes the hydrosphere, and biosphere of that soil. Flooding highly limits diffusion of air in soils. The O_2 supply can not meet the demand of aerobic organisms and facultative and anaerobic organisms proliferate using oxidized soil substrates as electron acceptors in their respiration. Consequently the redox potential (Eh) falls sharply according to a sequence predicted by thermodynamics and CO_2 and HCO^{-1}_3 concentrations increase to a very high levels. As a result the soil pH of acid soil increases while that of sodic and calcareous soils decreases, stabilizing between 6.5 and 7.2. Flooding and puddling render moist soils as ideal growth medium for rice by supplying abundant water, buffering soil pH near neutral (Pennamperuma, 1972).

The major gaseous end products of anaerobic fermentation in submerged soils produce an array of organic substances, many of them transitory and not found in aerobic soils. The major gaseous end products are CO_2, H_2S and CH_4 formation mainly takes place in the

reduced topsoil where easily degradable organic substances are available. If the subsoil is saturated with water the B horizon may also become a source of CH_4. If the topsoil is saturated with water CH_4 oxidation may predominate in B horizon. CH_4 oxidation also takes place in the floodwater-soil interface (Bont *et al.*, 1978) and in the rice rhizosphere (Sass *et al.*, 1991a). Methanogenic bacteria are strict anaerobes and intolerant of O_2 exposure for growth, although they may not be killed by short exposure (Knowles, 1993) to oxygen.

Twenty genera of methane-producing bacteria have been described but only a few, including *Methanobacterium* and *Methanosarcina* have been isolated from rice soils (Rajagopal *et al.*, 1988). *Methanospirillum* and *Methanocorpusculum*, which were isolated from freshwater sediments, as well as methanogens found in endosymbionts in sapropelic amoebae may also be present in wetland rice fields (Neue and Roger, 1993). Most described species are hydrogenotrophs and use formate or acetate while methylotrophs use 1-C compounds such as methanol or methylated amines (Garcia, 1990). Most of them can fix CO_2 and need H_2 as their electron donor (energy source) even if they use acetate as a C source (Knowles, 1993). In wetland rice soils, the major substrates for CH_4 production are acetate and H_2-CO_2 (Zeikus, 1977). Neue *et al.* (1990) amalgamated conditions for high CH_4

production in wetland rice soils into six crucial parameters : water regime, Eh/pH buffer, carbon supply, temperature, texture and mineralogy, and salinity. Rice soils that are prone to CH_4 production mainly belong to the orders of Entisols, Inceptisols, Alfisols, Vertisols and Mollisols.

Temperature :

Rice is grown under widely differing temperature regimes. The temperature of flooded rice soils at planting may range from 15 °C in northern latitudes to 40 °C in equatorial wetlands. The soil temperature of flooded soils varies in response to the meteorological regime acting upon the atmosphere-floodwater and floodwater-soil interfaces. Hackman (1979) reported that floodwater temperatures are above the minimum air temperature but below the maximum air temperature if diel amplitudes of air temperature are high, like in subtropical regions or at high altitudes in the tropics. Floodwater temperatures are above maximum air temperatures if diel fluctuations are low as in tropical lowlands. The temperature of the puddled topsoil layer (0-15 cm) closely follows the temperature of the floodwater and decreases with depth. Diel amplitudes reached upto 8 °C and decreased to less than 1 °C in and below the dense plough pan (Neue, 1991). In tropical rice soils maximum soil temperatures occur mostly early in the afternoon and minimum soil

temperatures are found in the morning. Schütz *et al.* (1990) found that the diel soil temperature pattern of flooded soils in Italy changed with depth and maximum temperature showed an increasing phase shift to later daytime probably because of time dependent heat transport. Rice soils in the US also reveal maximum temperatures in the later afternoon (Sass *et al.*, 1991a).

Methane emission increases by a factor of 1.5 to 2.0 for every degree increase in soil temperature and shows a maximum at 34.5±0.5 °C. The CH_4 flux decreases sharply above this soil temperature (Parashar *et al.*, 1993).

Variations in CH_4 production and emission from natural and agricultural wetlands have been correlated to soil temperature by a number of researchers (Crill *et al.*, 1988; Conrad, 1989; Bowman, 1990). At soil temperatures found in flooded tropical soils, CO_2 and CH_4 formation occur sooner and in larger amounts than in cooler climates (Tsutsuki and Ponnamperuma, 1987). Holzapfel-Pschorn and Seiler (1986) reported a marked influence of soil temperature on the CH_4 flux with doubling of emission rates when temperature increased from 20 to 25 °C. Sass *et al.* (1991a) observed maximum CH_4 production in rice soils at about 37 °C irrespective of differences in CH_4 production potentials. Most isolates of methanogenic bacteria are mesophilic with temperature optima of 30 to

40 °C (Vogels *et al.*, 1988). Psychrophilic acetate-utilizing methanogens with a temperature below 20 °C seem to occur in acidic peat (Svensson, 1984).

Diel variation of CH_4 fluxes is highly correlated with temperature fluctuation. Temperature affects the solubility of CH_4 in the soil solution and floodwater. Less CH_4 is solubilized with rising temperature during daytime. Additional factors like oxygen and substrate supply modify the relationship, especially at later growth stages of the rice crop (Schütz *et al.*, 1989a). Thus as simple comparison and field measurements over a whole season may not show a clear temperature correlation. Since upto 90% of the produced CH_4 may be oxidised within the soil floodwater system (Holzapfel-Pschorn *et al.*, 1986), temperature effects on methanotrophs may have substantial impact on the activation energy of CH_4 emission. Similar activation energies for CH_4 production suggest that emission is a faster process than production, and a large buildup of CH_4 in a flooded soil grown to rice should not be expected (Sass *et al.*, 1991a).

Redox Potential (Eh):

The supply of biodegradable carbon and the activity of the adoption are the key factors to most of the characteristic biochemical and chemical processes in flooded soils (Neue, 1991). These processes include soil reduction and associated electrochemical changes

alongwith the release of CH_4. Since CH_4 is produced only by strictly anaerobic bacteria (methanogens), a sufficiently low Eh is required. Wang *et al.* (1993) showed that the critical soil Eh for initiation of CH_4 production is between -150 to -160 mV. Between -150 mV and -230 mV the relationship of CH_4 production and soil Eh becomes negatively exponential. A rapid initial decrease of Eh after flooding in most soils is caused by high decomposition rates of organic substrates and a low buffer of NO_3^- and Mn oxides. The most important redox buffer systems in rice soils are Fe (III) oxyhydroxides/Fe(II) and organic compounds. Soils low in active iron with high organic matter may attain Eh values of -200 to -300 mV within 2 weeks after submergence (Ponnamperuma, 1972). In soils rich both in iron and organic matter, the Eh may rapidly fall to - 50 mv and then slowly declines over weeks and level off. Soils where the redox potential is controlled by a ferruginous or oxidic mineralogy and/or the soil reaction is strongly acidic or alkaline are less prone to CH_4 formation (Neue *et al.*, 1990).

pH :

Most methanogens are neutrophillic with a relatively narrow pH range of 6-8. Few alkaliphilic isolates with optimum growth at pH 8-9 have been reported in the genera *Methanosarcina, Methanobacterium,* (Blotevogel *et al.*, 1985; Worakit *et al.*, 1986) and *Methanohalophilus* (Mathrani *et al.*, 1988). No

acidophilic strains have been reported. Wang *et al.*, (1993) found highest CH_4 production rates at pH of 6.9 to 7.1 in an acidic rice soil. Small changes in pH sharply lowers CH_4 production. Below pH 5.75 and above 8.75 CH_4 production was inhibited completely. Acharya (1935) reported that during decomposition of organic substrates the preliminary stage of acid formation is more tolerant to pH reaction, but CH_4 formation is greatly impeded outside the range of pH 7.5 to 8.0. Parashar *et al.*, (1990) found highest CH_4 emission rates at a pH of 8.2 in some Indian rice soils. The actual optimum pH for CH_4 production may slightly differ between soils because of differences in substrate supply and to intimate linkage between pH and Eh. In calcarious and alkaline soils it may take weeks before CH_4 is formed. In very acid soils, CH_4 may not be formed at any time (Neue and Roger, 1993).

Methane production is restricted to Eh lower than -200 mV (Conrad, 1989). In laboratory experiments with rice soil cores CH_4 production started in the second week after incubation (Takai *et al.*, 1956).

In soil samples the methane production rate at 30 °C exceeded the rate at 17 °C by a factor of 2.5 to 3.5 (Conrad *et al.*, 1987); a recent investigation revealed even higher ratios between the CH_4 production rates at 25 °C and 35 °C (Yagi *et al.*, 1990). Since the microbial process involved in supplying methanogenic

substrates are thought to be more temperature sensitive than the formation of CH_4 itself, the temperature of the *in situ* production of CH_4 may predominantly reflect the impact of temperature changes on microbial process involved in substrate production for methanogens (Conrad *et al.*, 1987).

The total CH_4 production in soils of Italian rice paddies reached maximum values of more than 214.3 mg $m^{-2}hr^{-1}$. The CH_4 production increased during the season, although the population density of methanogens remained relatively stable (Schütz *et al.*, 1989a).

Wassmann *et al.*, 1993) compiled available field data describing methane emission rates from different parts of the world (Table 8).

Short term observation periods or less than an entire annual cycle are not feasible for an accurate extrapolation. Observation period covering a single year can yield misleading results due to specific weather conditions that differ from the long term average. The observed emission rates revealed pronounced regional variations. CH_4 emission was found to respond to short-term temperature changes, e.g. by diurnal dynamics, there is no clear cut correlation between the average temperature and the emission integrated over the entire season.

The application of organic manure generally seems to enhance CH_4 emission, although the extent of the enhancement reported in different studies exhibits

great variation. Addition of rice straw resulted in a significant increase of emission rates in Italy (Schütz *et al.*, 1989b) and Japan (Yagi and Minami, 1990), whereas the application of organic manure and compost only slightly altered CH_4 emission (Schütz *et al.*, 1990; Yagi and Minami, 1990).

The effect of mineral fertilizers on CH_4 emission is even more complex to survey. One type of fertilizer may increase or reduce methane production in non-identical conditions. A drastic example for inverse effect caused by the same fertilizer is ammonium sulfate that was found to result in five fold increase in CH_4 emission (Cicerone and Shetter, 1981) and a reduction by 50% (Schütz *et al.*, 1989b). Apparently, the mode of fertilizer application is an important factor for CH_4 emission (Schütz *et al.*, 1989b).

The temporal variations observed in different investigations were extensively variable in both, diurnal and seasonal cycle. Apparently, a direct response of CH_4 emission on temperature changes results in a diurnal cycle with a midday maximum and lowered emission rates during nighttime, as observed in Italy (Schütz *et al.*, 1989a).

The seasonal courses of CH_4 emission observed by several authors cannot directly be attributed to temperature changes (Cicerone *et al.*, 1983; Seiler *et al.*, 1984; Schütz *et al.*, 1990), but similarities in

the general trend were found (SchÜtz *et al.*, 1990). Therefore, indirect effects, i.e., the availability of methanogenic substrates, seem to modulate the seasonal patterns of CH_4 emissions from rice cultivation. This view is consistent with the finding that high emission rates after flooding are related to the degradation of the initial stock of organic matter in the soil. Additional input of rice straw into soils enhanced the early maximum of CH_4 emission (SchÜtz *et al.*, 1989b), whereas soil with low organic matter content did not exhibit a high methane release during this period.

The flooded soil experiences wide redox conditions ranging from well oxidized to strongly reduced. In an oxidized soil (aerobic) soil changes from about + 400 to + 600 mV, whereas, in most reduced (anaerobic) soils the Eh varies from about -300 to +100 mV. Moderately reduced soils are characterized by an Eh between +100 and +400 mV. Although it is known that methanogenic processes occur under strongly reducing soil conditions (SchÜtz *et al.*, 1989), the link between soil oxidation-reduction status on CH_4 emission from rice soil is not well defined. The identification of the link between soil and CH_4 emission will be important in determining the most effective mitigation to prevent increasing emission based on agricultural practices and scientific knowledge. The establishment of soil redox conditions below -150 mV resulted in a stimulation of methanogenic bacteria and led to

evolution of CH_4 from the flooded soil (Masochelyn *et al.*, 1993). Basically, CH_4 formation can be considered as a reduction of CO_2 to CH_4. The biochemical process and pathways involved in CH_4 formation in rice paddies have been recently reported by Kimura *et al.* (1991) and Schütz *et al.* (1989).

The correspondence of soil Eh to CH_4 emissions from a rice paddy soil was studied by Masscheleyn *et al.*, (1993). A Louisiana rice soil was equilibrated under controlled redox levels, ranging from + 500 to -250 mV, and the amount CH_4 evolved quantified. A soil redox value of -150 mV was critical for CH_4 emission to occur. The lower is the soil redox level the greater is the CH_4 emission rates. A 50 mV decrease in soil redox level resulted in approximately a 10 fold increase in CH_4 emission rate for the -150 mV to - 250 mV range. Upto -150 mV CH_4 flux is linear after which it increases.

A laboratory incubation experiment on rice soil was conducted to study the critical initiation soil Eh, the optimum soil pH, and the interaction of Eh and pH on CH_4 production. The critical soil Eh for initiation of CH_4 production observed was approximately from -150 to -160 mV. Between -230 and -150 mV, the relationship of CH_4 production and Eh appeared to be negatively exponential ($Y = a10^{-bx}$, where Y is the CH_4 production rate, $\mu g\ g^{-1}\ d^{-1}$; x is the Eh, mV; and a and b

are constants). The optimum pH for CH_4 production was near neutrality. A small decrease in pH resulting from the introduction of acidic materials significantly decreased CH_4 production. A slight increase in soil pH (about 0.2 unit higher than the natural soil suspension pH) however resulted in an enhancement of CH_4 production by 11 to 20% and 24 to 25% at controlled Eh of -250 and -200 mV respectively. Results suggests that a decrease in CH_4 emissions could be obtained by a small reduction in soil pH.

Cicerone and Shetter (1981) observed a flux of 32 mg CH_4 $m^{-2}d^{-1}$ from unfertilised rice field. When that field was fertilised by 140 kg N $ha^{-1}yr^{-1}$ as $(NH_4)_2SO_4$ the flux reduced to 1.5 mg CH_4 $m^{-2}d^{-1}$.

2.3 METHANE EMISSIONS FROM OTHER SOURCES

2.3.1 Landfills

Published estimates for worldwide landfill methane emissions range from 9 to 70 Tg yr^{-1} (Bogner and Spokas, 1993). The highest and most widely disseminated estimate is the Bingemer and Crutzen (1987) figure of 30 to 70 Tg yr^{-1}. Olrich's (1990) estimate of 33 Tg yr^{-1} is at the low end of the Bingemer and Crutzen range, and Richard's (1989) highest number is roughly half of the Olrich estimate.

For landfills Thom *et al.* (1993) assumed a carbon fraction of 20% by weight is converted to methane and a 10% net CH_4 production occurs from the amount of

converted organic carbon in a year.

Soil temperature has been correlated with emissions from several habitat types. However, the form of relationship between temperature and flux varied from that approaching a step function (Wilson *et al.*, 1989) to a logerithemic function (King and Wiebe, 1978). Although emissions from marsh sites along a tidal creek were logarithmically correlated with soil temperature (Bartlett *et al.*, 1987), emissions from the sites differed in seasonally, with peak emission occurring at different times and the period of high emission varying in length. Plots of flux and soil temperature indicated that equivalent temperatures in the autumn resulted in significantly higher emissions than in the spring. Although there is a general correspondence between flux and temperature in virtually all seasonal flux studies, in most cases attempts to correlate emissions to such simple environmental variable and to extrapolate them more widely have been generally unsuccessful.

Direct measurements of landfill methane emissions are sparse, with rates between 3.15 and 315; very high rates of 400 kg $m^{-2}yr^{-1}$ have been measured at a semiarid unvegetated site (Bogner and Spokas, 1993). Decomposition of refuse in landfills occurs through a complex series of microbial reactions, predominantly under anaerobic conditions. Acetic acid is a major aqueous intermediate. The terminal reaction in the production of CH_4 by methanogenic bacteria, which are

strict anaerobes, require a low Eh, and function best at neutral pH. The major gaseous products of refuse decomposition, collectively termed "landfill-gas", are CH_4 and CO_2. At a small percentage of sites, landfill gas is recovered commercially for fuel use; the largest facility is a 50 MW steam-turbine power plant in Southern California, USA, fueled exclusively by landfill CH_4. Gaseous emissions from landfills are becoming subject to increasingly stringent regulatory controls in many countries of the world.

2.3.2 Wetlands

Bartlett and Harris (1993) reviewed progress on estimating and understanding both the magnitude of, and control on, emissions of CH_4 from natural wetlands. They also calculated global wetland emissions using the extensive flux data base and wetland areas compiled and published by Mathews and Fung (1987). Tropical regions (20 °N - 30 °S) were calculated to release 66 Tg CH_4 yr^{-1}, 60% of the total wetland emission of 109 Tg yr^{-1}. Flux data from tropical wetlands reported only within the last four years, are currently restricted in geographic coverage. Additional data from other regions will be required to confirm these calculated large emissions. Although emissions from subtropical and temperate wetlands (45 °N-20 °N and 30°S-50 °S) were relatively low at 5 Tg yr^{-1}, the process oriented focus of most of the research in this region suggests that

work at these latitudes may serve as models to examine controls and possible uncertainties in estimating fluxes. These types of efforts are frequently not possible in more remote, globally significant wetlands. Northern wetlands (North of 45° N) were calculated to release a total of 38 Tg CH_4 yr^{-1} (34% of total flux); 34 Tg yr^{-1} from wet soils and 4 Tg yr^{-1} from relatively dry tundra. Methane emission in tropical wetland is 66 Tg/yr and in temperate wetland 5.4 Tg/yr of the total estimated annual wetland flux of 110 Tg.

The world's wetlands represent a large source of CH_4. Due to the anaerobic fermentation by bacteria in the water covered soil (Neue and Scharpenseel, 1984), they emit around 115 (Mathews and Fung, 1987) or between 40 and 345 (Aselmann and Crutzen, 1989) million tonnes of CH_4 annually. Globally, wetlands are concentrated primarily in boreal region (i.e. 20 °N-30 °S). Bogs have largely boreal features, approximately 70% of which are forested. They are distributed throughout Alaska and extend in a Swathe stretching wetlands from Hudson's Bay, Canada, as well in the northwest of the former Soviet Union, and in Malaysia and Indonesia. Swamps and alluvial formations are located in the topics along the Amazon and Parana rivers, in the Chao and Mato Grosso regions of South America, in Africa and in Malaysia. Recent estimates suggest emission figures of 55 and 39 million tonnes from tropical and high altitude respectively (Watson *et al.*, 1990).

However Ehrlich (1990) reported that natural wetlands especially peat bogs in northern latitudes, are responsible for perhaps 50% of the total emissions from wetland sources.

The study of Mathews and Fung (1987) suggested that the tropical and subtropical peat-poor swamps lying between 20 °N and 30 °S constitute around 30% of the global wetland area and produce about 25% of the total CH_4 emission. About 60% of the total wetland emission comes from peat-rich bogs in the region from 50 to 70 °N. They concluded that the highly seasonal emission (i.e. 62 million tonnes within a period of 3-4 months) from those latter ecosystems is the main cause of the large annual oscillations observed in atmospheric CH_4 concentrations at these latitudes in the Northern Hemisphere.

Aselmann and Crutzen (1989) also compiled data on global fresh water wetland ecosystems in six categories (Table 9).

The global release of CH_4 from swamps has been estimated to be between 20 and 60 million tonnes per year (Enhalt, 1985). Enhalt (1974) estimated the annual global CH_4 emissions from swamps and marshes to be 130-300 million tonnes. However Bolle *et al.* (1986) found this figure to be quite high. Blake (1984) reported an average emission from swamps and marshes to be around 121 million tonnes per year. The measurements

of CH_4 flux, from a freshwater temperate swamp, conducted by Wilson *et al.* (1989) showed CH_4 emissions to be highly variable both between locations, and time for any specific location. The emissions varied over three orders of magnitudes.

Recent measurements in the Amazon flood plain indicated relatively high emissions from macrophyte beds : annual emissions for the Amazon basin as a whole were estimated at between 7.8 and 13.2 million tonnes (Mooney *et al.* 1987). Burke *et al.* (1988) estimated the changes that could have resulted from warming during the last 100 years. The result of their calculations indicate that the annual CH_4 emission from wetland increased from 83 to 111 million tonnes between 1880 and 1980. If, by the year 2080, the earth surface air's mean temperature rises by 3 °C (as has been predicted as a result of the doubling of atmospheric CO_2), the increase in CH_4 emissions from wetlands, over those for the year AD 1880, could reach 280 million tonnes per year.

Bartlett and Harris (1993) reviewed CH_4 emission from wetlands from different latitudes. At 26 °N (Everglades, Florida) :

	$mg/m^2/day$	Range
Wetland forest	59	3-274[a]
Saltwater mangroves	4	1.9-7.7[a]
Pond open water	624	11-2646[b]

[a]Harris *et al.* (1988)

[b]Burke *et al.* (1988)

Cicerone and Shetter (1981) observed a flux of 0.232 to 7.86 g CH_4 $m^{-2}d^{-1}$ while temperature changed from 26 to 31 °C from fresh water lakes.

Harris & Sebacher (1982) reported CH_4 flux measurements made over a 17 month period in the Great Dismal Swamp Virginia. These flux measurements indicate that Great Dismal Swamp soils can act as both a source and sink for atmospheric methane. In a waterlogged condition, swamp soils are a net source of CH_4 to the atmosphere with seasonal variations in emission rates ranging from <1 to 20 mg CH_4 $m^{-2}d^{-1}$. During drought conditions, swamp soils consume atmospheric CH_4 at rates of <1 to 5 mg CH_4 $m^{-2}d^{-1}$. While these results should not be extrapolated to all swamp soils, they illustrate the potential complexity of process which regulate net flux of CH_4 between wetland soils and the atmosphere.

Moore and Knowles (1987) studied rates of net CH_4 evolution from four subarctic fens over one summer ranged from 0-7 m mol CH_4 $m^{-2}d^{-1}$. Annual flux of CH_4 is estimated to be 0.13-0.80 g CH_4 m^{-2} which, although low compared to other wetlands, becomes a substantial atmospheric contribution when the large area occupied by subarctic peatlands is taken into account.

More than 95% of world peat areas occur in the former Soviet Union, Canada, U.S.A., Sweden, Norway, Finland and U.K. Harris *et al.* (1985) reported the first survey of CH_4 emission from northern peatlands of

U.S.A. Emission ranged from 0.003 to 0.94 g CH_4 $m^{-2}d^{-1}$, with half of these values between 0.1 and 0.4 g CH_4 $m^{-2}d^{-1}$. The frequency distribution is log normal and the mean emission rate is 0.337 g CH_4 $m^{-2}d^{-1}$. Such fluxes are higher than most values reported for other ecosystems, suggesting that northern peatlands may be an important source of global tropospheric CH_4.

The CH_4 flux from any wetland ecosystem is affected by a range of variables including i) soil temperature, ii) soil moisture, iii) the quantity and composition of the decomposing organic substrates, and iv) the type of vegetation present (SchÜtz and Seiler, 1989). Methane flux measurements made, during the productive season, in different wetland ecosystems have ranged, for example, from <0.001 g $m^{-2}d^{-1}$ arising from Great Dismal Swamp, Virginia (Harriss & Sebacher, 1982) to >0.25 g $m^{-2}d^{-1}$ for an alpine fen in the Alaskan range (Sebacher *et al.*, 1986). Differences in substrate productivity is the primary cause of flux variations (Mathews and Fung, 1987). SchÜtz and Seiler (1989) reported that the measured CH_4 flux from natural wetlands varied over a wide range, depending upon the environmental characteristics and the location. Generally low rates (i.e. <10 mg $m^{-2}h^{-1}$) have been reported from the drier, nutrient poor sites of northern and mid-latitudinal peatlands. Wet peatlands, however, exhibited emission rates upto 80 mg $m^{-2}h^{-1}$. Average rates range from 0.06 to 27.7 mg $m^{-2}h^{-1}$. Higher CH_4

emission rates as compared to boreal peatlands were reported from swamps ponds of subtropical and tropical regions reaching individual values upto 51 mg $m^{-2}h^{-1}$.

Methane releases from swamps and marshes are subject to more uncertainties. They vary over four orders of magnitude at the same temperature (WMO, 1986a). Schütz and Seiler (1989) indicated that, although CH_4 emission rates as high as 90 mg $m^{-2}h^{-1}$ were reported from some sites of salt-water marshes, the average rates range between 0.1 to 11 mg $m^{-2}h^{-1}$.

Glachenko *et al.* (1989) estimated that the CH_4 flux from freshwater lakes is in the range 92-280 g $m^{-2}y^{-1}$. Schütz and Seiler (1989) reported that CH_4 flux from freshwater lakes in the USA and Canada range from 0.01 to 327.5 mg $m^{-2}hr^{-1}$, with average values of between 0.2 and 28.2 mg $m^{-2}hr^{-1}$.

The emissions of CH_4 from a wetland ecosystem depend upon the temperature. From their measurements, Baker-Blocker *et al.* (1977) suggested that the relationship between the CH_4 flux (F) from a wetland, in g $cm^{-2}d^{-1}$, and the mean temperature T, in ^{o}C, can be expressed as

$$F = 4.6 \times 10^{-5} - 5.6 \times 10^{-6} + 2.6 \times 10^{-7}T^2.$$

In their study of methane emission from Amazon floodplain Wassmann *et al.* (1992) found that the highest ebullition rates (mean value, 69 mg CH_4 $m^{-2}d^{-1}$) was in flooded forest, covering the higher areas of the

floodplains with a long subaerial period. Significantly lower averages of the gas bubble flux were recorded in the permanently aquatic areas of the lake (mean value, 29 mg CH_4 $m^{-2}d^{-1}$) and in the intermediate area with floating grass mats (mean value, 23 mg CH_4 $m^{-2}d^{-1}$). Ebullition was the predominant mechanism for the CH_4 transport from the Varzea sediment into the atmosphere with maximum values of upto 200 mg CH_4 $m^{-2}d^{-1}$. The diffusive flux remained below 29 mg CH_4 $m^{-2}d^{-1}$ at all sites throughout the entire annual cycle.

2.3.3 Coal mines

For coal mines, existing data collected by other researchers on underground mines are compared with the U.S. Environmental Protection Agency (EPA) data on emissions from surface mines to provide an estimate of global emissions of 43 Tg yr^{-1}. CH_4 from natural gas production, transmission, and distribution systems is estimated to be 4.4 Tg yr^{-1} for the United States (Beck, 1993).

2.3.4 Biogas pits

Biogas is a cheap and efficient fuel and its feedstock is a renewable resource. The manure produced from biogas plants is better than FYM. The social benefits of biogas include checking of deforestation by reducing indiscriminate felling of trees for fuel, improvement in rural sanitation and easy cooking. Biogas obtained from feedstocks available to villagers in a

negligible cost is a very economic fuel. Biogas has become an instrument of socio-economic change.

According to a rough estimate, 50% of India's total energy consumption comes from non-commercial energy sources. The large majority of rural people are surviving on these sources. On an average, this covers 84% of rural household's energy demand. A substantial portion, ranging from 1/3 to 1/2 of the recoverable cattle dung, is burnt as fuel. The annual requirement of fuel-wood was estimated as 133 million tonnes whereas the total annual production from recorded sources was only 49 million tonnes. A deficit of 84 million tonnes is left unaccounted (Vimal, 1985). Total number of biogas plants installed upto 1984/85 was 457100 (Khandelwal and Madhi, 1986). According to DNES report (1992) the number of biogas plants in the country is now 1.8 million. From the outlet areas or the exposed areas of the biogas plants gas (60-70 % methane) is escaped to the atmosphere causing loss as well as environmental pollution.

CH_4 budget from modern China is 23 Tg yr^{-1} from rice fields and <1 Tg yr^{-1} from biogas pits (Khalil *et al.* 1993).

2.3.5 Others

Williams (1993) measured the extent of CH_4 emissions from the waste of free-range dairy cows. There was considerable variability in the flux from

individual cowpats ranging from more than 6 mg/hr to near zero. The emission rate was strongly influenced by the cowpat temperature. Some flux measurements were also recorded on the swampy cesspit area into which the manure from the dairy floor were washed. Although the extent of this swampy area varied according to climatic conditions, it appeared to be an efficient producer of CH_4 with emission rates in the range 0.3-1.5 g $m^{-2}hr^{-1}$.

Anaerobic waste stabilization ponds have been used successfully to treat municipal and industrial wastewaters. Methane production rate mainly depend on the temperature. The theoretical amount of CH_4 produced during the anaerobic process is 0.7 m^3 for 1 kg of ultimate BOD removed (Toprak, 1993). The rate of gas production from the sludge layer is a sensitive measure of the biological activity in the bottom layers of an anaerobic pond. According to Gloyna (1971) there is approximately a fourfold increase in gas production for every 5 °C rise in temperature between 4 °C and 22 °C. Benefield and Randall (1980) investigated the effect of water temperature on gas production rate. They found gas production rates at constant BOD load to be 0.0028 m^3 biomass/m^2-day for water temperature below 15 °C and 0.0462 m^3 biomass/m^2-day for water temperature of 23 °C. Iwema *et al.* (1987) found CH_4 production of 2325 to 2720 ml/m^2-day in a facultative wastewater stabilization pond in summer. For winter conditions, CH_4 production rates

were measured between 166 and 348 mL/m^2/day. BOD reduction in anaerobic ponds is a function of temperature and increases with increasing temperature above 15 °C. Benefield and Randall (1980) reported CH_4 production rates as 0.0021 m^3/m^2/day for water temperature above 23 °C, considering CH_4 content is about 75%. The result of the theoritical approach is almost the same with Benefield and Randall's value for water temperature above 23 °C.

Ojima *et al.* (1993) found that increased N addition in temperate forest soils in the north-eastern U.S.A. decreased CH_4 uptake by 30 to 60% and increased N fertilization and conversion to crop land in temperate grasslands decreased CH_4 uptake by 30 to 75%.

Williams and Craford (1984) studied the rates of CH_4 emission in Minnesota peats. Surface (10-25 cm) peats produced an average of 228 m mol of CH_4 per g (dry weight) per hr at 25 °C and ambient pH. CH_4 production was temperature dependent, increasing with increasing temperature (4 to 30° C), except in peats from deeper layers. Maximal methanogenesis from these deeper regions occurred at 12 °C. CH_4 production rates were also pH dependent. Two peats with pH values of 3.8 and 4.3 had an optimum rate of CH_4 production at pH 6.0.

The overall critical review of literature leads one to conclude that there is not sufficient work on methane emissions from different sources in our

country. So, the current study is purposeful to identify the potentiality of different sources and the physical parameters associated with them.

Table 3. Methane emissions from different sources ($Tg\ Yr^{-1}$)[a]

Source of CH_4	Reference to investigation										
	[1,2]	[3]	[4][b]	[5]	[6]	[7]	[8][c]	[9]	[10][c]	[11]	[12]
Wetlands	130-300	-	150	115-345	100-200	60-180	47±22	100-200	25-70	11-300	40-160
Termites	-	5-50	-	-	10-100	10-50	25±7	10-200	-	28	2-5
Oceans and fresh water	2-42	6-13	23	-	6-45	-	-	6-45	15-35	-	15-35
Rice paddies	280	25-75	95	60-170	25-170	70-170	120±50	60-170	70-170	30-350	70-170
Domestic animals	100	100	120	65-100	65-100	70-100	86±13	65-100	70-100	75-100	66-90
Biomass burning	-	25-110	25	50-100	20-80	20-110	79±23	50-100	55-100	20-110	55-100
Fossil fuel production	16-50	29-80	40	50-95	40-100	32-90	69±8	50-95	65-75	30-100	65-75
Landfills	-	-	-	30-70	20-70	30-60	-	30-70	-	30-70	30-70
Other	-	-	100	-	0-100[d]	10-30	2±1	0-100[d]	1-2	-	1-2

[a] If the year is not specified, estimates can be assumed to be for the year prior to that of publication

[b] Values estimated for 1978 and increase about 10 million tonnes every year[4].

[c] Figures are for 1980

[d] Future destabilisation of methane hydrate

1. Enhalt (1974)
2. Enhalt and Schmidt (1978)
3. Klug (1985)
4. Khalil and Rasmussen (1983)
5. Lashof and Tirpak (1990)
6. Watson et. al. (1990)
7. Enhault (1985)
8. Seiler and Conrad (1987)
10. Cicerone and Oremland (1988)
11. Bolle *et al.* (1986)
12. Aselmann and Crutzen (1989)

Badr *et al.*, 1991

Table 4. Estimated trends of Global Emission Rates, in Tg Yr^{-1}, from individual Sources (Bolle *et al.*, 1986)

Source	1940	1950	1960	1970	1975	1980.
Rice paddies	64.5	74.5	89.0	105.0	115.0	117.0
Ruminants	35.5	58.0	68.5	78.5	84.0	86.0
Swamps and marshes	79.0	73.0	63.0	54.0	51.0	47.0
Other biogenic sources	15.5	18.0	20.5	23.0	24.0	25.0
Biomass burning	49.0	57.0	65.0	71.0	75.0	79.0
Coal mining	19.0	19.0	26.0	29.0	31.0	35.0
Natural gasleaks	2.0	5.0	11.0	24.5	30.0	34.5
Total	283.0	305.0	343.0	385.0	410.0	423.0

Bolle *et al.*, 1986

Table 5. Estimated trends of Methane Emission Rates (Tg Yr^{-1}), from Individual Sources

Source	Year 1988[a]	2000	2020
Natural wetlands	115	130	160
Rice paddies	110	125	160
Ruminants	80	90	110
Biomass burning	55	63	80
Natural-gas leakages	45	73	160
Termites	40	40	40
Landfills	40	45	55
Coal mining	35	45	70
Oceans	10	10	10
Freshwaters	5	6	7
Total	535	627	852

[a] Mean value estimated by Cicerone and Oremland (1988)

Glachenko *et al.*, 1989

Table 6. Methane sources and sinks (Tg Yr^{-1})

Sources	Estimate	Range
Natural sources		
Wetlands	115	100-200
Termites	20	10-50
Ocean	10	5-20
Freshwater	5	1-25
Anthropogenic sources		
Coal Mining, Natural gas & Petroleum Industry	100	70-120
Rice Cultivation	60	20-100
Entericric Fermentation (Anaerobic)	80	60-100
Animal Wastes	25	20-35
Domestic sewage treatment	25	NR
Landfills	30	20-70
Biomass Burning	40	20-80
Sink and Accumulation		
Reaction with hydroxyl (OH)	420	340-500
Removal by soils	30	15-45
Removal in the stratosphere	10	5-15
Atmospheric Accumulation	37	34-40
Total sources = Total sinks + Accumulation	500	420-600

NR - Not reported

IPCC, 1992a

Table 7. Global annual methane emission from rice as estimated by different authors

Reference	Estimate ($Tg\ CH_4\ y^{-1}$)
Koyama, 1964	190
Enhalt and Schmidt, 1978	280
Cicerone and Shetter, 1981	59
Khalil and Rasmussen, 1983	95
Seiler *et al.*, 1984	35-39
Blake, 1984	142-190
Crutzen, 1985	120-200
Hozapfel-Pschorn and Seiler, 1986	70-170
Cicerone and Oremland, 1988	60-170
Schütz *et al.*, 1990	80-150
Aselmann and Crutzen, 1989	30-75[a] 60-140[b]
Schütz and Seiler, 1989	70-170
Wang *et al.*, 1990	60-120
Neue *et al.*, 1990	25-60
Bowman, 1990	53-114

[a] accumulated from mean emission rates
[b] calculated from temperature dependency of emission rates

Rennenberg *et al.*, 1992

Table 8. Methane production from different wetland rice soils

Flux ($mg/m^2/hr$)	Region	Fertilizer treatment	Reference
7.4-47.0	Zhejan	nil	O
7.7-35.4	-do-	694 kg/ha K_2SO_4/KCl	O
7.9-44.0	-do-	694 kg/ha K_2SO_4/KCl 1042 kg/ha rape seed cake	O
6.0-50.6	-do-	1042 kg/ha rape seed cake	O
1.3-120.0	Sichun	not documented	W
3.0-16.0	-do-	-do-	K_1
60	-do-	-do-	K_2
0.4-16.3	Japan	6 t/ha rice straw	Y+M
1.9-3.8	-do-	12 t/ha compost	-do-
0.2-2.9	-do-	mineral fertilizer	-do-
1.4-2.8	-do-	no N	-do-
6.25-7.5	California	140 kg/ha N-fertilizer	C+S
9.1-11.7	-do-	220 kg/ha N-fertilizer	C
8.7	Texas	149 kg N/ha	S_1
2.5	-do-	190 kg N/ha	S_1
4.1	Spain	200 kg N/ha	S_2
8.3-24.2	Italy	various fertilized or not	H+S
6.3-17.5	-do-	not documented	H
6.6-15.8	-do-	unfertilized	S_3
19.6-25.0	-do-	6-12 t straw + 200 kg N/ha	-do-
4.2-15.8	-do-	200 kg N/ha	-do-
9.6-28.3	-do-	3-12 t/ha straw	-do-

O = Wassmann *et al.*, 1993

W = Wang *et al.*, 1988

K_1 = Khalil *et al.*, 1990

K_2 = Khalil *et al.*, 1991

Y+M = Yagi and Minami, 1990

C+S = Cicerone and Shetter, 1981

C = Cicerone *et al.*, 1983

S_1 = Suss *et al.*, 1991

S_2 = Seiler *et al.*, 1984

H+S = Holzapfel-Pschorn and Seiler, 1986

H = Holzapfel-Pschorn *etal.*, 1986

S_3 = SchÜtz *et al.*, 1989b

Wassmann *et al.*, 1993

Table 9. Global wetland methane emissions

Natural wetland ecosystem	Area (10^2 m ha)	Methane flux (Tg/yr)	Methane flux ($mg/m^2/day$)
Swamps	1.13	18-35	57-112
Fens	1.48	7-52	28-216
Marshes	0.27	12-30	137-399
Flood plains	0.82	5-19	50-200
Bogs	1.87	0.4-18	1-50
Lakes	0.12	1-4	17-89
Total	5.69	40-160	

Aselmann and Crutzen, 1989

MATERIALS AND METHODS

MATERIALS AND METHODS

The field investigations pertaining to the methane flux from paddy soil, were conducted at the Indian Agricultural Research Institute (I.A.R.I.), New Delhi, farm.

Investigations were also done in Distilleries, Compost pits, Najafgarh drain, Fruit and vegetable market wastes and Biogas plants.

3.1 CHARACTERISATION OF SOIL

The alluvial soil (*Typic Ustochrept*) of the experimental site was slightly alkaline with sandy loam texture and low organic matter. The general Physico-chemical properties of the soil are given in the Table 10.

3.2 IN SITU MEASUREMENTS

In situ measurements were done to know the pH, temperature and Eh at the sites under natural conditions. Water samples were collected to measure EC in the laboratory.

3.2.1 Measurement of pH

The pH of water bodies at different locations was measured using portable pH meter (Systronics Griph 'D' pH Meter, Model No. 327). The combined electrode alongwith its protecting plastic lead was dipped in the water bodies and pH readings were taken. Buffer readings were adjusted before taking pH readings of the water

bodies.

3.2.2 Measurement of Redox Potential (Eh)

Eh readings were recorded using a battery operated pH cum mV meter. The glass electrode was replaced by a Platinum micro-electrode specially prepared in the laboratory. Here a small piece of Platinum wire was welded to a Cu wire and kept inside a long narrow glass capillary. About 5 mm length of Pt wire remained outside the capillary tube at one end and the Cu wire at another through which electrical connection was to be made. The Pt tip was inserted into the medium under investigation at desired depth. The instrument was first adjusted to 245 mV using Zobbel buffer and then the Platinum electrode was inserted in a suitable depth. Calomel electrode was placed at the surface only to maintain electrical contact (Pennamperuma, 1972). After the settings the electrodes suitable time was allowed to stabilise the mV reading and then it was noted.

3.2.3 Measurement of Temperature

The ambient and water temperature of the experimenting sites were measured by ordinary mercury thermometer and Pt-100 respectively. The temperatures of the rice fields were measured using PT-100 and Multimeter which was calibrated against known temperatures of water in the laboratory and a regression equation was derived. The equation was

$$Y = 3.715X - 390.876$$

where, Y = Temperature (^{o}C)

X = Resistance (ohm)

As the temperature in the soil increased with the effect of sunlight the electrical resistance increased which was measured by the multimeter attached to the Pt-100 and the temperature was calculated very accurately using the regression equation.

For water bodies ordinary mercury thermometer was suitable enough to measure the temperature at suitable depths.

3.3 Measurement of Biological Oxygen Demand (B.O.D.)

Biological Oxygen Demand (B.O.D.) was determined to know the relative O_2 requirements of distillery effluents. Effluent samples were collected from the distilleries and were tested in the laboratory following the method described by APHA (1992).

3.4 Collection of gas samples

3.4.1 Rice fields

Collections of gas samples were carried out by closed chamber technique described by Hutchinson and Mosier (1981). For the rice fields 50 cm X 30 cm X 70 cm chambers made of 6 mm thick acrylic sheets were used. An alumi nium channel was used with each chamber to make it air tight when placed in the field. One Mediflex three way stop cock (Eastern Medikit Ltd., India) was fitted at the top of the chamber to collect gas samples.

Three replicates were taken from each plot and the average was taken as representative value for that plot. Head space inside the box was recorded which was used in calculations.

3.4.2 Water bodies

For water body a smaller stainless steel columnar chamber of 25 cm diameter and 30 cm height was used and a pneumatic circular rubber tube was attached at the bottom of the chamber to make it floatable.

The chambers were put at the sampling sites and at suitable time intervals gas samples (14 ml) were collected from the chambers through the three way stop cock by 20 ml air tight syringe. Then the gas was transferred to pre-evacuated Vacutainer tubes (12.5 ml) by hypodermic needle (26 gauge). The gas in the tubes remained in a little bit higher pressure than that of the atmosphere which helped to avoid contamination or dilution. After the collection of gas samples the butyl rubber stoppers of the tubes were sealed by glue (Elephant Super Glue, *Richbond*, Japan). These tubes were then brought to the laboratory and could be stored for a considerable period for the analysis of methane by Gas Chromatograph (GC).

3.4.3 Compost pits etc.

The same container used for the water bodies was used in these cases. The only difference was that the floating arrangement was absent here. The container

was pressed in the debris to make it air-tight and depth was noted, waited for a suitable period (10-15 min) to get the equilibrium condition restored which might have been disturbed during the placement of the container and then gas samples were collected at 5 min intervals.

3.5 ANALYSIS OF METHANE

3.5.1 Procedure

Methane concentration in the gas samples collected from natural ecosystems was estimated using Gas Chromatograph (Packard, Model No. 438) fitted with a flame ionisation detector (FID), 6' X 1/8" stainless steel column packed with Molecular Sieve 5A (60-80 mesh) maintained at 80 °C. Carrier gas was Nitrogen and the flow rate was 15 to 20 ml/min. Injector and detector were kept at 130 °C. Volume of gas injected by gas-tight syringes was 1 ml and the retention time for methane was 1.9-2.2 minutes. The area under the peak was measured by means of a microprocessor based integrator attached to the chromatograph. The concentration of methane in a sample was determined by calculating it from the standard curve obtained by injecting standard gas mixtures containing the known amounts of methane under the same set of conditions. 2 ppmV methane in nitrogen was used as primary standard which were brought from National Physical Laboratory, New Delhi. GC was calibrated periodically using 2 to 150 ppmV methane gas standards prepared from 0.5% methane in nitrogen standard by static dilution technique. These gas samples

standard by static dilution technique. These gas samples were analized in the NPL first and then used for the preparation of standard curve. Standard gas mixture was injected at the starting at each session of analysis and at the intervals of every 10 injections used septums were replaced by a new one. After every 10 to 15 samples the column was heated to 250 °C for 15-20 minutes to restore from possible contamination of the associated gases such as water vapour, CO_2 and other hydrocarbons which reduce the activity of the column due to their adsorption at 70 to 80 °C. The integrator was set on area normalization mode with a stop time of 5 min., minimum area of 2000μV.Sec. and base line reading of 80-150μV.sec.

Calculation of concentration of Methane in sample:

Standard curve was made from the standard sample of known concentrations. Then gas samples of unknown concentrations were injected and the peak areas were noted. Using the peak area value and the standard curve the concentration values are taken.

3.5.2 Flux Measurement and Calculation

To measure flux, the chamber was fixed at the experimenting site and the change in CH_4 concentration in the chamber so formed, with time, was determined by taking replicate gas samples from the chamber head space by syringe and transported them to the laboratory for analysis. The following precautions were taken for

getting satisfactory results:

1) Gas samples were drawn from the head space immediately after placement and at equal time intervals thereafter over a period not exceeding 30 minutes.

2) A minimum of three samples were drawn to check the linearity of the increase in concentration.

3) The chamber was removed after the final sample had been taken to minimise the disturbance to environmental conditions within the chamber.

Calculation of Flux:

Cross-sectional area of the chamber = A m^2

Headspace = H m

Volume of Headspace = AH m^3 = 1000 X AH l

CH_4 concentration at 0 time = C_o ppmV

CH_4 concentration after time t = C_t ppmV

Change in concentration in time t = $(C_t - C_o)$ ppmV

= $(C_t - C_o)\mu l\ l^{-1}$

Volume of CH_4 evolved in time t = $(C_t - C_o)\mu l\ l^{-1}$ X 1000 X AH l

= $(C_t - C_o)$ X AH ml

When t is in minute, then flux is:

$F = [(C_t - C_o)\ X\ AH] / (A\ X\ t)$ ml $m^{-2}min^{-1}$

= Y ml $m^{-2}min^{-1}$ (say)

$F = Y\ X\ 16 / 22400$ g $m^{-2}min^{-1}$

= Y X 16 / 22400 X 60 X 1000 mg $m^{-2}hr^{-1}$

Hence,

$F = [(C_t - C_o) / t]$ X H X 42.857 mg $m^{-2}hr^{-1}$

This working formula was used to calculate methane flux in all the cases.

3.6 Experimental sites of methane sources

Gas samples were collected to determine the rates of methane emissions from rice field, open drains, dairy wastes and landfills at different locations in Delhi. Delhi is situated at 28°40′ N latitude and 77°12′ E longitude at an altitude of 228 m above mean sea level. The climate of Delhi is sub-tropical semi-arid.

3.6.1 Paddy Fields

A field experiment was conducted at IARI farm in the main block 14-C during the *Kharif* season (July to October) in the year 1993. For each treatment three plots of size 2.5 m X 2 m were taken (layout in Table 11). 15 days old rice seedlings of the variety PUSA-169 were transplanted. The spacing among hills were 10 cm X 20 cm. Management practices like weeding, irrigation etc. were kept same for all the plots. Water regime was also kept constant at 5 to 10 cm till the draining of water after the crop ripening stage. In the treatment plots nitrogen was added in a constant value of 120 kg in different forms. In Urea treated plot total nitrogen was applied in Urea form. In the BSS+Urea treated plot half of the 120 kg nitrogen added as Urea and the other half added as BSS. For this 12 t/ha BSS was applied. Similarly in FYM+Urea treated plot half of the nitrogen was added through FYM which was applied at the rate of 36 t/ha. Six hills were accommodated inside the chamber

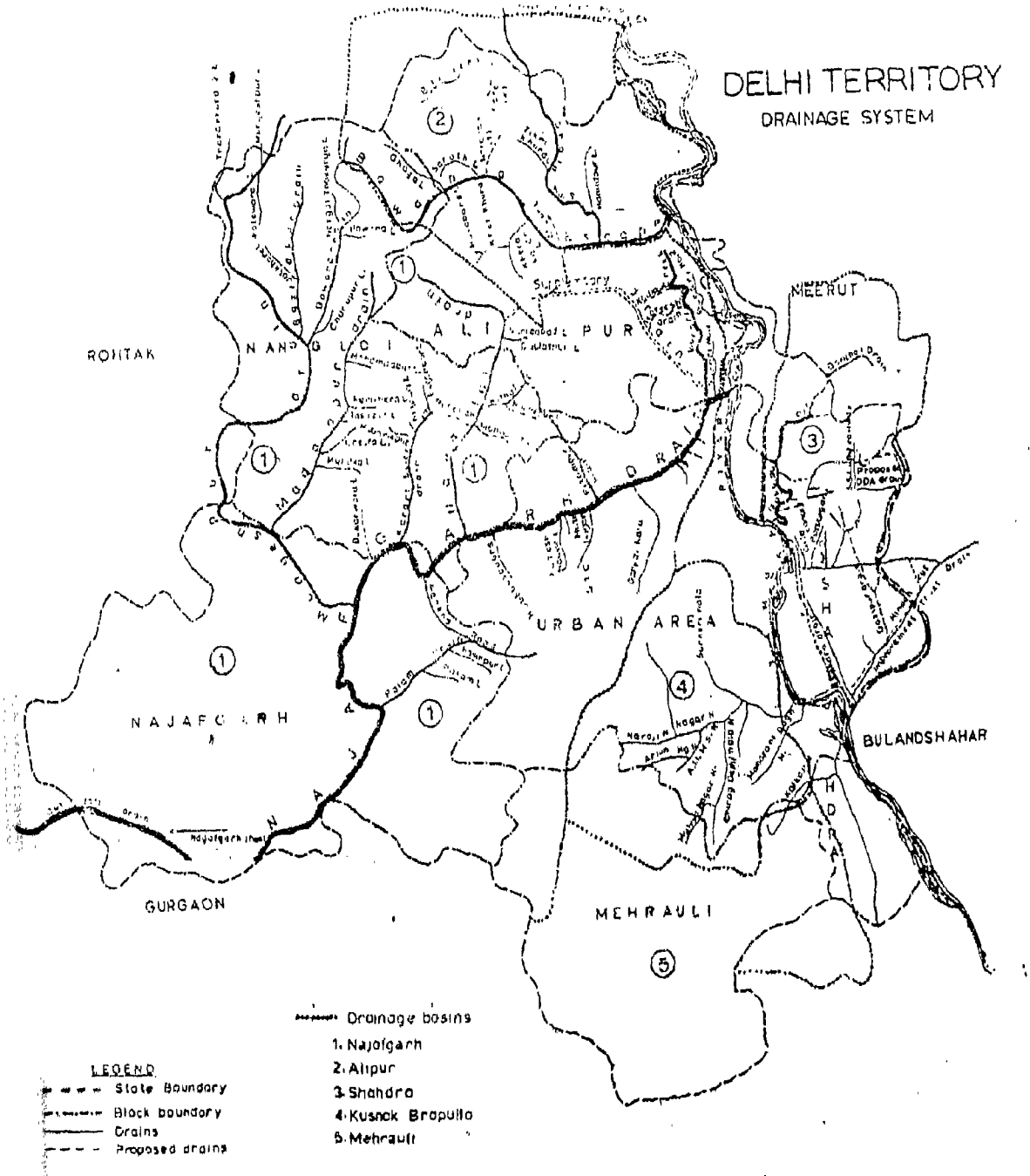
during gas samples collections. Three chambers were used at a time to reduce time. In rice fields samples were collected between 10.30 hrs. to 11.30 hrs. It is believed that at that period the emission rates were of the average value for the whole day.

3.6.2 Najafgarh Drain

In the Union Territory, Delhi ridge forms the main watershed. The drainage in the area East of the ridge is towards the Yamuna river which enters this area from the North near Wazirabad (28°43′ N; 77°14 E), at an elevation of 201 m and leaves it near Purana Quila (Old Fort) at 200.5 m above the sea level. In the West of the ridge, the drainage water passes into the Najafgarh drain which enters the area from about the middle of the western boundary and following roughly the north-easterly direction it joins the Yamuna river near Wazirabad (see the map).

On the basis of topographical characteristics, the Union territory of Delhi has been divided into five major drainage basins viz., Najafgarh basin; Alipur basin; Shadra basin; Kushak-Barapulla basin and Mehrauli basin (Sen, 1976).

The drainage system of Delhi is such that all waters collected through main drains and small rivulets are discharged into Yamuna river. Description of each basin along with its important surface drains is presented in the map.


DELHI TERRITORY
DRAINAGE SYSTEM
ROHTAK
MEERUT
BULANDSHAHAR
GURGAON
MEHRAULI
NAJAFGARH
URBAN AREA
Drainage basins
1. Najafgarh
2. Alipur
3. Shahdra
4. Kusnak Bropulla
5. Mehrauli
LEGEND
State Boundary
Block boundary
Drains
Proposed drains

Najafgarh basin includes a catchment area of approximately 735 sq. km, out of which about 573 sq. km is rural and the remaining is urban. The Najafgarh drain is the only outlet of this region originating from a low lying area known as Najafgarh jheel or lake. After originating from Najafgarh drain traverses a distance of about 61.6 km in north-eastern direction and finally joins the Yamuna river at Wazirabad. About 35 small and big link drains join the Najafgarh drain. The total area drained by these drains is approximately 544.2 sq. km. Total length of the main drains in all the basins is 220 km. The average width of Najafgarh drain is approximately 30 m. So it has an approximate surface area of 180 ha. The surface area of all the drains in the Union Territory with an average width of 20 m is 440 ha.

Samples were collected from the Northern bank at New Motinagar near Ring road. It was 300 ft. from the bridge and the width of the drain here was 60 m. The colour of the drain water was blackish with typical foul odour surrounding the area. Growth of water hyacinth was seen sporadically. At some places standing water was also visible. Heavy dark black sediments were present all over the year. There was profuse bubbling in summer months however during winter months bubbling was seen with lesser rate. Water level went down during winter season. Samples were collected once a week and the average was taken as the representative of that month.

Samples were collected between 12 o'clock to 1 o'clock during daytime.

3.6.3 Distilleries

In distilleries molasses is used to produce alcohol. In this process huge amount of water also is required. For one litre of consumable alcohol 12 to 15 litres effluent is discharged. This huge amount of effluent is stored in large lagoons. Sometimes this effluent is treated in the biomethanation plant to produce biogas which is used as a source of energy to operate various machines etc. So, pre-methanation effluent has much greater potentiality to produce methane and to pollute the atmosphere than the post-methanation effluent. In some distilleries the effluent is aerated by mechanical stirring as a primary treatment to reduce BOD. After lagooning the effluent is finally discharged in the municipal drains or canals etc. Hence it is a strong source of methane to the atmosphere. A strong typical odour of the effluent prevails in the entire distillery areas and the lagoons.

There are 246 distilleries of varying production capacities in India. The total annual installed capacity is 2215233 kl. Out of these 246 distilleries, primary biomethanation treatment plants are installed in 70 distilleries only covering annual installed capacity of approximately 898000 kl. This is only 28% of the total distilleries. Biomethanation

plants in 58 distilleries are under construction. So, at present 176 distilleries are without biomethanation plants. So, pre-methanation effluent discharged by them is 54132.86 kl/day and post-methanation effluent discharged by the distilleries is 36904.11 kl/day. Lagooning time varies from 30 days to 90 days in different distillaries. Taking an average value of 60 days lagooning and taking average depth of the lagoons as 5 m the surface area for premethanation lagoon will be 65 ha and the surface area for post methanation lagoon will be 45 ha and final lagoon 110 ha keeping in mind that the amount discharged per day is kept in the lagoons for 60 days and the same amount is discharged afterwards.

Gas samples were collected from Shamli, Shimbhauli, VAM Organics, Rampur and Doon Valley Distillery at different times in the year 1993.

3.6.4 Exposed Areas of Biogas Plant

Samples were collected during 1993. Every month of the year 1993 one trip was made to the AFPRO farm at Aligarh, Uttar Pradesh. Gas samples were collected in between 11 AM and 2 PM in triplicates and the average was taken as the representative emission rate for that month. Gas samples were collected from the outlet area. Slurry temperature at 30 cm depth), pH (of slurry at exposed areas) and Eh were also noted. The outlet areas was partly covered with cement slabs. So, the slurry temperature became higher than the

atmospheric temperature within this confined volume. Types of plants investigated were Deenbandhu, KVIC and Janta, the capacities 3 m^3 in all the cases.

It was assumed that the emission rates during the collection period of 11 AM to 2 PM were more or less the average of that day. Slurry temperature, pH and Eh were measured at the same time.

3.6.5 Compost Pit

Gas emissions were recorded from the compost pits, situated behind the division of Agronomy, IARI, New Delhi. Two sites were selected. Site I was situated in an open place where clear sunshine prevails. The second site of composting pit (II) was inside the dairy and in semishaded condition. Upper surface of Pit I remained almost dry whereas Pit II was somewhat moistened. Dairy wastes comprising of dry grass, straw, cowdung, etc. were dumped in these pits everyday. The agricultural wastes were also mixed in the pit I.

3.6.6 Landfill Areas of Fruits and Vegetables wastes

Azadpur fruits and vegetables market is situated at North-East Delhi. It is the biggest one of this type in Asia. The amount of wastes discharged from this market is 30000-40000 tonnes/year. Out of this (60-70 %) is wet waste which consists of partly rotten greenery, fruit peels etc. Maximum amount of wastes is produced in the months of January to April and November to December. The landfill area is situated inside the

newly developing Swarupnagar locality situated at the eastern side of the Grand Trunk Road which is about 10 km away from the market. Wastes are carried and dumped here by the market vehicles round the year. Gas samples were collected by the close chamber technique adopted for dairy wastes, and along with this atmospheric air samples (10 cm above the waste heaps) were also collected. Temperature below 10 cm of the heaps were also noted. Samples were collected fortnightly from three points and the average of all the points were taken as the representative for that month. Samples were collected in between 11.30 to 13.30 hrs.

Table 10. Physico-chemical characteristic of initial soil (0-15 cm) from the experimental field.

Property	Values	Method
Mechanical Analysis		Piper (1967)
Sand (%)	66.00	
Silt(%)	17.10	
Clay (%)	16.10	
Textural Class	Sandy loam	
Bulk density (g cm^{-3})	1.33	Keen and Raczkowski (1921)
pH (1:2 soil:water)	8.20	Richards (1954)
Electrical Conductivity (dS m^{-1})	0.32	Jackson (1973)
Organic Carbon (%)	0.41	Walkley and Black (1947)
CEC [cmol(p^+) kg^{-1}]	7.30	Bower *et al.* (1952)

Table 11. Layout of the rice field.

C = Control U = Urea B = BSS+Urea F = FYM+Urea

F	B	C	U	F	U	B	C	B	C	F	U

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Results and Discussion comprises of following headings:

4.1 Standardization of the GC technique for gas samples analysis

4.2 Methane emissions from Rice field

4.3 Methane emissions from Najafgarh Drain

4.4 Methane emissions from Distillery effluents

4.5 Methane emissions from exposed areas of Biogas plants

4.6 Methane emissions from Compost pits of dairy wastes

4.7 Methane emissions from Landfill areas of fruits and vegetable wastes

4.1 STANDARDIZATION OF THE GC TECHNIQUE FOR GAS SAMPLES ANALYSIS

4.1.1 Analytical technique

Efforts were directed for the development of a GC technique for the estimation of methane in the gas samples. Since methane is a hydrocarbon, possibility of its detection by GC as such was examined using flame ionisation detector (FID).

The analysis using GC fitted with FID was highly satisfactory and the method could be used for the quantitative analysis of methane. The essential pre-requisites for the development of GC technique are choice of a suitable column and selection of suitable oven temperature for good resolution of methane peak for detection by FID.

4.1.2 Selection of suitable column

Molecular sieve 5A 60-80 mesh was the best suitable column. The column was made of stainless steel and the dimension was 6' X 1/8". The carrier gas was N_2 and the flow rate was 15 ml min^{-1}. H_2 was taken as fuel gas with a flow rate of 25 ml min^{-1}. Zero Air was taken as a supporting gas for combustion. The flow rate of air was 250 ml min^{-1}. Hence the total flow rate became 290 ml min^{-1}.

4.1.3 Choice of suitable column temperature

Column temperature was kept at 80 ^{o}C for the separation of methane from other hydrocarbons in the gas

samples. A column temperature of 80 ^{o}C gave the best resolution of methane with distinct peak. The detector temperature was kept 130 ^{o}C.

4.1.4 Preparation of standard curve

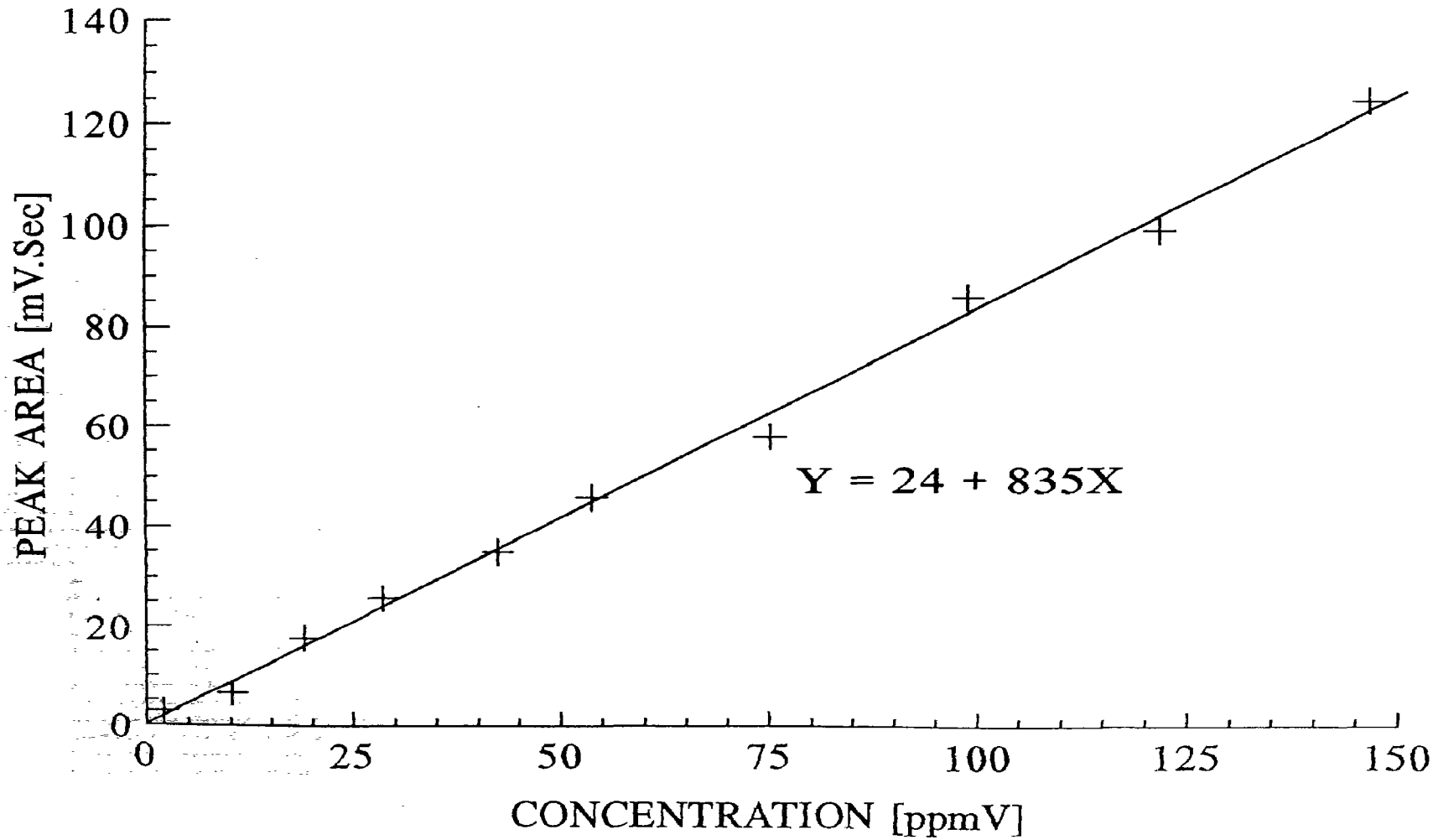
Five replications were taken for each concentration and the means were taken as the representative peak area for that concentration. Coefficient of variation was calculated for each set of data against a single concentration. It was seen that the coefficient of variation ranged from 1.2% to 7.5%. The peak areas corresponding to various concentration ranging from 2 ppmV to 150 ppmV of methane are presented in Table 12. The linear regression equation was **Y = 24 + 835X** with a squared value of regression coefficient of 0.996. Digits after the decimal were rounded in the equation.

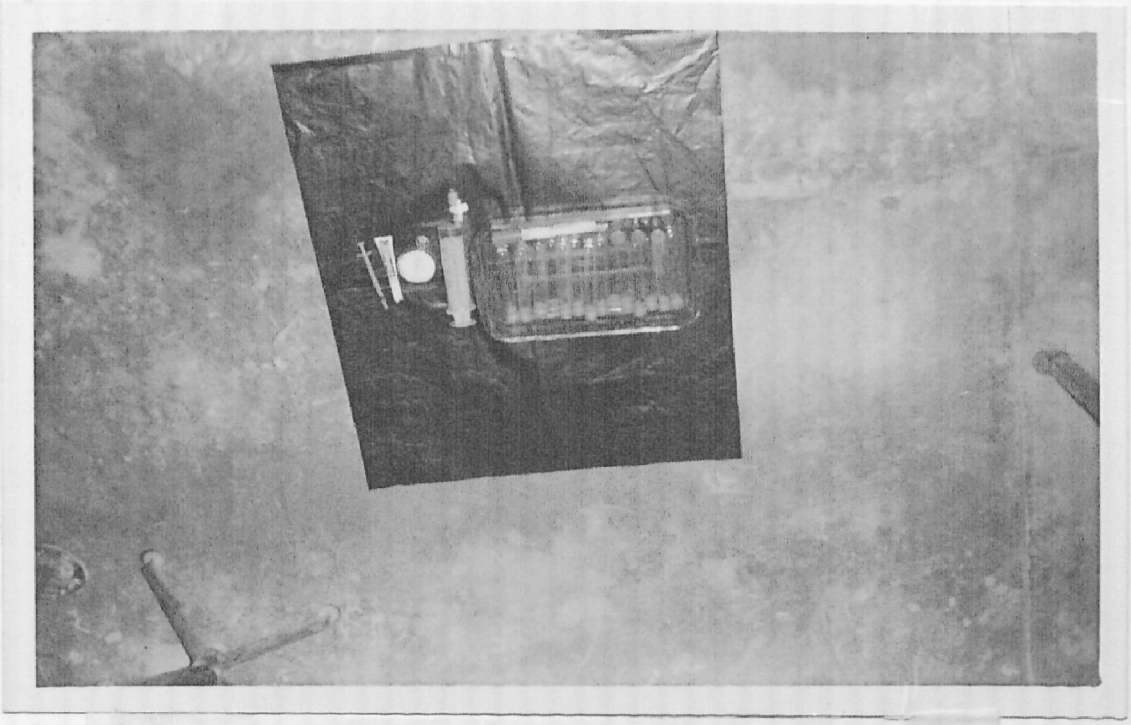
The calibration graph of concentration versus peak areas for methane has been shown in Figure 2. The curve shows linearity over the range from 2 ppmV to 150 ppmV of the methane concentrations.

Table 12. Calibration of methane by G.C. technique

Concn. (ppmV) (X)	Mean area in 5 replicates (μV.Sec) (Y)	Coeff. of variation (%)
2.03	2786	1.7
10.23	6264	3.1
19.08	17538	4.7
28.56	25478	2.9
42.25	34739	5.1
53.60	45727	1.2
74.84	57669	2.3
98.30	85323	4.6
121.06	98482	5.8
145.58	123569	7.5

Fig. 2. Calibration curve for methane estimation





1. Gas samples collection accessories

2. Samples analysis in G.C.

4.2 METHANE EMISSIONS FROM RICE FIELD

Methane flux measurements were carried out from the transplanted rice field during the *Kharif* season of 1993. Gas sampling was initiated after the transplanting of 15 days(d) old rice paddy and concluded 5d before harvest. CH_4 emissions from the flooded plots were highly variable among control and treated plots. The seasonal changes in daily CH_4 emissions from the rice plots as affected by the treatments and related to rice growth stages are graphically presented in the Figure 3.

An overview shows that during early submergence and before harvesting period CH_4 emissions were at their lowest values. After transplanting only a 3d lag period was observed. Thereafter CH_4 fluxes steeply increased over the next 12d and reached the first maximum peak (FM). CH_4 then steadily decreased over the next 20d and again increased for the next 11d and reached the second maximum peak (SM) at 7d after panicle initiation. Over the next 3 weeks CH_4 fluxes decreased and reached a plateau region about the time that the rice plants had reached 50% heading stage (pollination stage). During this period CH_4 emission from the treatment plots were higher than from the control plot. CH_4 emissions rapidly increased over the next 5d and reached the third maximum (TM) which corresponded to the grain-ripening stage. Emissions of CH_4 then decreased until harvest with a small increasing

trend 1d after drainage which reached to the maximum after 4d of drainage. This increase might be due to the release of soil-entrapped CH_4 bubbles after removal of flood water layer. Over most of the growing season, in general, higher CH_4 emissions were measured from the treated plots and relatively lower fluxes were recorded from the control plots. Emissions of CH_4 reached the minimum plateau twice in the growing period. The first plateau (FP) came at 35d after transplanting (DAT). for both the treated and control plots except FYM+Urea treated plot (30 DAT). The second plateau (SP) came at 55 to 64 DAT at treated and 50 DAT at control. CH_4 emissions from treated plots were much higher than the control in these two plateau. CH_4 emissions from the control plots followed more or less same trends to that of the treated plots. Fluxes of CH_4 recorded from treated plots were consistently higher up to TM than the control. In all the cases the FM, SM and TM values came at 15 DAT, 46 DAT and 69 DAT.

In the control plot FM, SM and TM peak values were 0.84, 1.68 and 2.37 mg $m^{-2}hr^{-1}$ respectively. In the FP emission rate was 0.18 mg $m^{-2}hr^{-1}$ and in the SP it was 0.14 mg $m^{-2}hr^{-1}$.

In Urea (alone) treated plot the FM, SM and TM peak values were 1.78, 2.16 and 2.96 mg $m^{-2}hr^{-1}$ respectively and the FP and SP were 0.57 and 0.71 mg $m^{-2}hr^{-1}$ respectively. FM here was 2 times higher than

the control and SM and TM were little bit higher than the control. The FP and SP were 3 and 5 times higher than that of the control.

In the BSS+Urea treated plot the FM, SM and TM values were 1.90, 2.79 and 4.05 mg $m^{-2}hr^{-1}$ respectively. The FP and SP were 0.66 and 0.62 mg $m^{-2}hr^{-1}$. All the peak values were nearly 2 times of the control. When compared to the Urea treated plot the FM value was little higher and SM and TM values were nearly 1.4 times higher. The FP and SP values were 4 times higher than that of the control. When compared to the Urea plot the FP and the SP values were more or less same. In general the emission values between Urea and BSS+Urea treated plots did not differ much throughout the growth period. After 69 DAT the emission rates in control, Urea and BSS+Urea plots were more or less same till harvesting at 100 DAT.

A quite high difference in CH_4 emission rates were observed in FYM+Urea treated plots than that of the other treated and control plots throughout the entire growing season. Where for the other plots the emission rates at 1 DAT were below 0.02 mg $m^{-2}hr^{-1}$, the emission rates in FYM plot 0.19 mg $m^{-2}hr^{-1}$ and which increased to 0.51 mg $m^{-2}hr^{-1}$ at 3 DAT. This 3 DAT value was 10 times higher than that of the control and BSS+Urea treated plot. At FM the emission rate was 4.52 mg $m^{-2}hr^{-1}$. This value was 2.4 times of the BSS+Urea treated plot and 5.4 times of the control. Similarly the SM peak value was

2.54 mg $m^{-2}hr^{-1}$ and it was little bit lower than the BSS+Urea treated plot and nearly 2 times of the control. The same trend was seen in the TM peak value. The TM value was 4.86 mg $m^{-2}hr^{-1}$ which was nearly same to the BSS+Urea treated plot and 2 times of the control. The FP came at 30 DAT and the value was 1.78 mg $m^{-2}hr^{-1}$ which was 6.4 times higher than the control and nearly 2 times higher than the BSS+Urea plot. The higher emission rate prevailed till harvest.

Seasonal fluxes of CH_4 from IARI rice field were highly variable and summarised in the Table 13. In the early growing season (1 to 5 DAT) no significant differences in CH_4 fluxes were observed between treated and control plots except with a higher value in FYM+Urea treated plot. This was probably due to elevated Eh conditions shortly after flooding. Between 10 DAT and 64 DAT significant differences between treated and control CH_4 emission rates were observed. In FYM+Urea treated plot higher emission rates continued up to 100 DAT.

The effect of soil and environmental parameters on CH_4 emissions was also evaluated. Seasonal changes in soil Eh, soil and air temperature and pH were observed. Seasonal changes in the Eh have been shown in the Figure 4, for all the plots. In Figure 5 the comparisons between emission rate and Eh are shown for all the treated and control plots. Soil Eh shows the characteristic steady drop after submergence for the

first 15 DAT. Redox values then remain fairly stable over the remainder of the growing season with occasional variation of 50 to 75 mV until the field was drained. The soil Eh goes up as the soil dries also shown by Patrick and DeLaune (1977). Redox values taken between 5 DAT and 90 DAT at each gas sample collection date were highly variable in treated and control plots except during 64 to 69 DAT. The large variation in Eh reading were due, in part, to the proximity of the Pt electrodes to the oxidised or reduced zones surrounding the rice roots (Reddy and Patrick, 1984). CH_4 emissions increased as soil Eh values dropped below -100 mV and were not detected or negligible when positive Eh values were measured. Similar observations have also been made by Cicerone and Shetter (1983) who showed a positive correlation between CH_4 emissions and soil Eh. In treated and control plots the Eh were lowest at 15 DAT. Here Eh values varied from -348 (FYM) to -302 (control) mV. Patrick (1981) suggested Eh <-200 mV for the onset of methanogenesis. But CH_4 emissions were detected above -200 mV also. So it appears that the CH_4 was produced also from the Pt electrode level (10 cm) where Eh might be lower than -200 mV. Eh increased steadily from 80 DAT due to drying of the field and became positive at 100 DAT. At this the emission observed might be from the deeper layers and entrapped CH_4 in the soil pores.

The plots were in continuously submerged condition up to 69 DAT (5 to 10 cm). No relationship

between floodwater depth and CH_4 emission could be established. This would support the findings of Seiler *et al.* (1984) which demonstrated that CH_4 diffusion through the flood water and CH_4 ebulition process are of minor significance compared to CH_4 transported by the plant system. They stated that about 95% of the CH_4 released to the atmosphere was through the plant.

Soil temperatures over the 100d ranged from 24.4 to 28.8 ^{o}C and air temperatures 1 m above the collection chamber fluctuated from 28.5 to 33.5 ^{o}C. Soil temperature (at 15 cm depth) and air temperature recorded between 11:00 to 11:30 in the morning did not show any positive correlation with CH_4 emissions measured over the growing season. Floodwater in the field acted as an insulating layer keeping the soil temperature fairly uniform over the growing season. Soil and air temperatures declined during the period of maximum CH_4 emissions and the decrease in soil temperatures may be partially due to shading of the soil surface by the maturing rice plants and lower air temperatures. Schütz *et al.* (1989a) conducted detailed soil temperature experiments in Italian rice paddy and found a positive correlation between CH_4 emission rates and temperature. In an earlier study, Cicerone and Shetter (1983) showed poor correlation between CH_4 measurements and soil temperatures recorded at the 10 cm depth. The emissions measured from the IARI rice plots

were comparable to published research data. Cicerone and Shetter (1981) measured CH_4 fluxes from a flooded California rice paddy and the emissions ranged from 0.15 to 7.50 mg $m^{-2}hr^{-1}$ with the fertilised plots emitting the highest CH_4 fluxes which agrees with our field results. They also showed that the main transport mechanism to the atmosphere was through the rice plant. Holzapfel-Pschorn and Seiler (1986) and Schultz *et al.* (1989a) also investigated the effect of fertiliser type on CH_4 emissions from Italian rice paddies. They concluded that CH_4 emissions from fertilised plots were comparable to that of unfertilised treatments, but the type of fertiliser and method of application greatly influenced the emission rate. The CH_4 emissions measured from Louisiana, USA rice field showed a strong seasonal dependence which has been shown by many researchers (Cicerone and Shetter, 1983; Holzapfel-Pschorn *et al.*, 1986; Holzapfel-Pschorn and Seiler, 1986; Schultz *et al.* 1989a). Cicerone and Shetter (1983) observed CH_4 fluxes ranging from < 0.04 mg $m^{-2}hr^{-1}$ to maximum emission rates measured 2 or 3 weeks prior to harvest (205.83 mg $m^{-2}hr^{-1}$). Seiler *et al.* (1984) measured CH_4 fluxes from rice paddies in Spain and emission rates ranged from 2.08 to 14.17 mg $m^{-2}hr^{-1}$ with the maximum values occurring at the end of heading and flowering stages. The two maximum (SM and TM) CH_4 emission rates have been observed in the Lousiana rice field by Holzapfel-Pschorn *et al.* (1986) and Lindau *et al.* (1991). Schultz *et al.*

(1989a) observed the FM before the rice tillering stage and the SM occurring during the rice reproductive stages with CH_4 emissions ranging from 6.67 to 15.83 mg $m^{-2}hr^{-1}$ from unfertilised Italian rice fields. They also observed a strong diurnal variation in CH_4 emission rates with maximum fluxes being measured in the late afternoon and the lowest fluxes recorded in the early morning. Lindau *et al.* (1991) observed two emission peaks (SM and TM) which occurred about 11d after panicle initiation and during ripening stages and fluxes were higher in the treated plot than in the control.

The FM in IARI field is exceptional. It may be due to the sudden and steep drop in Eh to almost minimum due to degradation of readily degradable organic matter left in the previous cropping season. But the peaks in the treated plots were highest due to the presence of higher organic C added from the organic amendments. In Urea (alone) treated plot the higher emission rates might be due to added N which enhanced the vigor of the plants than the control. In FYM treated plot the peak was much higher due to higher addition of organic C than the BSS treated plot. After 15 DAT Eh values raised slightly due to the buffering capacity of the soil where emission rate came down from the peak. The SM might be due to degradation of existing organic matter and dead roots and root exudates present in the anoxic soil. The TM peak might be due to the organic

root exudates or root litters from the rice plants (Schultz *et al.*, 1989a,b). The fact that lower peaks were observed only in Urea-N treated plots than the BSS+Urea or FYM+Urea treated plots might be due to higher amount of C which was added through BSS and FYM. The higher rate of emissions were the combined effect of the presence of higher organic C, increased concentrations of root-exudates and greater root growth and development due to amendments.

The results from our study have shown that CH_4 emissions increased with the addition of amendments. Maximum evolution of CH_4 to the atmosphere occurred at about 15 DAT, 46 DAT (3d after panicle initiation) and again during the rice ripening stage (69 DAT). CH_4 emissions increased as Eh decreased. Soil temperature measurements did not correlate well with CH_4 emission rates. More detailed research is required to predict accurately total CH_4 emissions from rice paddies under a variety of management and cropping practices. In addition, extensive research is needed to identify farming practices that can reduce emissions of CH_4 from flooded rice without affecting crop quality and grain yields.

After 64 DAT there was no significant difference in CH_4 emission rates between treated plots and control except in FYM+Urea treated plot. It might be due to more or less same Eh values and most probably the added effect of BSS and Urea had been diminished due to

using up the extra substrate from BSS by methanogenesis and Urea by plants. In FYM organic C was higher which might have been not used till then and emission rates remained higher.

Soil pH is another important factor. The optimum pH for CH_4 production in soils, specially at controlled Eh conditions is not well defined (Wang *et al.*, 1993). Any change of soil pH would affect soil Eh as given by inverse relationship of Eh and pH in Nernst equation (Ponnamperuma, 1972). The decreases in CH_4 production caused by increasing acidity might be due to the combined effect of inhibiting activity of methanogens and increasing soil Eh chemically. Therefore, it is necessary to investigate CH_4 production at controlled soil Eh and pH conditions in order to provide specific information on the effect of both the variables on CH_4 emission. Wang *et al.* (1993) in their soil incubation study in the laboratory reported highest production rate in the pH range of 6.8 to 7.0 after 15d when the pH was more or less stabilised. In submerged condition pH tends to go near 7.0 for both acid and alkali soils after prolong submergence (Pennamperuma, 1972). But in our case it remained mostly between 7.5 and 8.5. Relationship between pH and emission rates for various treatments and control are shown in the Figure 6. No perfectly conclusive effect of pH on emission was found. Further meticulate study is needed to get proper

conclusion under field conditions.

The average emission rates can be calculated from the average of all the emission rates observed. At 11:00 to 11:30 hrs in the morning the emission rates might be predicted to be the average for that day. The average emission rate in the control was 0.49 mg $m^{-2}hr^{-1}$. Hence for the entire season (100d) the emission is 11.76 kg ha^{-1}. Similarly emission from the only Urea treated plot was 20.88 kg ha^{-1}. The emission from BSS+Urea treated plot was 22.08 kg ha^{-1}. The emission from the FYM+Urea treated plot was maximum of 49.44 kg ha^{-1}. In FYM+Urea treated plot the average emission was 4.2 times greater than the control plot and more than 2.2 times higher than the BSS+Urea treated plot and 2.4 times higher than the only Urea treated plot. Yagi and Minami (1990) in their study on the effect of organic matter on CH_4 emission from some Japanese paddy fields observed that application of compost (lower C:N ratio) only slightly increased the CH_4 emission whereas the application of rice straw (comparatively higher C:N ratio) increased the emission 1.8 to 3.5 fold when compared to mineral fertilisation. They also concluded that the emission was closely related to the Eh in paddy soils. BSS is having comparatively lower C:N ratio (12:1) than to the FYM (20:1).

The yield from the control plot was 1.94 t ha^{-1}. The yields from the only Urea, BSS+Urea and FYM+Urea treated plots were 3.34, 2.94 and 2.85 t ha^{-1}

respectively. So the yields in the organic matter amended plots were in general identical but the emission in FYM treated plot was much higher. Emission from BSS+Urea treated plot was slightly higher than that of only Urea treated plot. So, BSS+Urea is strongly recommended instead of FYM+Urea and the former causes lesser pollution to the environment without any subsequent reduction in yield. Raw components of FYM should be biodigested to produce BSS generating biogas which may be used as the energy source both for the farm implements and domestic uses and then the BSS can be used in the field. Use of BSS instead of FYM may be one of the mitigation strategy of CH_4 emission in rice cultivation where both of them are available.

Table 13. Summary of seasonal methane flux from IARI rice field

DAT	Temperature (°C)		Redox (mV)				pH				Flux (mg $m^{-2}hr^{-1}$)			
	Ambient	Soil	Con.	Urea	BSS+U	FYM+U	Con.	Urea	BSS+U	FYM+U	Con.	Urea	BSS+U	FYM+U
1	30.0	27.0	10	10	13	12	7.99	7.97	8.01	8.00	0.01	0.01	0.02	0.19
3	29.3	26.1	-85	-99	-90	-103	8.11	8.11	8.05	8.01	0.05	0.03	0.05	0.51
5	29.0	26.0	-155	-153	-167	-178	8.15	8.15	8.10	8.05	0.13	0.14	0.14	0.80
10	31.0	26.2	-274	-287	-311	-308	8.23	8.63	8.31	8.31	0.49	0.77	1.03	2.42
15	28.5	26.2	-302	-312	-337	-348	8.45	8.75	8.62	8.80	0.84	1.78	1.90	4.52
20	28.5	24.4	-250	-264	-320	-311	8.36	8.41	8.40	8.23	0.50	1.29	1.67	3.27
25	30.7	26.7	-210	-253	-269	-275	8.19	8.19	8.35	8.19	0.35	1.09	1.48	2.35
30	32.7	27.0	-245	-291	-280	-307	8.11	7.95	8.12	7.90	0.28	0.84	1.06	1.78
35	31.0	27.1	-264	-297	-310	-338	8.12	8.13	8.30	8.05	0.18	0.75	0.66	2.13
40	30.6	27.3	-261	-308	-284	-291	8.10	8.25	7.75	7.91	0.34	0.57	0.70	2.27
46	30.0	27.5	-300	-298	-301	-283	8.15	8.14	7.70	8.08	1.68	2.16	2.79	2.54
50	30.3	27.5	-263	-267	-287	-293	8.11	8.10	7.85	8.03	0.14	1.07	0.86	1.73
55	30.5	27.6	-220	-263	-270	-289	8.00	8.02	7.81	7.98	0.35	0.71	0.62	1.70
60	30.1	27.2	-190	-221	-211	-217	7.92	8.18	7.92	8.15	0.34	0.73	0.68	1.44
64	30.2	27.5	-204	-217	-201	-227	8.01	8.00	7.87	7.95	0.48	0.94	0.57	2.91
69	33.0	30.0	-280	-271	-275	-298	8.12	8.22	7.80	7.81	2.37	2.96	4.05	4.86
74	33.5	27.0	-266	-257	-213	-295	8.11	8.28	8.00	8.06	0.72	1.00	0.44	3.35
80	33.0	26.5	-303	-283	-240	-292	8.10	8.09	8.11	8.14	0.87	1.06	0.95	2.91
84	30.0	26.7	-240	-234	-141	-163	8.12	8.15	8.10	8.23	0.53	0.73	0.42	2.05
90	31.3	26.9	-102	-97	-113	-119	8.02	8.08	8.15	8.17	0.14	0.31	0.10	1.07
95	32.2	27.5	-32	-37	-35	-45	7.91	7.93	8.09	8.05	0.02	0.06	0.02	0.43
100	31.7	27.3	183	176	181	145	7.95	7.92	8.03	8.09	0.01	0.02	0.01	0.18

Fig. 3. Methane flux from IARI rice field

(*Kharif* Season, 1993)

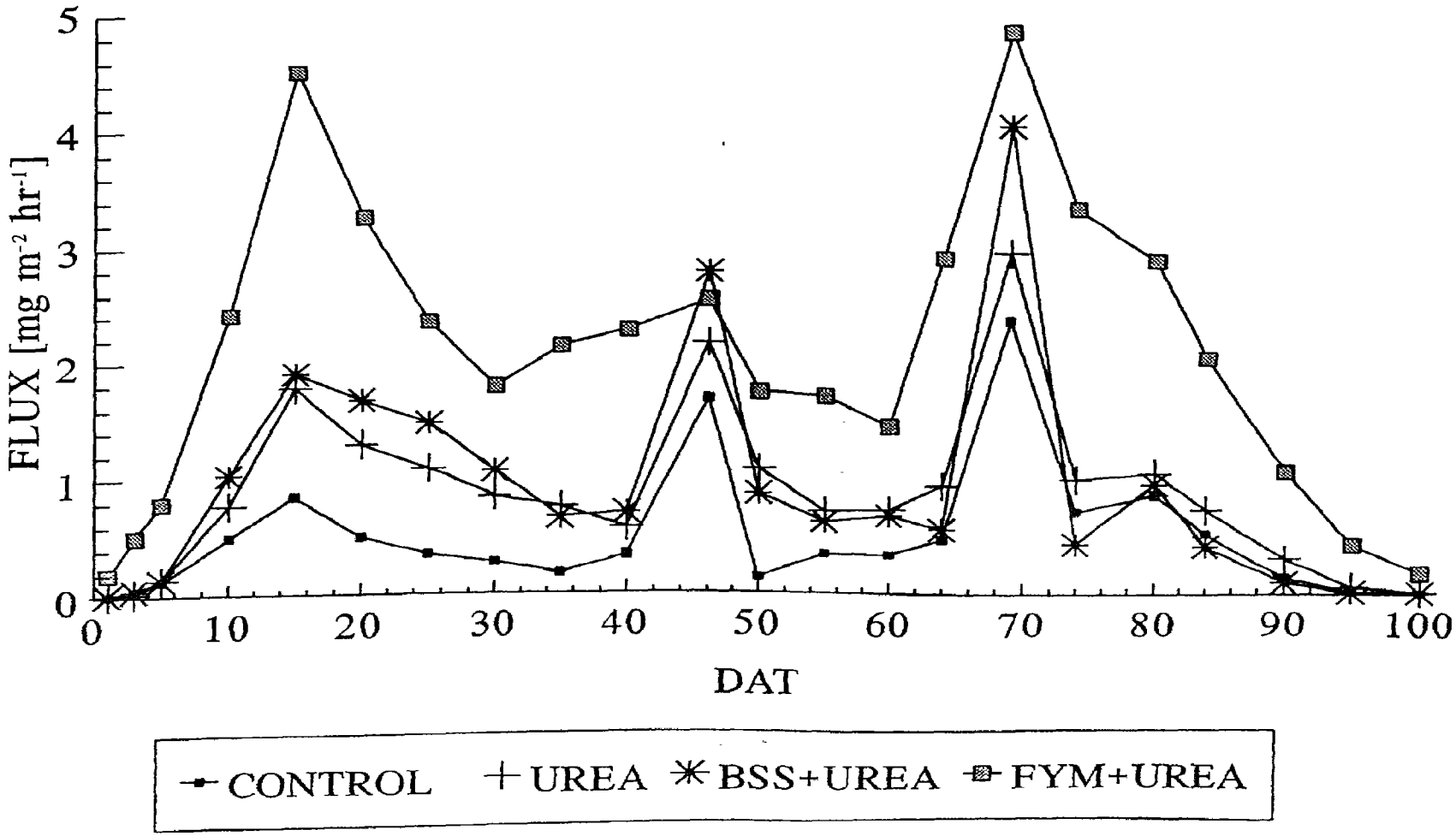


Fig. 4. Changes in Eh at IARI rice field
(*Kharif* Season, 1993)

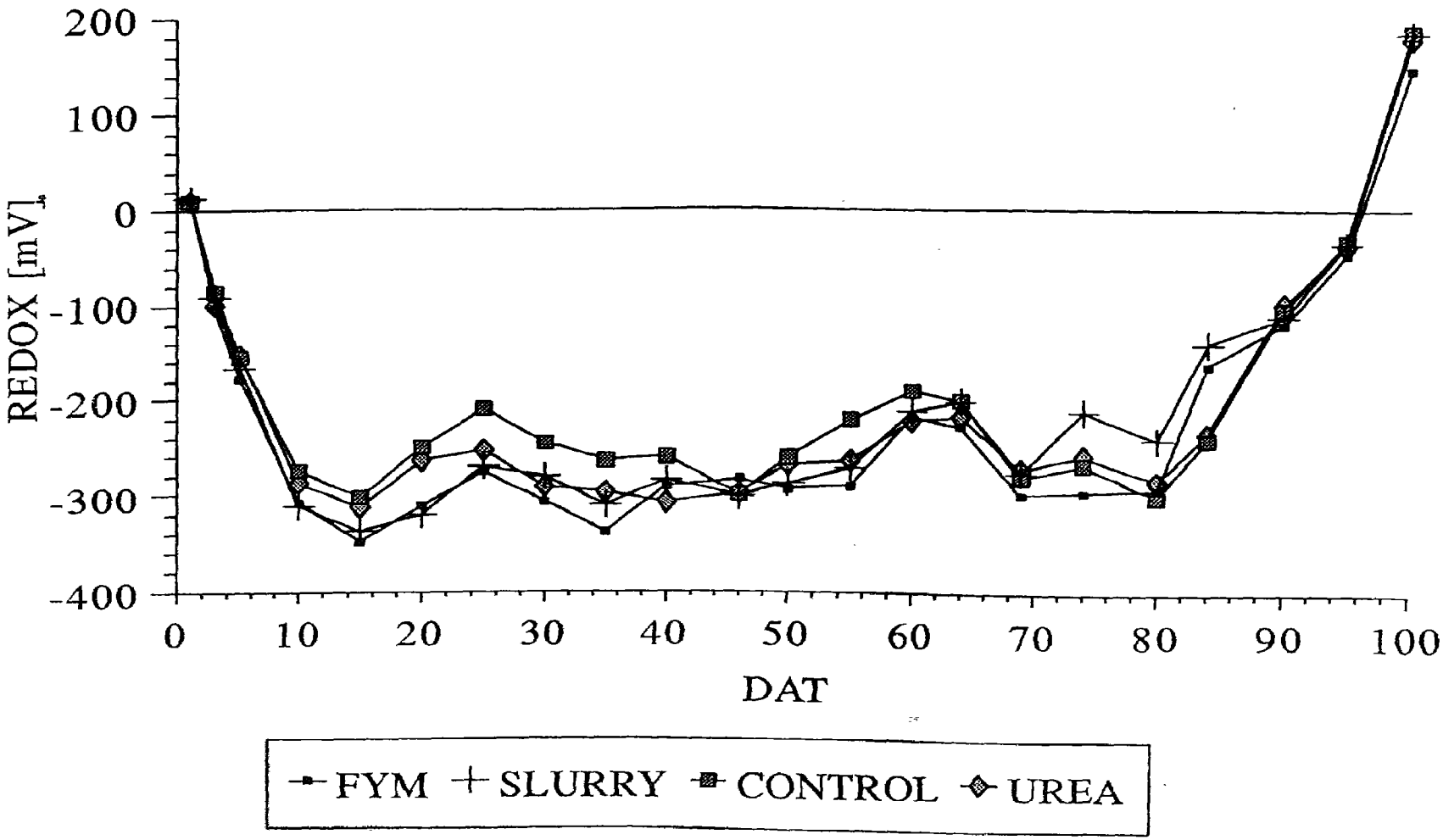


Fig. 5. Methane flux vs. Eh in different treatments

(*Kharif* Season, 1993)

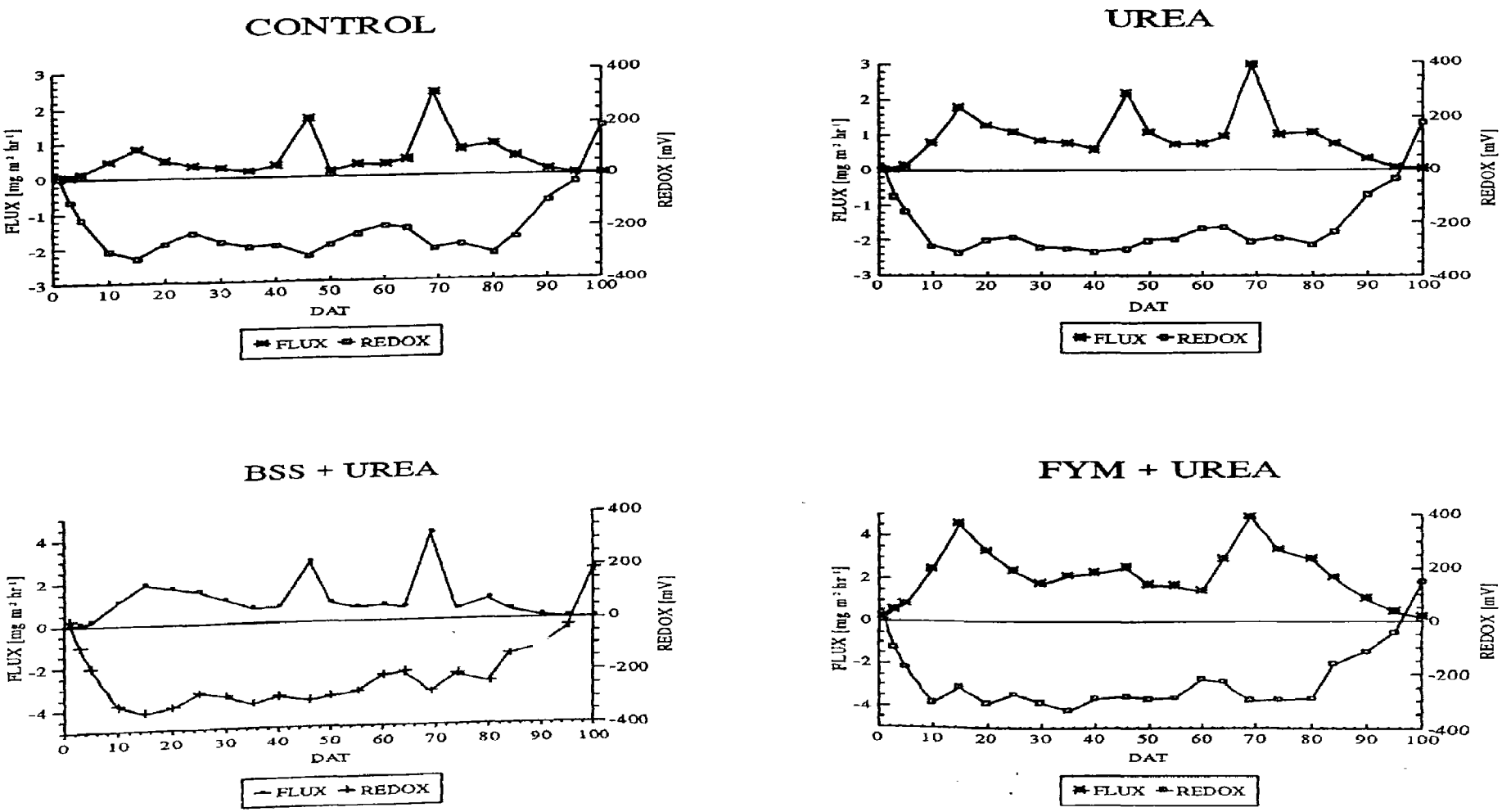
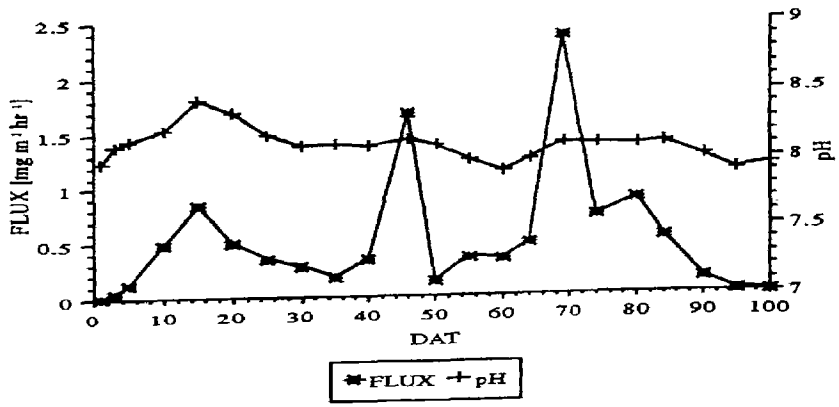


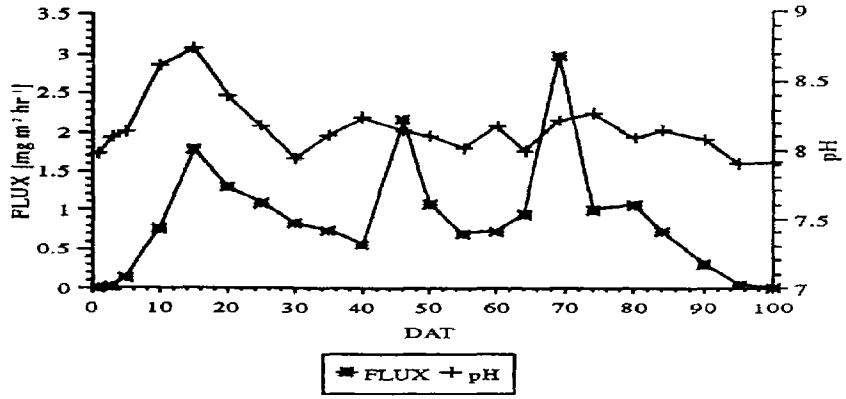
Fig. 6. Methane flux vs. pH in different treatments

(*Kharif* Season , 1993)

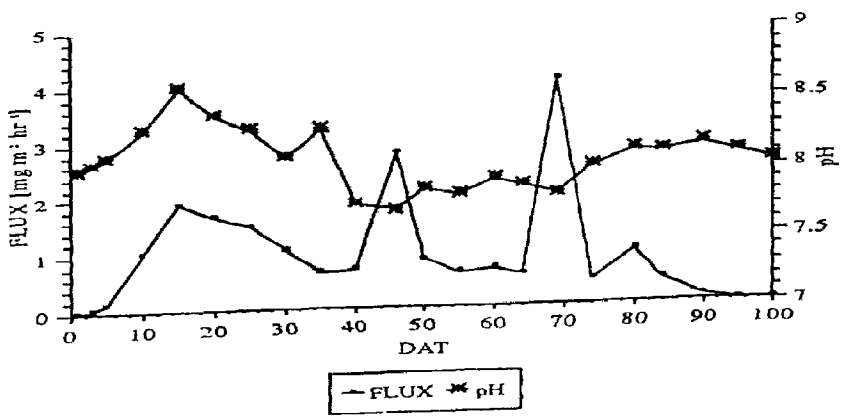
CONTROL



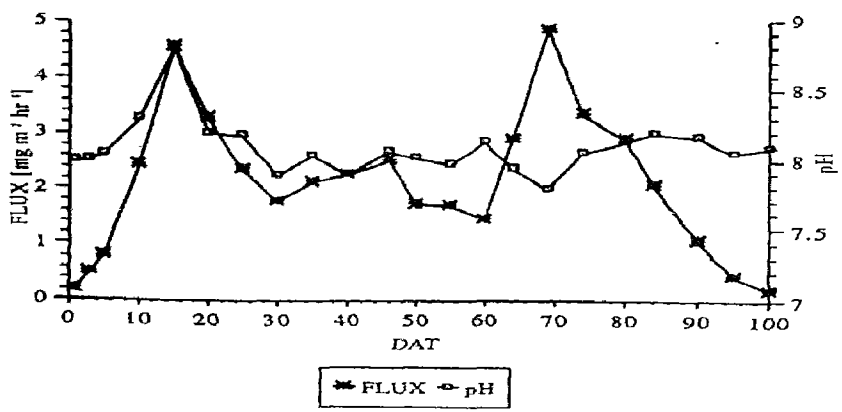
UREA



BSS+UREA



FYM + UREA



3. Gas samples collection in IARI rice field

4.3 METHANE EMISSIONS FROM NAJAFGARH DRAIN

Najafgarh drain is the largest drain in National Capital region of Delhi. Many hydrants are opened in this drain at different points. There was a difference of 40 cm in water level between summer and winter season. In the winter season the water level was low due to lack in rainfall and less spent domestic water compared to that in summer. A typical marshy odour prevailed around the area all over the year. This odour was much strong in summer months when the atmospheric temperature was high. In rainy season (July to September) there was a rise in the water level and subsequent increase in water flow. In other seasons the flow remained quasi-stationary. There was heavy sludge deposits under the water. The sediments were of coal-black colour. The colour of water was also light black. So, when one looks over the drain from the nearby bridge it appears like a pool of black water. Many aquatic weeds grew sporadically on the heavy sludge deposits. During summer months (April to June) profuse bubbling from the surface was seen. This bubbling was present in a little amount in the cold winter months (November to February). Where the water flow was virtually stagnant due to higher deposition of sediments the bubbling was higher compared to other locations. So, it was evident that methanogenesis occurred in the sediments. It is expected that emissions occurred by both ebullition and diffusion. However in the summer months ebullition

process was dominant. Gas samples were collected by floating chamber technique. Collection of gas samples and measurements of other parameters were made in the year 1993, four times in a month (once in a week) and the average was taken as the representative of that month (Table 14).

Results of the seasonal study of CH_4 emission are shown in the Figures 7 and 8. The average hourly rate of methane release during 12 month period and atmospheric concentrations vs. months are plotted there along with the drain water average temperature. In the Figure 9 and 10 change in atmospheric concentrations and flux per degree of absolute change in drain water temperature w.r.t. the previous month vs. months are plotted. There is a strong seasonal trend in the data. Emission rate increases during spring and summer to a maximum in June and then decrease in winter to a minimum in January. Some specific pattern were followed by atmospheric concentrations. In June the drain water temperature was all time maximum of 33.5 ^{o}C and flux was 720.83 mg $m^{-2}hr^{-1}$ and atmospheric concentration (taken 5 cm above the water surface) was the highest of 32.6 ppmV. Both the atmospheric concentration and emission rates were lowest in January, 2.6 ppmV and 9.88 mg $m^{-2}hr^{-1}$ respectively. The average drain water temperature was also lowest of 13.7 ^{o}C. Atmospheric concentrations and emission rates both increased or

decreased with the increases or decrease in atmospheric temperature as well as the drain water temperature. Drain water temperatures, atmospheric concentrations and emission rates increased from January to June. The rate of increase in the emission rates varied from 26.31 to 81.05 mg $m^{-2}hr^{-1}$ $^{o}C^{-1}$. In March there was a considerable increase of 50.73 and the maximum increase was in June which was 81.05 mg $m^{-2}hr^{-1}$ $^{o}C^{-1}$. For atmospheric concentration the rate of increase was fairly constant which varied between 0.7 (in February) to 1.8 (in April) ppmV $^{o}C^{-1}$. The rate of decrease in atmospheric concentrations emission rates were much sharper. Steepest decrease was in July. For atmospheric concentration it was -13.4 ppmV $^{o}C^{-1}$ (range -1.0 to -13.8) and for emission rates it was -108.33 mg $m^{-2}hr^{-1}$ $^{o}C^{-1}$ (range -13.9 to -108.33). In the autumn month of October there was a sudden rise in both atmospheric concentration and flux, 17.4 ppmV and 308.33 mg $m^{-2}hr^{-1}$ respectively with an increased rate of 2.4 ppmV $^{o}C^{-1}$ and 13.17 mg $m^{-2}hr^{-1}$ $^{o}C^{-1}$, respectively. The average atmospheric concentration for January to June was 17.7 ppmV and from July to December it was 13.2 ppmV and the average for the year was 15.4 ppmV. Similarly for the first half of the year the average emission rate was 356.86 mg $m^{-2}hr^{-1}$ and for the next half of the year it was 321.57 mg $m^{-2}hr^{-1}$ and round the year average was 339.21 mg $m^{-2}hr^{-1}$.

Other parameters measured were pH, EC and Eh.

pH values were fairly stable ranging from 7.10 to 7.26. EC values were also fairly stable ranging from 0.92 to 1.41 dS m^{-1}. EC and pH values were quite haphazard and did not follow any trend in both the atmospheric concentration and flux. Eh values also did not follow any definite trend. It varied from -139 to -230 mV. In natural conditions like Najafgarh drain it was also not unexpected. These data cannot show true relationship to CH_4 emission because the water and the sludge underneath was not perfectly stagnent. Again during gas sampling we get the dissolved CH_4 by diffusion from the drain water along with the ebullition from the sediments. Actual sites of the CH_4 production might be at greater distance from the banks where the depth of drain water as well as sediments were higher compared to the nearer places along the banks. Eh values were taken at 2 cm. depth of sediments and depth of drain water varied from 20 to 60 cm depending on the season. Only continuous monitoring can establish the true relationship of flux with these parameters. The drop in EC in rainy season (July to September) suggested the existence of lower concentration of suspended materials in the drain water. It might be due to the dilution of the drain water by rain water. Sharp decrease in atmospheric concentration and flux in July was definitely associated with temperature drop but the effect of the purification of atmosphere from suspended particles and methane

molecules by rain and addition of rain water to drain water could not be ignored. In September there was heavy rainfall. So, methane emissions in this condition was a complex phenomenon and to reach to a definite conclusion was virtually impossible within a year. But there was no doubt about the exceptionally high atmospheric concentrations and emission rates and their relationship with the increase in temperature.

The data presented here on seasonal release of methane from the Najafgarh drain to the atmosphere are of the type which perhaps has been attempted for the first time. No published data of this type of situation have been come across during the review of literature so far. A few near similar situations (e.g. marsh area, flood plains etc.) can be reviewed to realize the nature of emission rate in this situation. In a laboratory study of methane release from salt marsh soil-cores Atkinson and Hall (1976) calculated an annual release of 1 g m^{-2}. Data obtained from one or two sets of conditions can not possibly be to extrapolated to other set of conditions. The seasonal variability of methane release for the mid and short *Spartia* marshes seems to correlate well with the ambient temperature (King and Wiebe, 1978). Although the correlation of methane production with temperature has been reported in the literature (Zeikus and Winfrey, 1976), the extent to which methanogenesis is regulated directly by temperature is not known. Temperature is reported

(Jones, 1975) to express its regulatory nature as follows: (i) temperature directly affects the metabolic activity of methane-producing bacteria, (ii) temperature affects the metabolic activity of those microorganisms which produce the substrates for or inhibitors of methanogenesis. Anomalous activity such as the variable release pattern may be due to these two mechanisms differing in the degree of their expression in the different marsh types. King and Wiebe (1978) reported 53.1 g CH_4 m^{-3} released in Georgia salt marsh. High $SO_4^=$ concentration in salt marsh soils could induce a competition such as that observed by Winfrey and Zeikus (1977), who have shown that the presence of $SO_4^=$ in fresh water sediments causes a competition between $SO_4^=$ reducers and CH_4 producers for H_2 and acetate in which substrate becomes limiting for the CH_4 producers. During the study on CH_4 emissions from the Amazon floodplain, Wassmann *et al.* (1992), found a maximum emission of 200 mg CH_4 $m^{-2}d^{-1}$ from the varzea sediment. They got a concentration of 2.5 ppmV in ambient samples. The highest emission rates obtained by single measurements were 1 g $m^{-2}d^{-1}$. Microbial CH_4 can be formed in anaerobic environments by two different pathways. The first pathway is a fermentation of organic substrate such as acetate to CH_4, while the second is the reduction of CO_2 with H_2 as the electron source (Whiticar *et al.*, 1986). The former pathway is dominant in $SO_4^=$ free, freshwater

environments, whereas the latter is the principal methanogenic pathway in marine environments (Whiticar *et al.*, 1986). They also concluded that in the permanent aquatic areas the flux of gas bubbles was relatively high during the low water phase. So, sharp decrease in flux in Najafgarh drain during July-September was due to the increase in water level due to rain. In October rainy season was over and the water level came down and net sunshine hours were also increased due to clear sky; hence a rise in the emission rates were observed for this month. In the following months the temperature came down and emission rates were also decreased. Measurements in Varzea lakes also revealed ebullition as the main methane transport mechanism (Bartlett *et al.*, 1988; Devol *et al.*, 1988). Changes in the ebullition rate can be seen as the principal cause for the seasonal and spatial differences in Varzea (Bartlett *et al.*, 1990; Wassmann and Thein, 1991). So, high emission rates were caused by the frequent emergence of methane containing gas bubbles. Low emissions coincide with the absence of significant ebullition (Wassmann *et al.*, 1992).

In their study on temperature limitation on methanogenesis in aquatic sediments Zeikus and Winfrey (1976) found that the sediment was of brown to black colour, smelled of sulfide, and had an Eh below -150 mV. In our study the average was -165.8 mV. In their study the pH values were near neutral throughout the sampling

period which was also true for our observations on Najafgarh drain. They had shown that a rise in sediment temperature from winter to summer months correlated with an increase in methanogenesis; a decrease in sediment temperature from summer to winter months correlated with a decrease in the number of methanogens. In their incubation study of the lake sediment they found CH_4 emission from 4 to 60 °C and identified the optimum temperature for methane formation between 35 °C to 42 °C. 100 to 400 fold increase was observed in methane emissions with a change of 20 °C during the rise in temperature from 4 to 24 °C. In our study we found around 13 times increase in atmospheric concentration and around 74 times increase in emission rate during a change of 20 °C (13.7 to 33.7). Thus, the increased rate of methanogenesis that was associated with seasonal change is in part a reflection of increased numbers of methanogens and increased rate of metabolic activity when sediment temperatures more closely approximated the optimum temperature for methanogenesis.

Williams and Crawford (1984) in their incubation study of peats collected from different depth of Minnesota peatlands, USA, found that methanogenesis by surface peats was more responsive to temperature alterations than was that by deep peats. The year-round temperature below approximately 25 cm in the peatlands remained between 7 and 12 °C (Williams and Crawford,

1983). The methanogenesis temperature optimum for the deepest samples was within this range. So, continuous emissions of CH_4 in Najafgarh drain was possible in winter months.

Williams (1993) during his study of methane emissions from manure of free range dairy cows found a high flux of methane from the swampy cesspit area into which the manure from dairy floor were washed. He found that at 17 °C the emission rate was more than 720 mg $m^{-2}hr^{-1}$. In our study at 17.6 °C emission was 112.5 mg $m^{-2}hr^{-1}$ only. It proves the possibility of high emission rate at higher temperatures. It may be concluded that the high emission rate from the drain was due to heavy deposition of organic wastes from domestic waste water and wastes from food processing factories which helped in continuous supply of substrates to methanogenesis. Cicerone and Shetter (1981) also reported a considerably higher emission rate of 327.5 mg $m^{-2}hr^{-1}$ from fresh water pond.

Using a computer software CURVEFIT (Thomas, 1986) we tried to work out the mathematical relationship of atmospheric concentration and emission rate vs. the drain water temperature. We took only data from February to June only (the increasing trend). The best fit equations for atmospheric concentration was:

$Y = A + BX + C/X^2$ [2nd. order hyperbola]

$A = 107.90$

$B = -3349$

C = 28000

R^2 = 0.999

$R^2(C)$ = 0.998

for straight line fit :

Y = A + BX

A = -20.90

B = 1.60

R^2 = .996

$R^2(C)$ = .994

where Y is atmospheric concentration in ppmV and X is drain water temperature in ^oC.

For flux the best fit equation was:

Y = A + BX [Straight Line]

A = -509.19

B = 36.04

R^2 = .994

$R^2(C)$ = .992

where Y is flux in mg $m^{-2}hr^{-1}$ and X is drain water temperature in ^oC. Figure 11 shows the straight-line fits.

In an attempt to find out the annual average methane emission rate from the Najafgarh drain it was seen that the value was 339.21 mg $m^{-2}hr^{-1}$. If we extrapolate it to find out the total annual emission it becomes 29.72 t/ha and when the area is approximately 180 ha the emission is 5350 tonnes. The maximum emission was during the month of June 934.36 tonnes and minimum

was 13.23 tonnes/ha during January. If all drains of Delhi are considered, the average annual emission becomes 13075 tonnes.

It should be noted that methanogenesis as well as the emissions are a complex phenomena in this type of natural conditions. Atmospheric concentration may vary every now and then depending on wind velocity and water flow characteristics. Emission rates may also change due to unpredictable causes at any time. Long term and continuous monitoring is needed to predict the relationships and best fit equations for these emissions.

Table 14. Methane emissions from Najafgarh Drain

Month	Temp. (°C) Amb*.	water	EC (dS/m)	pH	Eh# (mV)	Atm. Conc.& (ppmV)	Flux (mg/m²/hr)	δ(atm. conc.) / δ(w. temp.)	δ(flux) / δ(w. temp)
JAN	19.8	13.7	0.95	7.26	-139	2.6	9.88	-	-
FEB	24.9	17.6	0.81	7.16	-165	8.2	112.50	1.4	26.31
MAR	26.8	19.9	1.05	7.23	-230	9.8	229.17	0.7	50.73
APR	35.7	26.3	1.10	7.20	-205	21.4	428.97	1.8	31.25
MAY	40.6	32.5	1.20	7.10	-175	31.4	639.79	1.6	33.97
JUN	39.4	33.5	1.41	7.15	-190	32.6	720.83	1.2	81.05
JUL	34.0	33.0	1.06	7.13	-177	23.3	665.99	-13.8	-108.33
AUG	35.5	31.1	0.92	7.21	-143	13.4	579.27	-5.2	-46.05
SEP	31.3	27.7	0.95	7.10	-169	9.9	262.50	-1.0	-93.10
OCT	28.8	24.6	1.11	7.17	-160	17.4	308.33	2.4	13.17
NOV	27.4	20.2	1.23	7.21	-134	10.6	95.83	-1.6	-48.30
DEC	23.6	14.6	1.07	7.20	-103	4.7	17.50	-1.1	-13.99

* Between 12.30 - 1.00 P.M., # At 2 cm sediment depth. & Above 5 cm of surface

Fig. 7. Water temperature vs. atmospheric methane concentration in Najafgarh drain in the year 1993

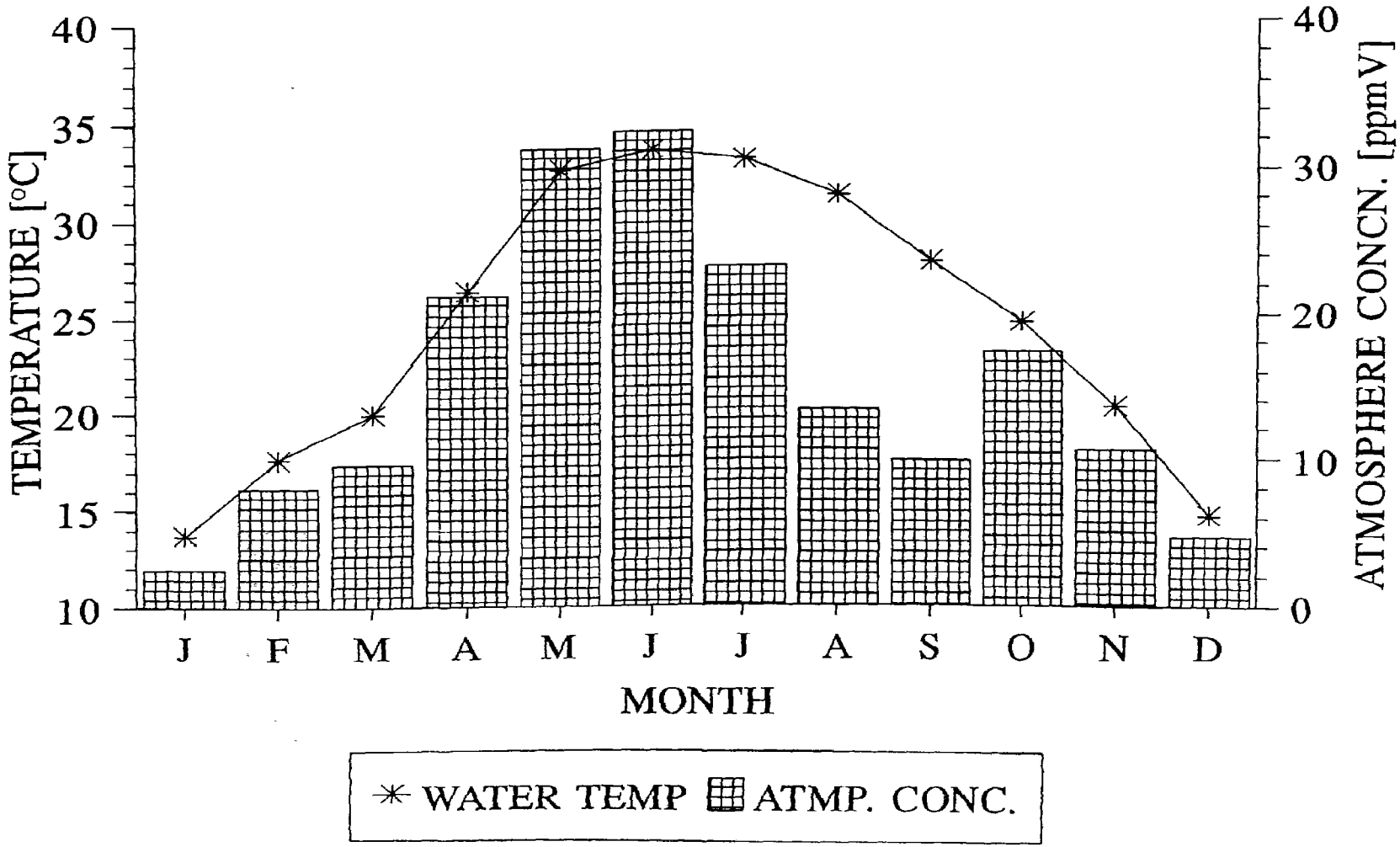


Fig. 8. Water temperature vs. methane flux from the Najafgarh drain in the year 1993

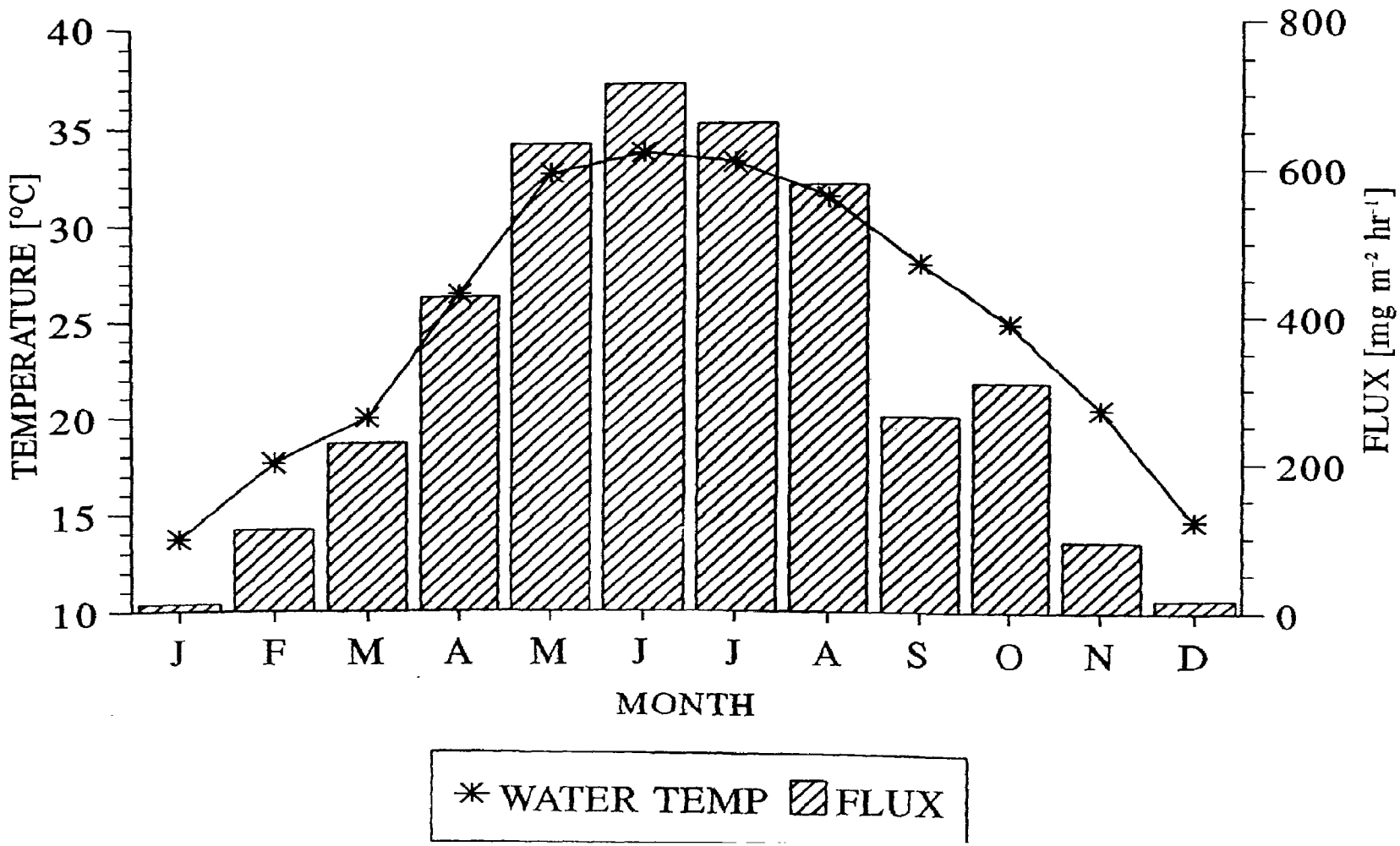


Fig. 9. Change in atm. methane conc. with per °C temp. change in Najafgarh drain water in the year 1993

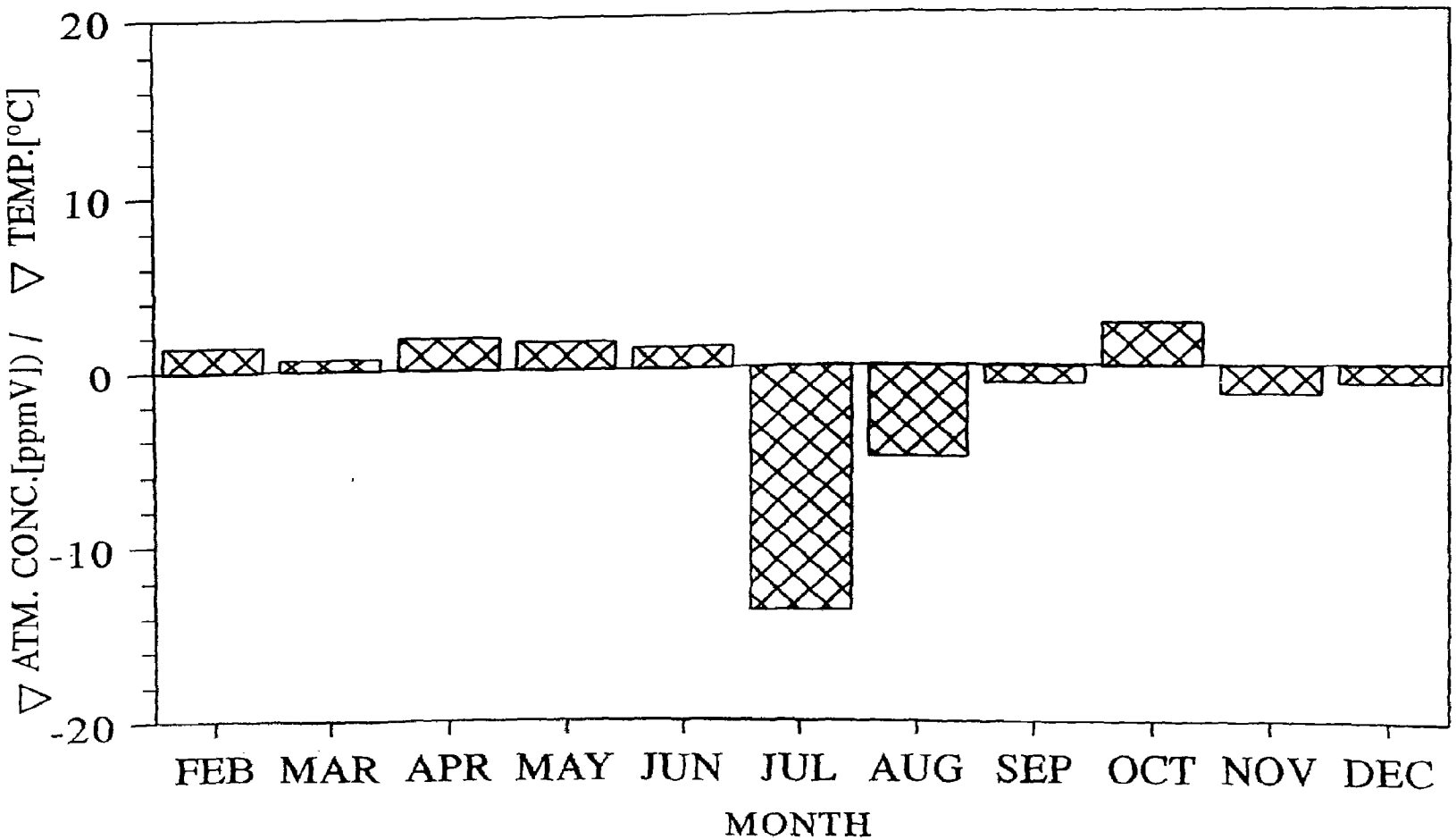


Fig. 10. Change in methane flux with per °C temp. in Najafgarh drain in the year 1993

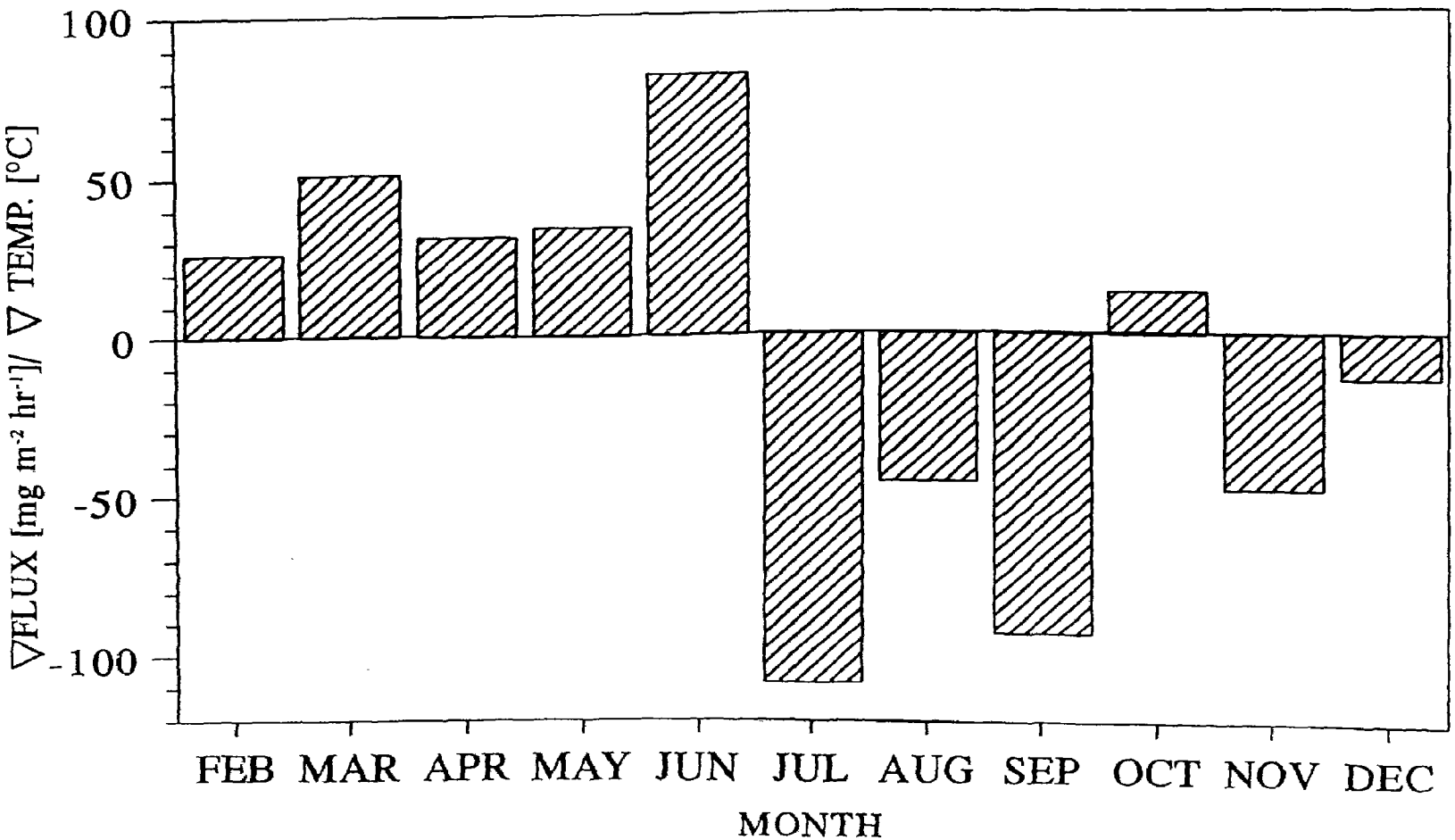
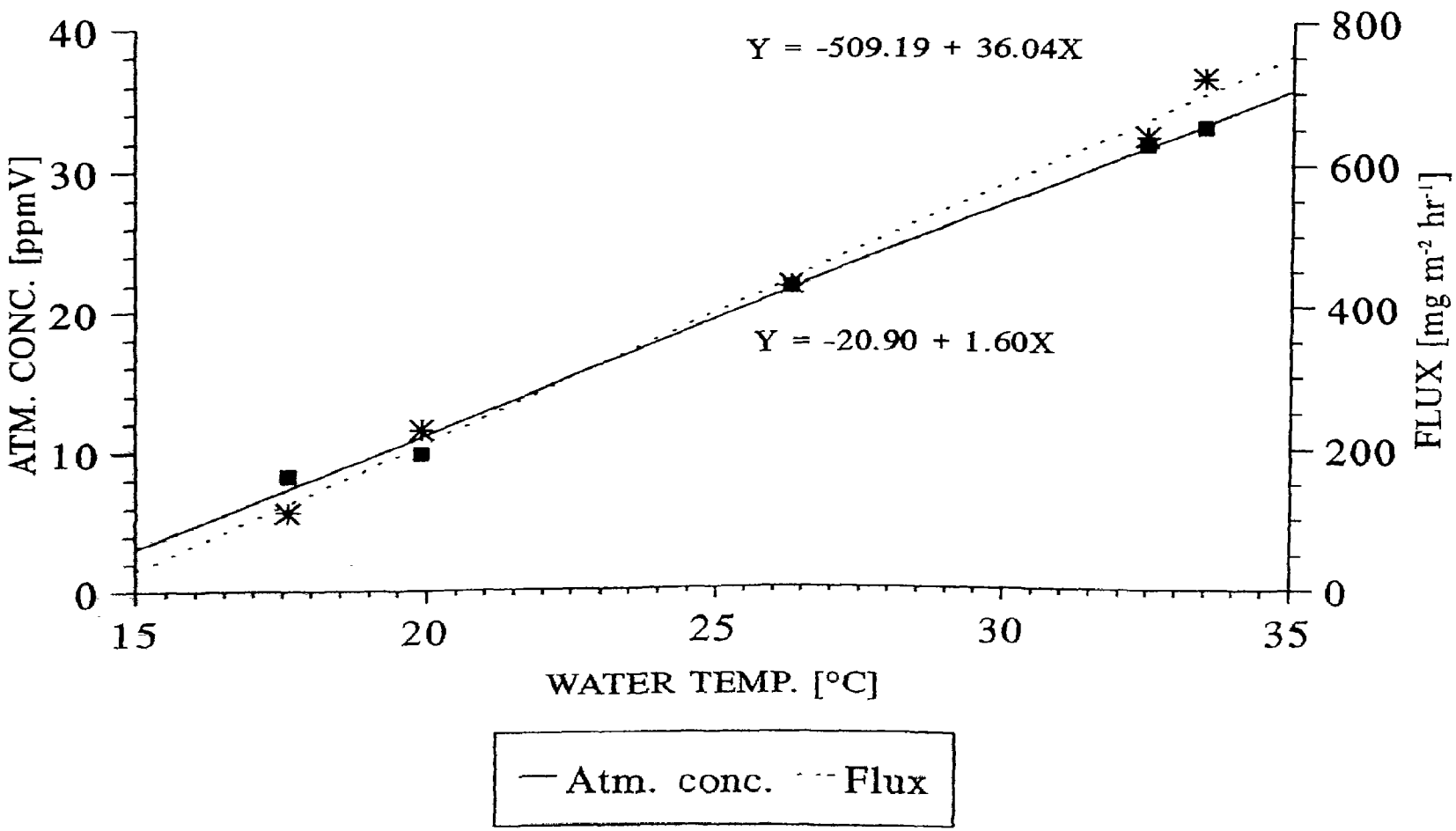


Fig. 11. Best fit equations for atmospheric concentration and methane flux vs. drain-water temperature in the year, 1993



4. New Motinagar site of Najafgarh drain

5. Gas samples collection at Najafgarh drain

4.4 METHANE EMISSIONS FROM DISTILLERY EFFLUENTS

Distillery effluents were found to be the strong source of methane emission from natural environment. Till now no effort has been made to identify its importance in CH_4 emissions. Indian distilleries generally use molasses as starting material in their fermentation chambers. Sometimes they use rice for the same purpose. After fermentation alcohol is distilled out from the mixture. The remaining liquid is drained out from the plant to effluent treatment chambers or aeration chambers or collected in the artificial lagoons. After lagooning for 30-90 days these effluents are discharged into nearby canals or rivers. In some cases farmers of the nearby fields use this effluent in their sugarcane fields for irrigation. It is claimed that the use of this effluent at a suitable concentration not only reduces the use of commercial fertilizers but also minimizes the attack of termites to sugarcanes. However its use at a higher concentration may be fatal to the sugarcanes in early stages. Due to the immense potential of this effluent to produce CH_4, a few distilleries have established primary treatment plants in which methanation is aggravated by maintaining suitable temperature and methanogens. CH_4 thus produced is used as supplementary energy source for various operations. It is claimed that there is at least 60% saving in electricity expenditure. It was found that the post methanated effluent has adequate potential to

produce CH_4. But according to the distilleries a secondary methanation plant has a high cost:benefit ratio which makes its use uneconomic. However, from pollution point of view it is a must. When somebody approaches a distillery more specifically the lagoon area a typical strong odour of effluent along with that of molasses results in a suffocating condition. A large population of house flies is visible in the entire lagoon area specially during summer months.

In some distilleries the pre-methanation or post- methanation effluents are treated in aeration tank. In aeration tanks effluent is mechanically stirred to increase the oxidation or diffusion of methane before final discharge so that no aquatic pollution hazard occurs in the nearby water sources. The effluent has a deep brown colour which leaves brown to black marks on the walls of canals through which it runs. Due to its dark colour and due to high temperature in distillation tank the effluent temperature is usually higher than the ambient temperature in the lagoons which were directly receiving effluent from the distillation tanks.

From every sampling site gas samples were collected in three sets and the average of fluxes from each set was taken as representative emission rate of that site.

4.4.1 Collection of gas samples from the distilleries in Uttar Pradesh.

Gas samples were collected from different

distilleries in Uttar Pradesh during May-June and December months. The distilleries undertaken in the present studies were 1) Shimbhauli, 2) Rampur, 3) VAM organics, 4) Shamli and 5) Doon Valley distillery. Collections from post-methanation, aeration tank or from final effluent tank or lagoons were situation specific and couldn't be systematic due to local restrains. All the pre, post and final effluent samples were not available in any single distillery (Table 15). But we got characteristic emission rates for those situations. Profuse gas bubbling was observed in the lagoons at all these sites.

4.4.1.1 Shimbhauli Distillery

Samples were collected twice from Shimbhauli distillery. First visit was made during last week of May and gas samples were collected from the final storage tank. In this distillery, effluent was first discharged in to a lagoon. The effluent discharge from this distillery was 375 kl d^{-1}. After a certain period this effluent was shifted to another lagoons and from where the farmers used to collect it by tankers. The other alternative was to pump it out to a nearby canal. The distillery has two methanation plants but only one was operational. So, the discharged effluent in real sense should have been only post methanated. However for comparison Pre-methanation (PR), Post-methanation (PS) and final (F) effluent samples were collected for laboratory studies. The atmospheric concentration of CH_4

at 10 cm above the effluent surface was 4.7 ppmV in final tank and 9.6 ppmV in post-methanation tank. The effluent temperature was 41.9 ^{o}C, Eh was -21 mV at 20 cm depth in final tanks and -3 mV in PS tank. The pH of PR, PS, and F samples were 4.5, 8.1 and 8.0, respectively. Similarly ECs were 23, 12 and 1.8 dS m^{-1} and BODs were 35000, 8560 and 7050 mg l^{-1} respectively. Methane flux were 188.63 and 324.21 mg $m^{-2}hr^{-1}$ in F and PS lagoons respectively.

Gas samples were collected from the same distillery in the month of June also. At that time the methanation plant was out of order. So, untreated effluent i.e. PR was directly discharged to the lagoons. Therefore first lagoon was full of untreated high BOD effluent and heavy bubbling was observed. pH, BOD and EC values were more or less same to that PR samples in the first observation. The effluent temperature was 43 ^{o}C in F lagoon. Atmospheric concentration (above 10 cm) at the first lagoon was 5.3 ppmV and at the final lagoon it was 2.5 ppmV. The lower value of atmospheric concentration at the first lagoon might be due to the higher wind velocity. The emission rate in the first lagoon was 1264.29 mg $m^{-2}hr^{-1}$ and at the final lagoon was 221.84 mg m^{-2} hr^{-1}. The BOD at the final lagoon was 9435 mg l^{-1}. So, it was not clear whether the rise in emission rate from the final lagoon was due to higher BOD or elevated temperature as compared to the values obtained before.

But it was clear from the first lagoon that higher is the BOD higher is the emission rate.

4.4.1.2 Rampur Distillery

Rampur distillery is the biggest distillery in UP and per day effluent discharge was 1200 kl d^{-1}. Here PS effluent discharge was stored in a concrete tank and after aeration (natural or mechanical) it was transferred to another concrete tank from where gas samples were collected. This effluent was finally discharged through drains which ran through the town and then to the agricultural fields and finally form a tributary of the river Jamuna. The typical odour prevailed in the drain water even at a distance of 5 km from the distillery and that too after a torrential rain the previous night. The temperature at the final tank (here PS was the final tank) was 45.6 °C and the atmospheric concentration (above 10 cm) there was 5.6 ppmV. EC of PR, PS and F (in the outgoing drain) were 22, 8.5 and 2.3 dS m^{-1} and pH values were 4.6 8.2 and 8.1 respectively. The BODs were 38333, 5550 and 5450 mg l^{-1} for PR,PS and F respectively. The emission rate from the tank was 185.36 mg $m^{-2}hr^{-1}$ which was lower than the emission rate at Shimbhauli where BOD was higher and though temperature was lower than Rampur. It is the distinct proof that higher BOD always results higher emission rates.

4.4.1.3 VAM Organics

In VAM Organics the situation was some what

different. Daily discharge of effluent from this distillery was 270 kl d^{-1}. They discharged the effluent from the distillation unit to a cemented tank and from there required amount of effluent was pumped out to the biomethanation plant whenever necessary. The PS effluent was then transferred to another tank where aeration was carried out and finally shifted to a lagoon from where it was discharged out through drains. Gas samples were collected from PR and F lagoons. The atmospheric concentration over PR and F lagoons were 36.1 ppmV and 4.9 ppmV respectively. ECs of PR, PS and F were 18, 12, 2.3 dS m^{-1} respectively. pHs were 4.3, 8.3 and 8.1 and BODs were 38000, 3300 and 3225 mg l^{-1} respectively. The Ehs at PR and F were 6.7 and 13.8 mV. The temperature of effluent at PR was 47.9 and F was 46 °C. The BOD of F was minimum among all the distilleries but the emission rate was maximum of 446.25 mg $m^{-2}hr^{-1}$. It may be due to very high temperature. The emission rate from the PR lagoon was maximum among all distilleries and that was 2705.15 mg $m^{-2}hr^{-1}$. BOD of PR was very high i.e. 38000 mg l^{-1}. The high BOD associated with high temperature was the probable cause of so high emission rate.

4.4.1.4 Shamli Distillery

The samples were collected in June. The effluent discharge from this distillery was only 9 kl d^{-1}. The effluent temperature was 45 °C and the atmospheric concentration over the aeration tank was 7.5

ppmV. ECs of PR, PS and F effluents were 36, 21 and 1.5 dS m^{-1} respectively. The BODs of PR, PS and F were 37500, 7000 and 6650 respectively. Gas samples were collected from the storage tank after aeration. The emission rate was very low and it was 112.179 mg $m^{-2}hr^{-1}$. The low emission rate after aeration was specially noticeable.

4.4.1.5 Doon Valley Distillery

Doon Valley distillery was visited in the winter month of December, 1993. The temperature of the effluent was 23.5 °C in the PR and 23 °C in the F tank. The PR effluent pH was 4.3 and after aeration it increased to 5.3. The BOD of the PR effluent was 38450 mg l^{-1} which became 7165 mg l^{-1} after aeration. The methanation plant was not in a working condition. The emission rate from the PR effluent from the lagoon was 189.74 mg $m^{-2}hr^{-1}$. After aeration treatment the emission rate went down to 96.73 mg $m^{-2}hr^{-1}$. The comparatively lower rate of emission from the untreated or PR effluents may be due to low temperature than that in summer months in other distilleries. Another important observation was that after aeration the emission rate decreased almost to the half of the initial rate. The atmospheric concentration over the initial tank was 15.8 ppmV and after the aeration it became 5 ppmV. Relatively higher atmospheric concentration may be due to stagnation of air over the lagoons as there was no wind movement.

4.4.2 Diurnal Variation

To study the effect of temperature during whole day observations were carried out in Doon Valley Distillery in the second week of March, 1994. The biomethanation plant was still not in full operation. The BOD of the PR lagoon was 33,000 mg l^{-1} and in the aeration cum final lagoon 10,000 mg l^{-1}. pH values were the same as were in December, 1993. EC (measured at 50 cm depth of the effluent) were 22 and 6.13 dS m^{-1} in PR and F lagoons. Eh in the PR was -15 mV whereas in F tank was 45 mV. The PR lagoon did not have any lining and was an earthen one. Effluent was fed to it by pipes using pumps. In the morning hours there was a cover of froths on the surface. The frothing disappeared as the sunshine and wind velocity were increased. This frothing has direct relationship with the environmental parameters like wind velocity and temperature as well as sunshine. Frothing was only observed in PR but not in aeration lagoon. So, frothing was related to higher EC or BOD of the effluent. The frothing totally disappeared at 11.00 hrs. Again at 13.00 hrs. there was a semi-cloudy condition and the wind velocity lowered down and hence again frothing started which disappeared at about 15.00 hrs. as there was sunlight again. After 16.00 hrs. again there was cloud in the sky and the sunlight disappeared and frothing in the PR was seen. So, it is quite sure that as the evaporation increases frothing decreases. In

PR lagoon profuse bubbling was seen but in F it was negligible as compared to PR. So, in PR the main emission process was ebullition where as in F there was negligible ebulition. Details of emissions from these two lagoons at different times of observation is given in the Table 16. Temperature was recorded at 10 cm depth of the effluent. At 8.30 hrs. the ambient temperature was 18 ^{o}C and PR effluent was 30.6 ^{o}C. The PR temperature was higher as it was coming directly from the distillation plant. The F temperature was only 17 ^{o}C. Flux from the PR and F were 85.34 and 53.75 mg/m^{2}/hr. In the PR tank there was heavy covering of froths. At 10.30 hrs. ambient temperature was 25 ^{o}C. The PR temperature was 31 ^{o}C. The F temperature was 21 ^{o}C. After 11.00 hrs. PR temperature was 30 ^{o}C which may be due to the little cooling effect of the increased wind. At 10.30 hrs flux from the PR and F were 119.21 and 92.19 mg $m^{-2}hr^{-1}$ respectively. At 12.30 hrs. the ambient temperature increased by 1 ^{o}C but the PR temperature decreased but F temperature remained same. The fluxes from PR and F were 135.15 and 52.25 mg $m^{-2}hr^{-1}$. The emission rate in PR might be increased due to removal of frothing cover but the cause of decrease in the F lagoon was not clear. At 14.30 hrs. the atmospheric temperature was 27.5 ^{o}C. The emission rate from the PR drastically reduced to 77.86 and in F it increased to 113.86 mg $m^{-2}hr^{-1}$. The lowered flux in PR might be due to formation of froths which reduced the rate of

ebullition. The increase in the emission rate in F might be due to increase in effluent temperature which increased the rate of diffusion. At 14.00 hrs the atmospheric concentration 5 cm above the lagoon surface was taken. In PR it was only 5.08 and in F it was 15.09 ppmV. It further strengthened the argument that frothing inhibits emission to a considerable extent. At 16.30 hrs. The PR and F temperatures were 29 and 20 °C and the flux were 63.32 and 94.80 $mg/m^2/hr$ respectively. The lower rate of emission was due to the lower temperature in the late hours of the day.

When we go for overall discussion of our studies of methane emissions from distillery effluents it was seen that in general pH of PR effluent varied from 4.3 to 4.6 which were in acidic range. The BODs were highest in PR effluents ranging from 35000 to 38000 $mg\ l^{-1}$ and ECs varied from 18 to 36 $dS\ m^{-1}$. Relatively higher EC suggested more suspended matters present in PR effluent than others (as Total soluble solids = 640 X EC). So, high BODs are generally associated with higher emissions. Low pH is generally not congenial for methanation. Perhaps the low pH levels were compensated by high level of organic substrate for methanogenesis and/or there may be specific strains of methanogens which are not present in the other methane producing natural ecosystems. High BODs associated with high temperature always gave high emission rates. The pHs of

final effluent was 8.1 to 8.2 i.e. in alkaline range. This was the optimum pH for methanation. So, in spite of relatively lower BODs the emission rates were appreciably high.

It was quite obvious that higher BOD does not necessarily mean higher emission rates. BOD alone cannot be an index of methane emission. Emissions are intimately related to other environmental factors. We have observed varied emission rates in PR and F lagoons in the whole day observation.

So, we can take only an average of these emission to take a rough estimate of total emission from all the distilleries. To do so we have taken the average of all the PR,PS and F all the distilleries. Approximate averages of PR, PS and F were 750, 250 and 170 mg $m^{-2}hr^{-1}$ respectively. The calculated all-India surface area of PR, PS and F lagoons are 65, 45 and 110 ha respectively. So, yearly emission from these lagoons are 4270, 985 and 1640 t. So total estimated methane emission from the Indian distilleries are 6895 t yr^{-1} i.e. approximately 6900 t yr^{-1}.

Exact relationships within emission rates and BOD, pH, EC, Eh and temperature need extensive, meticulate and years of observations. But for the mitigation strategy it can be safely advocated that those distilleries which have no methanation plant, should be immediately ordered to install it. Alongwith primary methanation plant secondary methanation plant

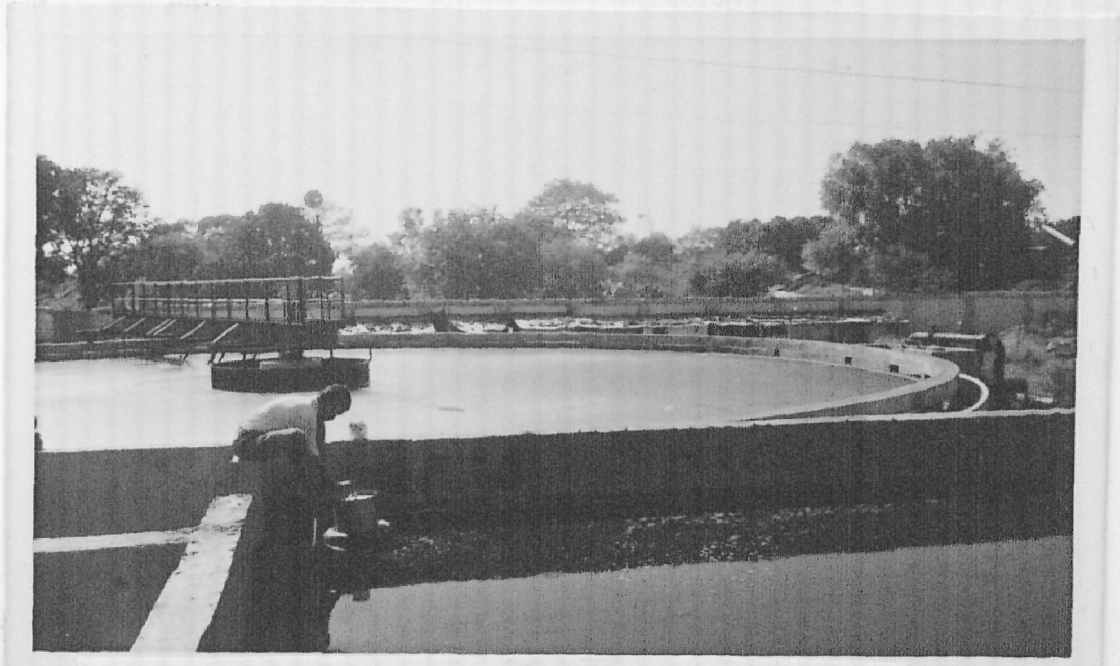
is preferable though the initial cost:benefit ratio may be high. Every distillery should provide aeration tank where post treated effluents should be aerated and then transferred to final lagoon or tank from where it is discharged out. Again instead of discharging the final effluent in rivers etc. it may be utilised as an efficient source of organic manures in the farmers fields which will, as well as, reduce water and air pollution problem. Pre-methanation effluent should not be used as manurial source because the very low pH generally damages the crops specially sugarcanes, in its early stages. There are reports of complete damage of the crop as well as degradation of the soil productivity with the use of premethanation distillery effluents around the distilleries. The properly treated effluents can be used with great profit and without fear of crop damage.

Table 15. Methane emission from different Distilleries in Uttar Pradesh

PLACE	ATM. CONC. (ppmV)	TEMP.(°C)			EC(dS/m)			pH			Eh(mV)			BOD(mg/l)			FLUX ($mg/m^2/hr$)	DISCHARGE (kl/d)
		PR	PS	F	PR	PS	F	PR	PS	F	PR	PS	F	PR	PS	F		
Shimbhauli (I)	4.7(F) 9.6(PS)	-	43.2	41.9	23	12.0	1.8	4.5	8.1	8.1	-	-3	-21.0	35000	8650	7050	188.63(F) 324.21(PS)	375
Shimbhauli (II)	2.5(F) 5.3(PR)	44.0	-	43.0	20	10.0	2.1	4.4	8.2	8.1	11.2	-	-7.0	35050	-	9435	221.84(F) 1264.29(PR)	-
Rampur	5.6(PS)	-	45.6	-	22	8.5	2.3	4.6	8.2	8.1	-	-	-	38333	5550	5450	185.36(PS)	1200
VAM	36.1(PR) 4.9(F)	47.9	-	46.0	18	12.0	2.3	4.3	8.3	8.1	13.8	-	6.7	38000	3300	3225	2705.15(PR) 446.25(F)	270
Shamli	7.5(F)	-	-	45.0	36	21.0	1.5	4.6	8.3	8.2	-	-	-	37500	7000	6650	112.18(F)	9
Doon	15.8(PR) 5.0(F)	23.5	-	23.0	24	-	1.9	4.5	-	5.3	-	-	-	38540	-	7165	96.73(F) 189.74(PR)	-

Table 16. Diurnal methane fluxes from Doon Valley Distillery

Time	Temperature (^{o}C)			Flux [$mg/m^2/hr$]	
	Ambient	Effluent			
		PR	F	PR	F
8.30	18.0	30.6	17	85.34	53.75
10.30	25.0	31.0	21	119.21	92.19
12.30	26.0	30.0	21	135.15	52.25
14.30	27.5	30.0	23	77.86	113.86
16.30	24.0	29.0	20	63.32	94.80



6. Gas samples collection at Rampur distillery

7. Aeration tank in Doon Valley distillery

8. Gas samples collection at Simbhauli distillery

4.5 METHANE EMISSIONS FROM EXPOSED AREAS OF BIOGAS PLANTS

Deenbandhu and Janta were of fixed dome type. In the Deenbandhu model the slurry temperature varied 19.6 to 40.7 °C. The pH varied from 7.01 to 7.41. Eh varied from -109 to -65 mV. The flux varied from 773.41 to 1314.39 mg/m^2/hr. Maximum emission was in May and the minimum rate was in December. The average emission rate through-out the year as calculated from the emission rates of individual months was 1.05 g/m^2/hr.Temperature has positive effect on methane emission. The correlation coefficient was 0.96. The best fit equation for temperature vs. methane emission rate was Y (flux, mg/m^2/hr) = 304.36 + 24.95X (Temperature, °C) (Table 17 and Figure 13).

In the Janta type of plant the emission varied from 810.38 to 1289.71 mg/m^2/hr. The pH values varied from 6.75 to 7.31. Eh varied from -67 to -113 mV. The slurry temperature varied from 20.1 to 39.8 °C. The average emission rate was 1.05 g/m^2/hr. The best fit equation for temperature vs. emission rate was Y = 415.12 + 21.42X and the correlation coefficient was 0.91.(Table 18 and Figure 14).

In the floating dome type KVIC model in I.A.R.I. the emission rate from the gap between digester wall and gas cylinder varied from 923.91 to 1406.43 mg/m^2/hr. The pH varied from 6.87 to 7.14. The Eh varied

from -65 to -115 mV. The slurry temperature varied in between 20.1 to 41.2 °C. The average emission rate was 1.10 $g/m^2/hr$. The straight best fit equation for temperature vs. flux was Y = 468.31 + 21.81X and the correlation coefficient was 0.80 (Table 19 and Figure 15).

In general emission rates did not vary much in all these various types of plants (Figure 12). The average emission rates were around 1 $g/m^2/hr$. In all these plants the emission rates were higher during summer months (May-June) due to the elevated temperature. In the winter months (December-January) the emission rates were low due to the low temperature.The correlation coefficient varied from 0.80 to 0.96 i.e. temperature had positive effect on methane emission from the exposed areas of the biogas plants. The slurry temperature varied only by 2-3 °C from the ambient temperature. The pH and Eh variations followed no definite trend with the emission rates. Table 20 shows the different emission rates from different types of biogas plants depending upon their exposed areas.

Table 17. Methane emission from exposed areas of Deenbandhu Plant

Month	Temperature (°C) Ambient	Slurry	pH	Eh (mV)	Flux (mg/m^2/hr)
Jan	23.3	21.2	7.04	-76	848.32
Feb	27.1	26.5	7.00	-95	989.72
Mar	31.3	31.0	6.88	-107	1120.51
Apr	36.0	36.2	6.82	-114	1189.53
May	40.5	40.7	7.01	-109	1314.39
Jun	37.2	37.1	7.07	-67	1243.03
Jul	30.3	29.7	7.06	-101	1160.16
Aug	28.9	30.4	7.09	-94	1019.91
Sep	32.7	29.3	7.41	-86	1043.57
Oct	31.4	30.4	7.14	-69	995.21
Nov	29.5	27.3	7.23	-65	938.02
Dec	23.7	19.6	7.19	-78	713.41

Table 18. Methane emission from exposed areas of Janta Plant

Month	Temperature (°C) Ambient	Slurry	pH	Eh (mV)	Flux (mg/m^2/hr)
Jan	23.9	20.1	6.75	-95	810.38
Feb	27.1	26.4	7.04	-81	1003.79
Mar	31.3	31.2	7.00	-106	1062.11
Apr	36.0	36.0	6.90	-93	1171.83
May	40.5	39.8	6.95	-94	1289.71
Jun	37.2	36.3	7.07	-87	1148.47
Jul	30.3	29.5	7.15	-110	1162.49
Aug	28.9	30.2	7.16	-113	1068.01
Sep	32.7	29.1	7.31	-75	1120.51
Oct	31.4	30.3	7.15	-80	997.68
Nov	29.5	26.9	7.14	-79	900.67
Dec	23.7	20.2	7.09	-67	870.54

Table 19. Methane emission from exposed areas of KVIC Plant

Month	Temperature (°C) Ambient	Slurry	pH	Eh (mV)	Flux (mg/m^2/hr)
Jan	23.3	22.4	7.02	-70	986.25
Feb	27.1	26.7	6.80	-67	1196.34
Mar	31.3	31.2	6.84	-84	1243.03
Apr	36.0	36.5	6.94	-115	1245.36
May	40.5	41.2	6.87	-110	1360.91
Jun	37.2	37.6	6.88	-98	1406.43
Jul	30.3	30.2	6.98	-50	1190.50
Aug	28.9	30.7	7.06	-84	998.31
Sep	32.7	29.6	7.32	-77	1085.36
Oct	31.4	31.1	7.08	-91	1027.10
Nov	29.5	28.3	7.11	-65	931.39
Dec	23.7	20.1	7.14	-73	923.91

Table 20. Annual methane emission from exposed areas of different type of Biogas Plants

Types of plant	Exposed Area (m^2)	Emission	
		Daily (g)	Yearly (Kg)
Deenbandhu			
2 m^3	1.68	40.3	14.7
3 m^3	2.40	57.5	21.0
4 m^3	3.60	86.3	31.5
KVIC			
3 m^3	0.99	23.9	8.7
Janta			
3 m^3	1.95	46.6	17.0
6 m^3	4.10	98.6	36.0

Fig. 12. Methane emissions from Biogas plants

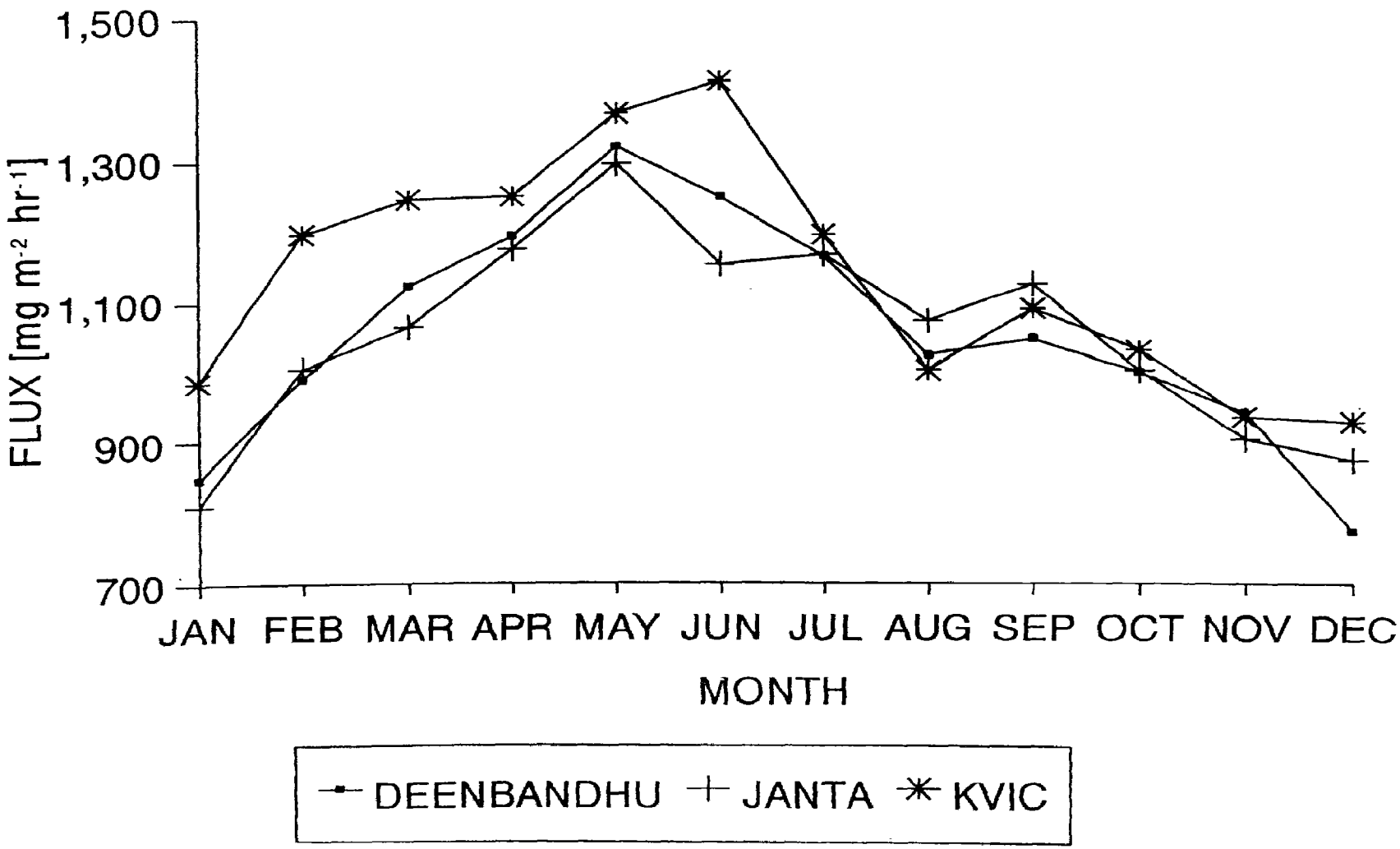


Fig. 13. Methane emissions vs. slurry temperature
[Deenbandhu plant]

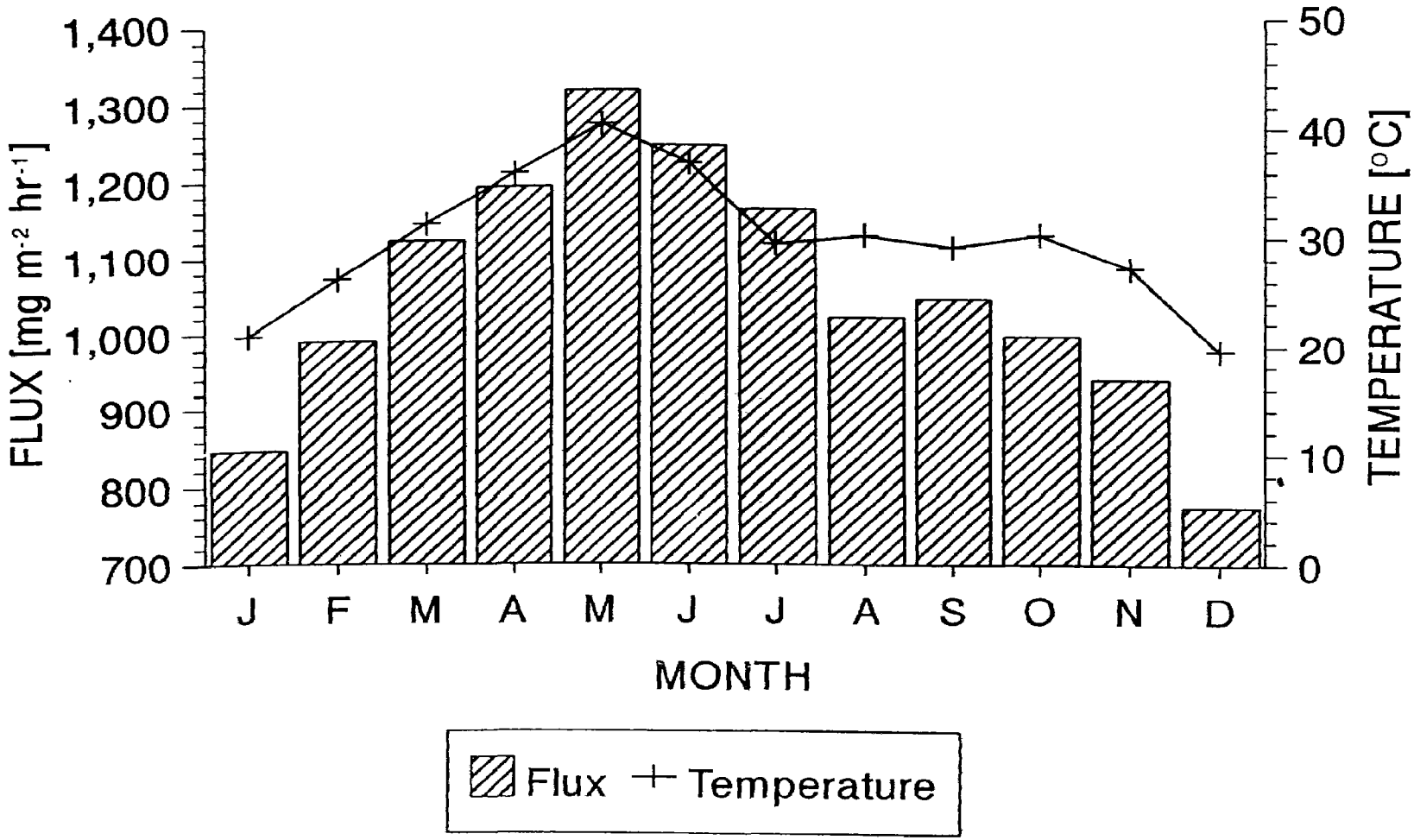


Fig. 14. Methane emissions vs. slurry temperature [Janta plant]

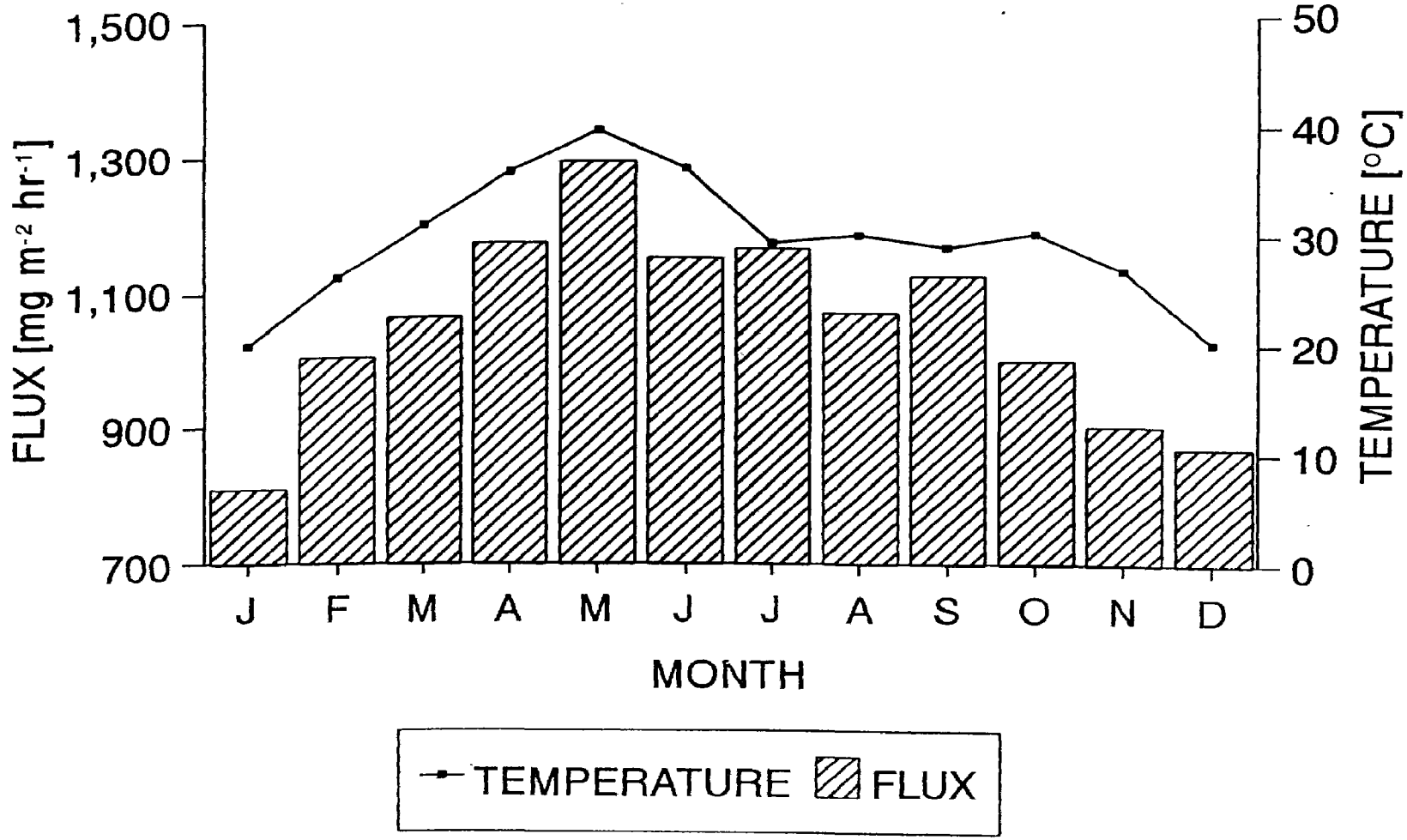
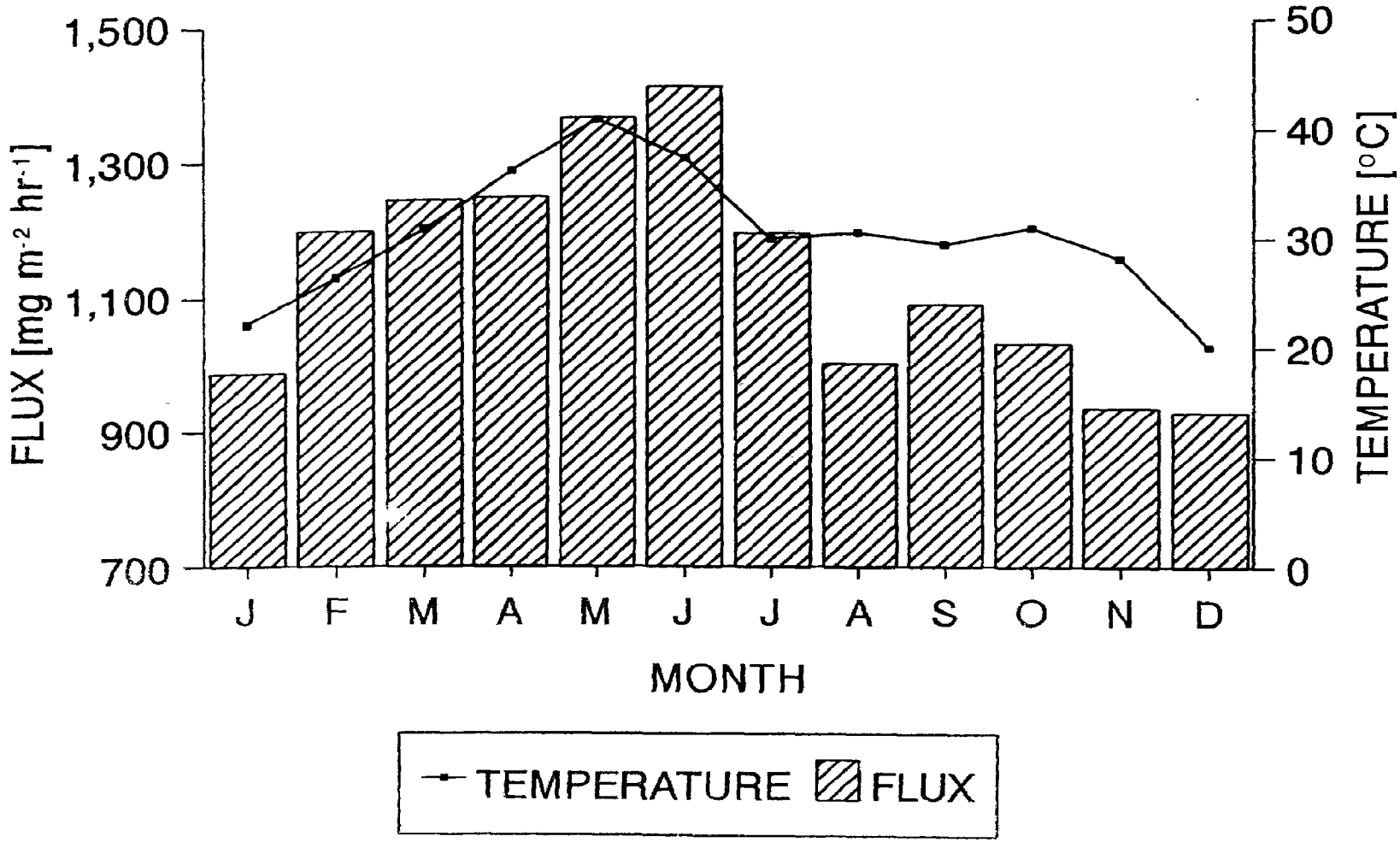


Fig. 15. Methane emissions vs. slurry temperature [KVIC plant]



4.6 METHANE EMISSIONS FROM COMPOST PITS OF DAIRY WASTES

The pits were situated behind the Division of Agronomy, IARI. These were being used to dump wastes from the dairy behind that Division. Of the two pits, first (Pit I) was situated adjacent to the field and the other (Pit II) inside the dairy. As pit II was inside the dairy the use of this was maximum to dump the wastes. Pit I was in a more open space and exposed to sunlight. Pit II was near the boundary wall of the dairy which was surrounded by trees in the southern side permitting less sunlight on the pit. These pits are lacking in similarity of a true compost pits where wastes are deposited inside a deep pit. Here wastes disposed as it was done in case of landfills. The wastes were not dumped on the same point everyday. So, considerable spatial variability was also present. We restricted to a single point for each pit in order to minimise spatial variability in sampling. The wastes consisted of cowdung, unused and chopped fodders, straws etc. Urine of the animals was in general absent. These wastes were carried from the cowshed by trollies and were disposed off here and there in the pit areas. Because of that, there was variability in the fresh amount and depth in the wastes in the entire pit area. The measurement was done to get the rough estimate of the methane emission rates from this type of natural environment.

Keeping in mind that a general trend or

relationship between emission rates and temperatures in the wastes heaps (below 10 cm) could not be available due to extreme variability in the measuring sites from time to time, it was decided that sample would be taken once in a week and averaged for a month throughout the year for each pit. Along with this only one physical parameter i.e. temperatures inside the heaps were taken. All gas samples were collected in between 11.30 A.M. and 12.30 P.M.

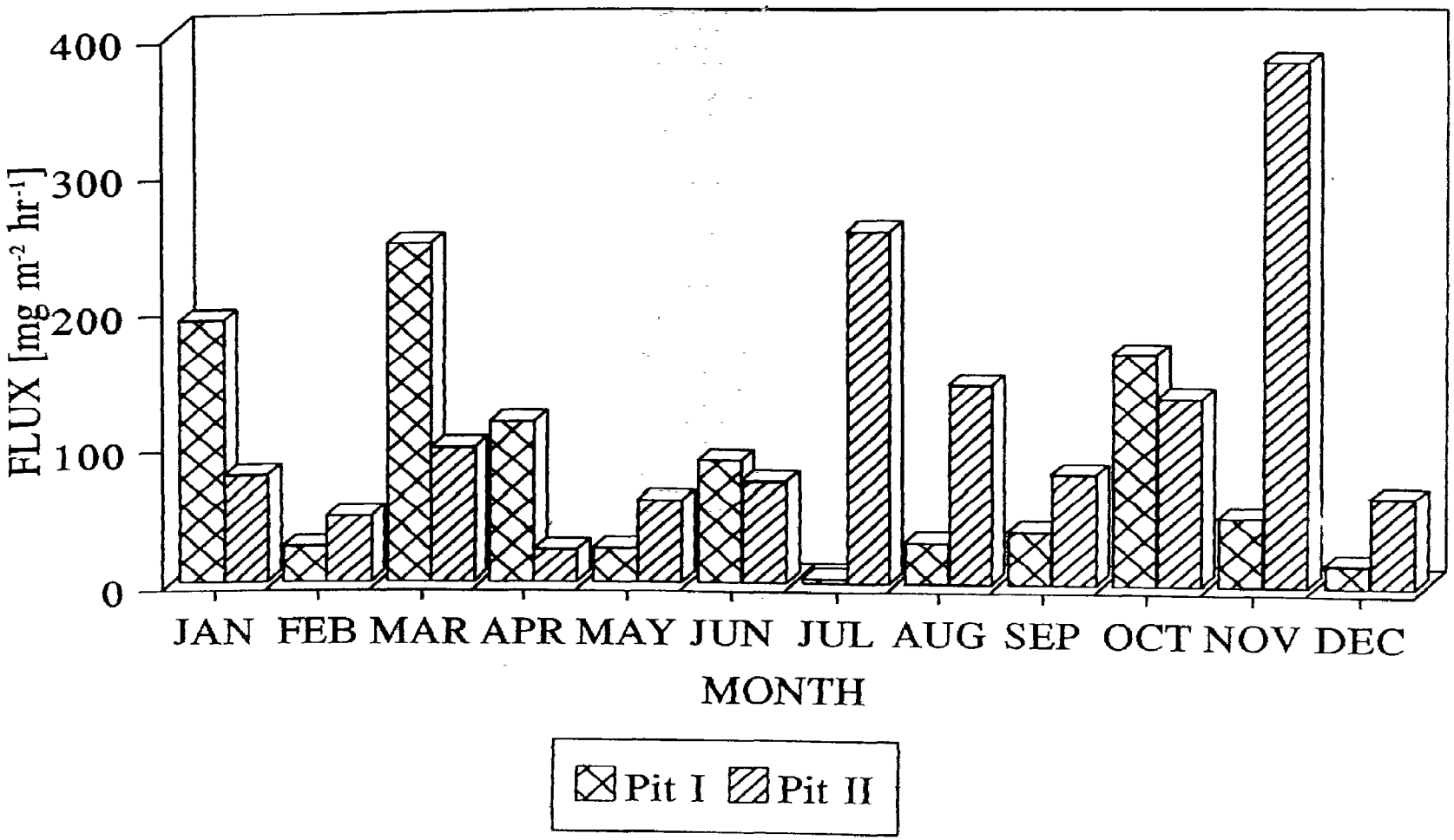
Monthwise atmospheric concentrations and emission rates were tabulated in the Table 21 and graphically presented in Figure 16 for both the pits. For pit I the atmospheric concentrations varied from 2.1 to 12.6 ppmV and the maximum was in March and the minimum was in July. Pit temperatures and the time of sampling at 10 cm depth varied from 23.0 to 38.2 ^{o}C with the maximum in May and the minimum in January. Maximum emission rates were found in March and that was 245.47 mg $m^{-2}hr^{-1}$ and minimum was 3.26 mg $m^{-2}hr^{-1}$. No relationship was visible between atmospheric concentrations, temperature and emission rates. Occasional low emission rates in the summer months may be due to very less moisture content in the heaps and lack of renewal of the sampling points by fresh wastes. It may be also due to oxidation of methane by methanotrophs. The same is true for high value in winter months when the reverse situation took place.

In the pit II similar haphazard emission rates and atmospheric concentrations were observed due to same reasons as were in pit I. The maximum rate was 475.43 mg $m^{-2}hr^{-1}$ in the month of November and the minimum was 22.93 mg $m^{-2}hr^{-1}$ in the month of April. The atmospheric concentrations ranged from 2.3 to 9.4 ppmV and the pit temperature varied from 15 to 39 ^{o}C. Again atmospheric concentrations varies with wind velocity, so increased atmospheric concentration did not show increased emission rates or higher pit temperatures. Drawing the relationship between emission rates and temperatures was not possible because the emissions were widely affected by the local conditions and the renewal of wastes at those points. A general conclusion can be drawn from the data that continuous renewal of wastes at one point increases the average emission rates. In pit I which was situated outside the dairy boundary where renewal was less than pit II, the monthly average was 81.43 mg $m^{-2}hr^{-1}$; whereas in pit II it was 118.57 mg $m^{-2}hr^{-1}$. No published research data were available in this aspect which can describe this specific natural system.

Table 21. Methane emission from compost pit of dairy wastes

Month	Atm Concn. (ppmV)		Temp (°C)		Flux (mg/m^2/hr)	
	Pit I	Pit II	Pit I	Pit II	Pit I	Pit II
JAN	5.5	3.9	23.0	15.0	190.82	77.13
FEB	6.9	5.7	25.0	22.0	25.73	47.35
MAR	12.6	7.1	26.2	28.0	245.47	96.34
APR	8.2	2.3	29.6	32.2	114.38	22.93
MAY	3.7	4.8	28.2	30.1	24.23	58.84
JUN	7.3	5.7	36.4	37.7	87.62	72.84
JUL	2.1	9.3	37.5	39.0	3.26	253.97
AUG	2.8	7.4	31.3	33.0	29.56	142.77
SEP	6.5	4.5	32.7	31.2	37.27	78.44
OCT	7.4	6.3	30.4	29.8	165.40	133.56
NOV	8.3	7.6	30.0	30.0	47.92	375.43
DEC	6.2	4.5	27.0	25.6	15.51	63.37

Fig. 16. Methane emissions from Compost pits of dairy wastes, 1993.



9. Gas samples collection from compost pit

4.7 METHANE EMISSIONS FROM THE LANDFILL AREAS OF FRUITS AND VEGETABLES MARKET WASTES

The fruits and vegetable wastes from the market premises is a real menace. The estimated total wastes from Indian towns is 18 crore tonnes each year. This value is increasing by 1.33 % per year. It has been estimated that 10000 tonnes of green vegetable wastes can produce 171000 m^3 cooking gas (70 % methane) which is equivalent to 117000 l disel or 73000 kg LPG or 103000 l kerosin. So, these wastes have tremendous potentiality to supply energy for various purposes (Azadpur Market Office, 1993).

It was observed that the minimum emission rate was in the cold winter of January 3.04 mg $m^{-2}hr^{-1}$. At that time the heap temperature was also minimum of 13.3 °C. The atmospheric concentration was 2.3 ppmV. During winter though the supply of wastes to the landfills were higher but the lack of moisture in the atmosphere as well as rainfall, it dried up quickly. In fact lack of moisture might be the key factor of low emission. This was also supported from the low emission rates in the strong summer months of May-June. In this period though the temperature was high the wastes dried up before sufficient rottening. Comparatively higher emission rates in the summer months might be due to high temperature and availability of moisture from the occasional thunder-storm. Highest emission rates were observed during August-September. During the year 1993

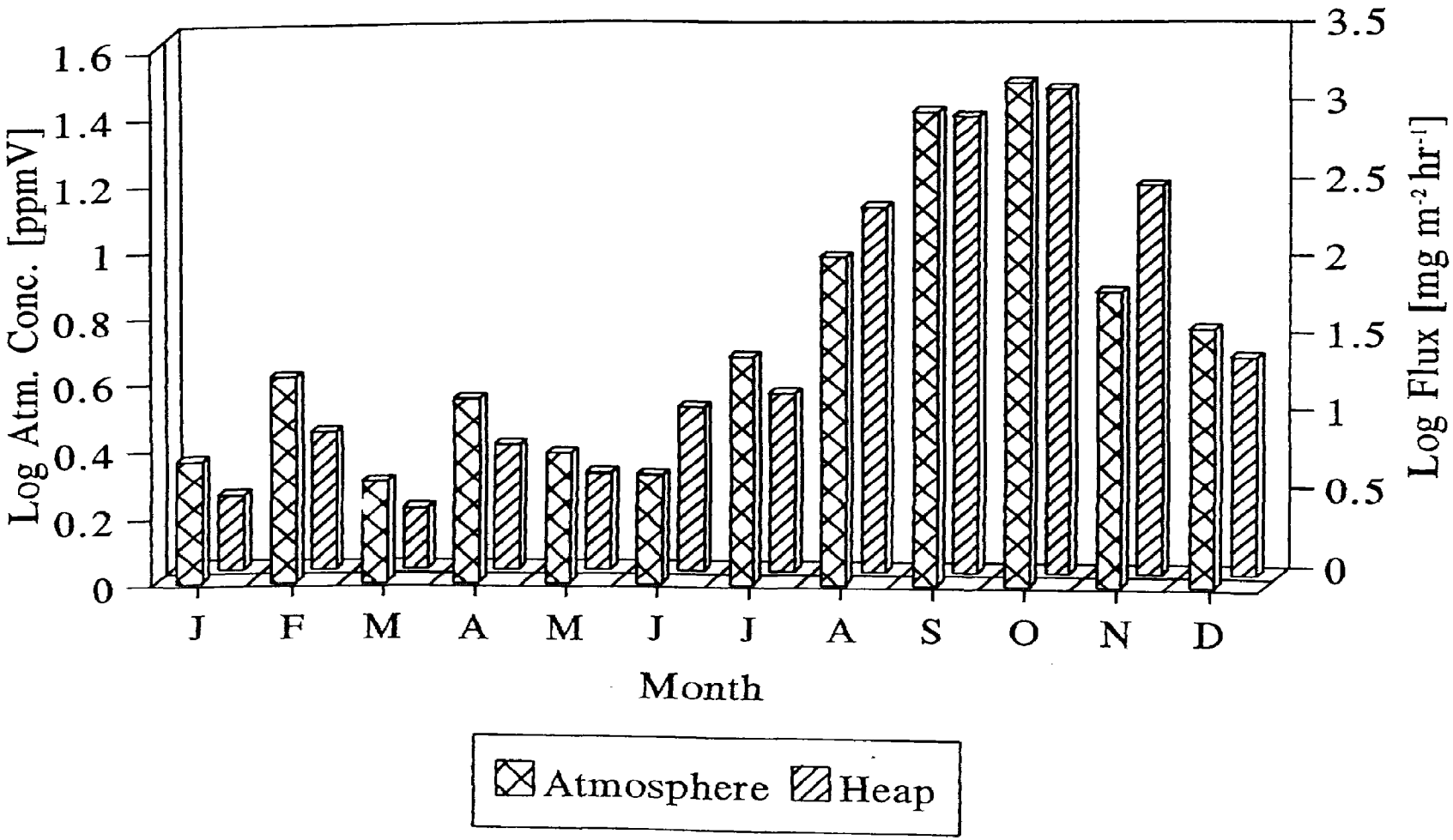
maximum rainfall was in these months. The area was engulfed with strong foul rancid odour. The wastes heaps soaked water and showed spongy appearance. The odour was a real nuisance on that entire locality. The emission rate was maximum in October when sunshine hour was increased which increased the temperature inside the heap. The emission rate was altime maximum of 1347.29 mg $m^{-2}hr^{-1}$. The average emission rate was 238.69 mg $m^{-2}hr^{-1}$. From this the yearly emission could be estimated as 2.09 kg m^{-2} (table 22 and Fig. 17).

Emission from this type of natural ecosystem is a complex phenomenon. It depends on moisture, temperature and recharge of the waste heaps by fresh addition of wastes. No relationship could be drawn between heap temperature and emission rates. No published research data were available so far which was comparable to this eco-system. In a study Bogner and Spokas (1993) showed a very high rate of 400 kg $m^{-2}yr^{-1}$ from a semiarid unvegetated site which was much higher than our observation. More prolonged study is needed in this aspect.

Table 22. Methane emissions from landfill areas of fruits and vegetable wastes.

Month	Atm. Concn. (ppmV)	Heap Temp. (°C)	Flux ($mg/m^2/hr$)
JAN	2.3	13.3	3.04
FEB	4.1	19.0	7.71
MAR	2.0	24.1	2.47
APR	3.5	27.6	6.35
MAY	2.4	29.7	4.15
JUN	2.1	32.5	11.30
JUL	4.7	34.2	13.76
AUG	9.3	30.0	227.71
SEP	25.1	29.4	890.56
OCT	30.7	32.3	1347.29
NOV	7.4	27.1	325.13
DEC	5.7	23.0	24.75

Fig. 17. Methane emissions from landfills of fruits and vegetables market wastes, 1993



10. Waste disposal from Azadpur market

11. Gas samples collection from landfill

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

After the Rio Summit global warming and greenhouse gases are of major concern. Measures are taken to know the sink and sources and possible mitigation strategies for these threatening gases. Methane is an important greenhouse gas emitting out from the rice cultivation in Agriculture and different natural ecosystems associated to our everyday life. Though concentration of methane in atmosphere is only 1.63 $\pm$0.12 ppmV but it is increasing in an alarming rate of 1.3 % each year. Each molecule of methane is 20 times effective in greenhouse effect over each molecule of carbon dioxide which mainly comes from the industrial sector. Methane contributes 15 % to global warming and it absorbs outgoing thermal infrared radiation in the *window* region. Methane has also direct role in ozone chemistry which causes depletion of ozone which acts as the protective cover against the unwanted ultra-violet radiation from the Sun. Global warming will bring sea-change in the earth's atmosphere and environment which will be perilous to the human civilization. Now-a-days every nation is feeling the urgency to escape out from that *dooms day* which is purely man-made. In the developed countries intensive research and extension work is in progress but unfortunately developing countries like India and other under-developed countries are lagging behind. So, we cannot neglect our duties to

contribute some effort to the understanding of the nature which will pay at least one drop of water in the sea- efforts of all the working mankind to save our planet's atmosphere for the future generations.

Keeping in mind that rice cultivation is one of the major sources in methane emission, investigation was carried out to estimate the rate of emissions and associated physical parameters. Natural wetlands are another major source of methane emissions. Being in the most polluted city Delhi, we are attracted to study the one of the major open drains - Najafgarh drain. Studies were also conducted to estimate methane emissions from the lagoons of the distillery effluents, mostly in the sugarcane producing area of U.P., which were potential sources of methane emissions. Emissions from the compost pits of dairy wastes, landfills of fruits and vegetable wastes, exposed areas of biogas plants were also investigated. The salient results obtained from these investigations are presented below:

1) **Rice cultivation**

i) In the rice cultivation in *Kharif* season of the year 1993 with the variety PUSA-169 three distinctive peaks in the methane emission were observed at 15, 46, and 69 DAT.

ii) In all the treatments highest peak was in 69 DAT.

iii) The first peak at 15 DAT was somewhat uncommon.

iv) The steepest drop of Eh to the minimum within two weeks of submergence.

v) There is no appreciable change in soil temperature with fluctuations in ambient temperature.

vi) In general methane emission increases with decrease in Eh.

vii) Role of pH to emission was inconclusive.

viii) FYM+Urea treated plot showed the maximum emission rate of 4.86 mg m^2 hr^{-1} with a total of 49.44 kg ha^{-1} for this season. This total emission was 4.2 times higher than the control (11.76 kg ha^{-1}), 2.3 times higher than the BSS+Urea treated plot (22.08 kg ha^{-1}) and 2.4 times higher than the only Urea treated plot (20.88 kg ha^{-1}).

ix) Yield in the control, only urea, BSS+Urea and FYM+Urea plots were 1.94, 3.34, 2.94 and 2.85 t ha^{-1} respectively.

x) So, in the consideration of yield and methane emission BSS+Urea was much more acceptable over FYM+Urea.

xi) The minimum Eh value was -320 mV.

xii) Ph values ranged between 7.5 and 8.5.

2) Najafgarh Drain

i) The entire area was observed typical odour round the year.

ii) The water was blackish with heavy sludge deposition.

iii) Maximum emission was in the summer month of June, 720.83 mg/m^2/hr when the maximum water temperature was 33.5 °C.

iv) Highest atmospheric concentration above the water surface (5 cm) was 32.6 ppmV in June.

v) The lowest atmospheric concentration was in January 2.6 ppmV and the emission rate was the lowest of 9.88 mg/m^2/hr. The lowest drain temperature was also in this month, 13.7 °C.

vi) During rainy season there was a decrease in emission rates which increased again in the month of October.

vii) The average annual emission rate was 339.21 mg/m^2/ha.

viii) pH ranged from 7.10 to 7.26.

ix) EC ranged from 0.92 to 1.41 dS/m.

x) Eh varied from -139 to -230 mV.

xi) Relationship with emission rate and EC, Eh and pH were inconclusive.

xii) In general emission rate increased with temperature.

xiii) The straight line best-fit equation for atmospheric concentration vs. drain water temperature was: Y (atmospheric concentration, ppmV) = -20.90 + 1.60X (drainwater temperature, °C).

xiv) The straight line best-fit equation for flux vs. drain water temperature was Y (flux, mg/m^2/hr)

= -509.19 + 36.04X (drain water temperature, °C).

xv) The rough estimate of yearly emission from the drain was 5350 tonnes.

3) Distillery effluents

i) Pre-methanation effluents has higher BOD and higher emission rates.

ii) pH of pre-methanation effluent is in acidic range (4.3-4.6). So, there should be specific strains of methanogens which work in acidic range.

iii) Eh values do not fall much (-21 to 45 mV) as compared to drain eco-system.

iv) Maximum emission rate was 2705.15 $mg/m^2/hr$ with a BOD of 38000 mg/l from the pre-methanation lagoon when the temperature of effluent was 47.9 °C.

v) Maximum emission from a final lagoon was 446.25 $mg/m^2/hr$ with a BOD of 3225 mg/l and effluent temperature of 46 °C.

vi) Minimum emission rate from the pre-methanation effluent was 77.86 $mg/m^2/hr$ with a BOD of 33000 mg/l and temperature of 30 °C.

vii) Minimum emission rate from the final lagoon was 52.25 $mg/m^2/hr$ with a BOD of 10000 mg/l and temperature of 23 °C.

viii) Emission is influenced by the diurnal variation and the weather conditions.

ix) pH of final effluent was in alkaline range (8.1 to 8.2).

x) The approximate average emission rates from pre-methanation, post-methanation and final effluents were 750,250 and 170 mg/m^2/hr.

xi) Approximate total emission rate from Indian distilleries was 6900 t/yr.

4) Exposed areas of Biogas plants

i) Generally emission is higher in higher temperature. In the summer months, the emission rates were higher.

ii) Minimum Eh was observed as -115 mV.

iii) PH range was 6.75 to 7.41.

iv) From Deenbandhu plant maximum emission was 1314.39 mg m^{-2} hr^{-1} and the minimum emission was 713 mg m^{-2} hr^{-1}.

v) From the Janta plant the maximum and minimum emission rates were 1289.71 and 810.38 mg m^{-2} hr^{-1} respectively.

vi) From the KVIC plant, the maximum and minimum emission rates were 1406.43 and 923.91 mg m^{-2} hr^{-1} respectively.

vii) The average emission rates from the Deenbandhu, Janta and KVIC plants were 1.05, 1.05 and 1.10 g/m^2/hr respectively.

viii) The straight-line best fit equations relating temperature (X, °C) and emission rates (Y, mg/m^2/hr) for Deenbandhu, Janta and KVIC plants were Y = 304.36 + 24.95X, Y = 415.12 + 21.42X and Y = 468.31 +

21.81X respectively.

5) **Emission from Compost pits**

i) Emission rates were widely irregular.

ii) Apparently emission rate was higher at higher temperature. The maximum and minimum emission rates were 375.43 and 3.26 $mg/m^2/hr$.

iii) Pit microenvironment specially moisture status might be the important controlling factor of the emission rates.

6) **Landfills of vegetable market wastes**

i) Due to rapid drying, the emission rates throughout the year in general was low.

ii) In general emission rates were high in the rainy season due to high moisture content.

iii) The maximum emission rate was 1347.29 $mg/m^2/hr$ and the minimum was 2.47 $mg/m^2/hr$.

From the overall preview of the results, it can be concluded that methane emission from various sources is an important phenomenon in our natural eco-system. Till now very little has been done in quantifying the amount of emission from these sources in our country. To work out the possible mitigation strategies, these types of study may be of great help in future.

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