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# **The Changing Role of Non-CO<sub>2</sub> Greenhouse Gases**

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## **Abstract**

During the last century, the concentrations of several greenhouse gases have increased considerably - most notably carbon dioxide, methane and nitrous oxide. In addition, new, entirely man-made gases have been put into the atmosphere that also cause the greenhouse effect; these include the chlorofluorocarbons. Calculations have shown that during the last century the non-CO<sub>2</sub> greenhouse gases could together be almost as effective as the increase of carbon dioxide in causing global warming. These and similar gases were therefore included in the Kyoto Protocol to develop a comprehensive plan for controlling potentially unfavorable climatic change. Studies show however that the other gases, with few exceptions, are likely to play a smaller than expected role in future global warming. The most significant non-CO<sub>2</sub> man-made greenhouse gases are methane and nitrous oxide. Methane rose from 700 ppbv some 200 years ago to about 1750 ppbv in recent times, while nitrous oxide rose from about 285 ppbv to 318 ppbv over the same time. These trends made methane the most important gas for global warming after carbon dioxide. But now, the rate of increase of methane has slowed down considerably. Budget analyses suggest that we may not see major changes of concentrations in the future comparable to the trends of the last century. Thus the role of methane in future global warming may be less than expected earlier. Nitrous oxide on the other hand, has increased slowly but steadily during recent decades. It is likely to become more important in the future compared with methane. While other greenhouse gases such as the perfluorocarbons, sulfur hexafluoride and hydrochlorofluorocarbons are included in the Kyoto Protocol, these are present in such minute concentrations that it is unlikely that they will have an important role in future global warming.

## 1. Introduction

In recent years it has become increasingly evident that human activities are increasing the concentrations of many trace atmospheric constituents, particularly the greenhouse gases that can warm the earth. Of these, carbon dioxide is the best known and is likely to be the most significant cause of future global warming. The non-CO<sub>2</sub> greenhouse gases individually have little potential for causing tangible global warming but there are so many that collectively they can rival the effects of carbon dioxide. This paper is about the present importance of the non-CO<sub>2</sub> greenhouse gases and the potential of these gases to cause global warming.

The global warming potential (GWP) is an index that is widely used to identify non-CO<sub>2</sub> greenhouse gases and to use these gases in creating a comprehensive environmental policy for controlling global warming.

$$\text{GWP} = \frac{\int_0^{\text{TH}} a \exp(-t/\tau) dt}{\int_0^{\text{TH}} a(\text{CO}_2) F(t) dt} \quad (1)$$

The GWP is the ratio of the integrated radiative forcing of a kilogram of a gas to the same for carbon dioxide.  $F(t)$  denotes the function describing the loss of a unit mass of CO<sub>2</sub> from the atmosphere, which for rough calculations can be taken as an exponential decay with a lifetime of 100 y similar to the expression in the numerator. The values of the radiative forcing “ $a$ ” change in time also, but for simplicity are usually assumed constant in most calculations. The length of integration is the time horizon (TH) that is often taken as 20 y, 50 y, 100 y or infinity. Under the special circumstances when  $\text{TH} = \infty$  and the assumption that  $F(t) = \exp(-t/\tau(\text{CO}_2))$ ,  $\text{GWP} = (a\tau) / [a(\text{CO}_2) \tau(\text{CO}_2)]$  which is just the ratio of the radiative forcings per kg multiplied by the ratio of the lifetimes. As such the GWP is seen to be a measure of the relative importance to global warming of a kilogram of a gas to a kilogram of CO<sub>2</sub>, or alternatively, one kilogram of the gas is “equivalent” to GWP kilograms of CO<sub>2</sub>. If the GWP is very high, the gas is seen to have a great potential for global warming. Gases with high GWPs are selected for inclusion in environmental management strategies such as the Kyoto Protocol. In general the non-CO<sub>2</sub> greenhouse gases have both a higher radiative forcing per kilogram of the gas put into the atmosphere and a longer lifetime than CO<sub>2</sub>, thus the combination leads to large values for the GWP. The GWPs and other data on the non-CO<sub>2</sub> greenhouse gases are summarized in Table 1 (IPCC, 2001 and references therein). Radiative forcing is commonly used as a measure of the effectiveness of the greenhouse gas because it is more definite than the actual temperature change at the earth’s surface caused by the addition of a gas to the atmosphere. The actual change of surface temperature due to an addition of a gas is complicated by myriad feedbacks, interactions and time delays.

Based on this background, the role of the non-CO<sub>2</sub> greenhouse gases is discussed in detail in the next section. The outcome of these investigations will define the importance of methane and nitrous oxide in the global warming issue and the potentially small role of the other gases included in the Kyoto Protocol.

Table 1: Radiative Forcing and Global Warming Potentials of Greenhouse Gases

	1998	1750	100 y GWPs	Lifetime (y)	Radiative Efficiency W/m <sup>2</sup> /ppbv
CO <sub>2</sub> (ppmv)	367	280	1	100	0.000015
CH <sub>4</sub> (ppbv)	1745	700	23	8.4	0.000370
N <sub>2</sub> O (ppbv)	314	270	300	120	0.003100
SF <sub>6</sub> (pptv)	4.2	0	22000	3200	0.52
Major PFCs (pptv)					
CF <sub>4</sub>	75	40	5700	50000	0.08
C <sub>2</sub> F <sub>6</sub>	2.9	0	11900	10000	0.26
C <sub>3</sub> F <sub>8</sub>	0.2	0	8600	2600	0.26
Major HFCs (pptv)					
CHF <sub>3</sub> (HFC-23)	24	0	12000	260	0.16
CF <sub>3</sub> CH <sub>2</sub> F (HFC-134a)	7.5	0	1300	13.8	0.15
CH <sub>3</sub> CHF <sub>2</sub> (HFC-152a)	0.5	0	120	1.4	0.09
Compiled Data from IPCC (2001) for gases included in the Kyoto Protocol. The mixing ratios are given as ppxv where x = b for parts per billion, m is for million and t is for trillion. The GWPs have been rounded. The radiative efficiency is denoted as “a” in the text but is discussed in units of W/m <sup>2</sup> /kg of gas.					

## 2. The Non-CO<sub>2</sub> Greenhouse Gases

Although the GWP is an index of the importance of a greenhouse gas as shown in Table 1, there are other factors that determine whether a gas can be significant in controlling or affecting global warming. The most important of these is the existing concentration in the atmosphere and the actual potential for future accumulations. One way to look at this issue is to consider the additional radiative forcing ( $\Delta RF$ ) that a gas is causing at the present due to human activities. This can be readily calculated from Table 1 as follows:

$$\Delta RF \text{ (W/m}^2\text{)} = a \text{ (W/m}^2\text{-ppbv)} \Delta C \text{ (ppbv)} \quad (2)$$

Here  $\Delta C$  (ppbv) is the change in the mixing ratio of a gas between now and the pre-industrial times, which we assume is due to human activities. This assumption is particularly accurate for

the PFCs, HFCs and CFCs, most of which, with the exception of  $\text{CF}_4$ , are entirely man-made. The results of these calculation are shown in Figs. 1 and 2.

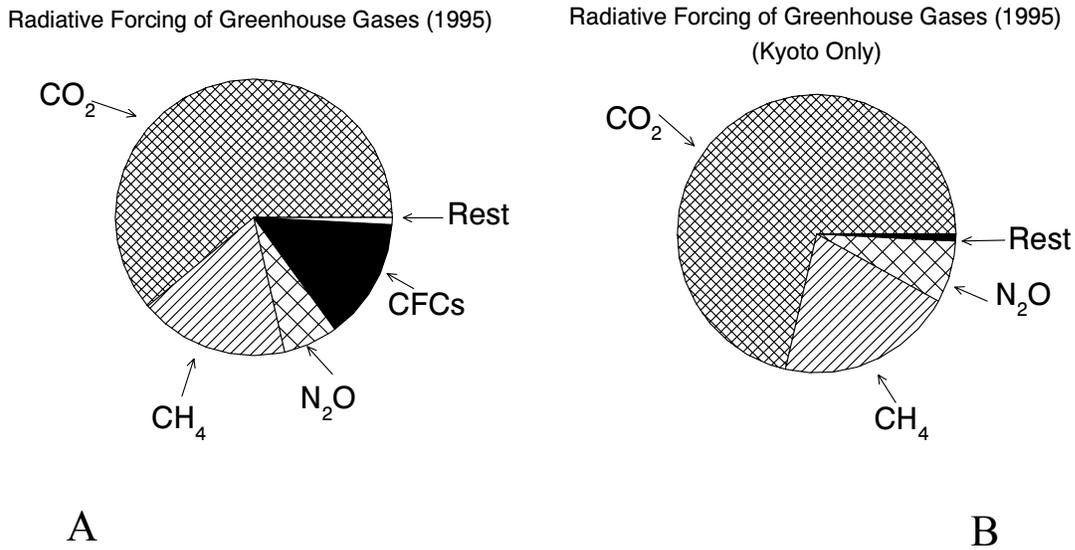


Figure 1. (A) The present radiative forcing due to increases of greenhouse gases over the last 200 years. The increases of the gases are assumed to be from human activities. (B) The same calculations excluding the effect of the chlorofluorocarbons (see text for details).

## GWP and Present Radiative Forcing

TH = 100 y

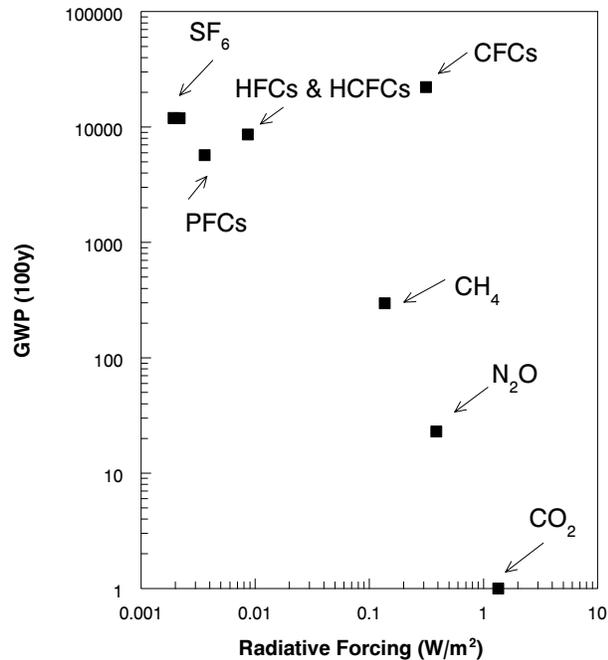


Figure 2. The present radiative forcing of a gas (Fig 1) as a function of the Global Warming Potential (GWP). Generally the gases that have the highest GWP are “industrial” and entirely man-made compounds and hence not emitted in very large quantities. Gases such as CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> are natural compounds increased by major sectors of human industrial and agricultural activities. These have smaller GWPs but have increased the most and hence dominate the present increased radiative forcing.

There are essentially two conclusions that can be drawn from these figures. The first is that collectively non-CO<sub>2</sub> greenhouse gases have been significant in the present increase of radiative forcing due to human activities. According to these calculations, CO<sub>2</sub> contributes about 60% to the additional radiative forcing since pre-industrial times, and the non-CO<sub>2</sub> gases currently contribute the rest or 40%. If the CFCs are taken out of the calculations, then CO<sub>2</sub> contributes about 70% and the other gases contribute 30% which is almost entirely due to methane and nitrous oxide, since the remaining gases in Table 1 contribute about 0.5%. If we assume that the change of global temperature over the last 50-100 years is due to the increase of these gases, then the proportions estimated above also approximately represent the contributions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O and the remaining gases in Table 1.

There are two reasons why the CFCs may be excluded from the present discussion. The first is that by depleting the ozone layer, the CFCs cause a feedback that cools the surface (Ramaswamy et al., 1992). The combined effect is smaller than the direct effect alone. The question of indirect effects or feedbacks, both positive and negative, is applicable to the other gases also, but the mechanisms are not as well understood as for the CFCs. The other reason for excluding the CFCs is that these gases are already banned from production under the Montreal Protocol and its Amendments. Hence, from a policy perspective, the CFCs no longer provide an opportunity to limit future global warming. Some may argue that the CFCs can be recovered from reservoirs and hence may still be of benefit in reducing future global warming. This may be so, but other factors such as cost and the limited amounts present may outweigh the global warming potentials of these gases.

The second conclusion from these figures is that the GWP is in itself not a complete indicator of how significant a gas may be in global warming. Gases that are presently causing the most man-made radiative forcing have the lowest GWPs starting with CO<sub>2</sub> which has a GWP = 1 and working up to the more exotic gases such as the PFCs which have GWPs = 6,000 to 12,000. This conclusion should not be interpreted to mean that these gases will forever remain as unimportant as they are now. It is questionable however, whether controlling them now, or trading them for CO<sub>2</sub> equivalents is a good idea. Because of their long lifetimes, trading them now based on the CO<sub>2</sub> GWP equivalent is the same as trading a large radiative forcing over a short time for a small forcing over a long time. In general, this trade is undesirable for managing the environment and climate.

It is also noteworthy that we do not expect that the non-CO<sub>2</sub> greenhouse gases other than methane and nitrous oxide will ever be emitted in very large quantities. This perspective is based on the nature of the human activities that produce these gases and how they are used. Most are manufactured for specific applications using small amounts and as such, despite increasing demands for consumer goods, will not be needed in large amounts. Moreover in some cases the gases can be recovered, as for instance the PFCs used in electronics manufacturing. This is in contrast to CO<sub>2</sub> which is a by-product of energy use, or CH<sub>4</sub> and N<sub>2</sub>O that are by-products mostly of agricultural activities. Both energy use and food production are major human activities.

Based on the developments in this section, methane and nitrous oxide emerge as the most important non-CO<sub>2</sub> greenhouse gases of the present and possibly for the future. In the next section the state of the knowledge of these gases is discussed.

### **3. Methane and Nitrous Oxide**

We look first at the changes in the concentrations of methane and nitrous oxide during the last two decades over which detailed global measurements have been taken. These data are from our flask sampling network and supplemented by new data from the NOAA/CMDL program (CMDL,

2001, Khalil et al. 2002). Although the samples were collected at various locations distributed over the polar, middle and tropical latitudes of both hemisphere, we show only the global average mixing ratios as these are most relevant to the present discussion. Before the start of these measurements, there are various data both from direct measurements in the atmosphere and from old air bubbles preserved in polar ice. These data are not discussed in detail here, but are used to establish the pre-industrial concentrations (see Table 1).

### 3.1 Methane

The methane concentration data are shown in Fig 3 and the trend is shown in Fig 4.

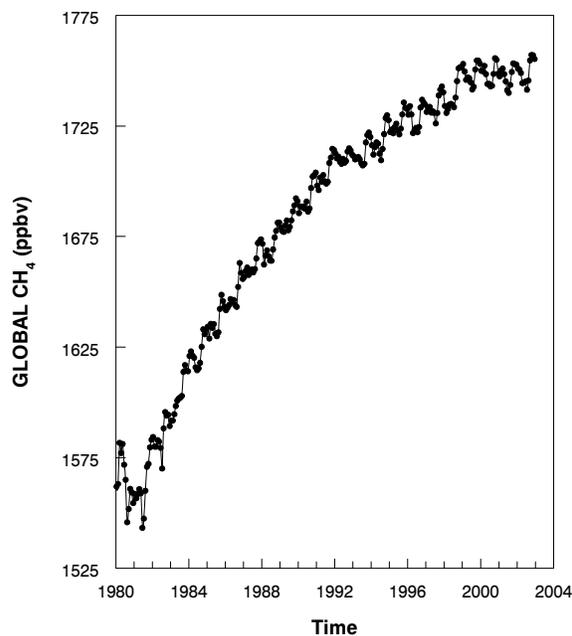


Figure 3. Concentrations of methane in ppbv taken as global and monthly averages. These data are from sites distributed over the globe and include high, middle and tropical latitudes of both hemisphere. The global average is latitudinally weighted. The original data set generally has triplicate measurements once a week.

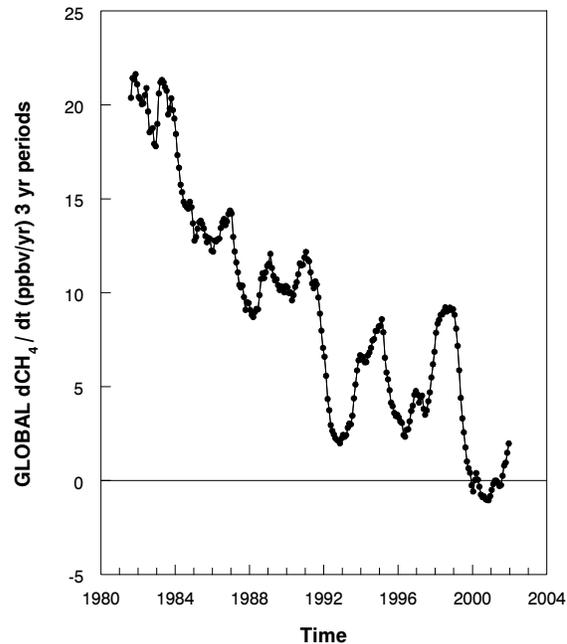


Figure 4. The trend of methane  $dC/dt$  in ppbv/yr taken from the data shown in Fig. 3. The rate of increase represented by this figure has continuously declined since intensive measurements began and has on occasion dipped below zero. These calculations are over 3-year overlapping periods of time. For example, the first point is the rate of change over months 1 to 36, the next is over months 2 to 37 and so on.

Inspection of the figures suggests the following conclusions. First, there has been significant increase of methane in the atmosphere. The average rate of increase between 1981 and 2002 is 8.9 ppbv/yr, but as both figures show, there has been a significant decrease of the trend which was approximately 20 ppbv/yr in the early 1980s and is presently only 1-5 ppbv/yr and has even dipped below zero in some years. Second, it is apparent that the trend has continually headed downwards since detailed measurements began, indicating that the decreasing trends are not a recent phenomenon. As we will soon see, this has important implications for the trends of anthropogenic emissions.

The changes of methane, or any other gas for that matter, can be described by a mass balance equation:

$$dC/dt = S - C / \tau \quad (3)$$

$$S_{\text{NATURAL}} = C_0 / \tau \quad (4)$$

$$S_{\text{ANTHROPOGENIC}} = S - C_0 / \tau \quad (5)$$

Here S is for sources (g/y), C is the burden (g), and  $\tau$  is the lifetime (y) due to the combined effect of all first order chemical reactions or physical processes. The observed trends (Fig 4) or the concentrations (Fig 3) can be caused by the change of emissions (S), the lifetime ( $\tau$ ), or both. Ordinarily this can greatly complicate the evaluation of why the concentrations are changing, but for the case of methane during the last 20 years or so, independent evidence suggests that the lifetime is not changing. This simplifies the understanding of the global methane budget and the trends. We can calculate the total anthropogenic emissions from Eqn. 5 by noting that  $\tau$  is constant (at about 8 y), taking  $C_0$  from the ice core data (Table 1) and calculating S from Eqn. (3).

Before going to the results of the calculation of the anthropogenic sources, a brief discussion of the lifetime and its constancy over the last two decades is warranted. The global lifetime of methane is dominated by its reactions with tropospheric hydroxyl radicals (OH or HO). Small amounts, perhaps some 10% - 20% are removed by soils and stratospheric OH. If tropospheric OH concentrations change in time, then some of the changes in the methane concentration can be driven by this sink process. One way to address whether the OH concentrations have changed is to consider the budget of methyl chloroform (Krol et al., 1998; Prinn et al., 2001). Methyl chloroform is an industrial degreasing solvent, currently banned from production under the Montreal Protocol. It is also destroyed mostly by reacting with OH radicals. Hence Eqn. 3 can be applied to it noting that  $1/\tau \approx K [\text{OH}]$  where K is the reaction rate constant determined in the laboratory. Knowing the emissions (S) of methylchloroform from industry records and the concentrations from atmospheric measurements (C and dC/dt) we can calculate the concentrations of [OH] for each year over which we have methyl chloroform measurements. Such measurements span about the same length of time as the measurements of methane and nitrous oxide (and from the same sites). The results of such a calculation are shown in Fig. 5 based on our transport-chemistry model (Butenhoff, 2002) which is more complex than Eqn. 5 but based on the same principles. It is apparent that there have not been any major changes in the OH concentrations. If anything, there are indications of a small downward trend in the recent decade which according to Eqn 3 (applied to methane) would require that the sources must be decreasing slightly relative to a calculation in which OH is assumed to be constant.

Using the result that the lifetime of methane has not changed over the last two decades we can calculate the anthropogenic emissions based on Eqn. 5. The results are shown in Fig. 6.

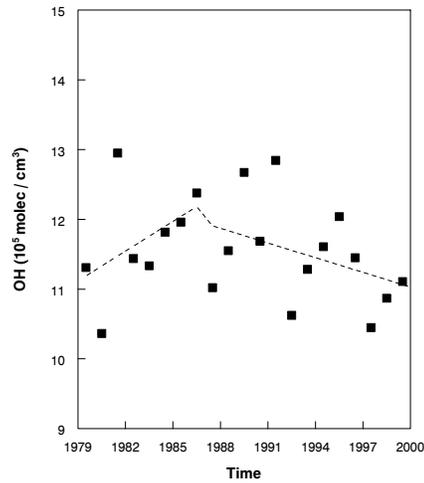


Figure 5. Time series of calculated globally and annually averaged concentrations of OH radicals in molecules per cubic centimeter. These calculations are based on the budget of the industrial solvent methyl chloroform (see text for details).

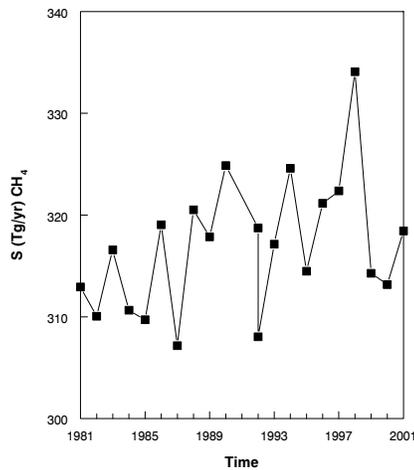


Figure 6. Estimated emissions of methane in Tg/yr from all human activities. The calculation is based on the assumption that the natural sources are constant. Some of the inter-annual variations may not be due to human activities but rather due to natural processes which may not be constant from year to year. The trends of these emissions however are likely to be well represented by these calculations since it is unlikely that the natural emissions have systematically increased or decreased over the time for these calculations.

Inspection of Fig.6 suggests that the total anthropogenic methane emissions have not changed much over the last two decades, with the difference between maximum and minimum values being only  $\pm 1\%$  of the mean. There is a suggestion of a slight increasing trend in the emissions but this is not likely to be of practical significance. In addition we see some ups and downs from year to year. These may be due to inter-annual changes in either natural or anthropogenic sources. We have assumed here that the natural sources do not change from year to year since the anthropogenic source is calculated as a residual between the total source required by the mass balance (Eqn.3) and the presumed constant natural source. What is important in the present calculation of the anthropogenic source is the trend in emissions. As long as the assumption that the natural sources do not have long-term trends is valid, the result that anthropogenic sources have been relatively constant during the last two decades would also be valid.

Although the total and even the anthropogenic sources are constrained by the measured time series of concentrations, the exact causes of the nearly stable emissions of methane over the last two decades are presently only qualitatively explained. The major sources of methane and nitrous oxide are shown in Table 2. It is evident that agricultural activities such as rice agriculture and cattle are important anthropogenic sources of methane. Present research suggests that both these sources may be declining because of much slower increases in the number of cattle and hectares of rice harvested as well as declining emission factors. The global rice and cattle data are shown in Fig. 7. The stabilization of the agricultural sources, or indeed a reduction in these sources may be partially offset by some of the energy based sources leading to a near stable anthropogenic source over the last two decades. Once again this conclusion is based on the assumption that natural sources have not systematically increased or decreased during this time.

Table 2: The sources of methane and nitrous oxide

CH <sub>4</sub> - Methane			N <sub>2</sub> O - Nitrous Oxide		
Sources	Emissions (Tg/year)		Sources	Emissions (Tg/year)	
	Natural	Man-made		Natural	Man-made
Wetlands	110				
Termites	20		Soils	12	
Ocean	4		Oceans	3	
Geological	10				
Fires	2				
Rice Agriculture		65	Biomass Burning		1.6
Ruminant Animals		79	Nylon Manufacturing		0.7
Manure		15	N-Fertilizer		1.0
Landfills		22	Sewage		1.5
Waste Water Treatment		25	Manure		0.5
Biomass Burning		50	Aquifers-Irrigation		0.8
Coal Mining		46	Automobiles		0.8
Natural Gas Leakage		30	Land Use Change		0.7
Low Temperature Fuels		17	Atmospheric Formation		?
Other		13	Global Warming		0.3
Totals	150	360	Totals	15	8
Total All Sources		510	Total All Sources		23

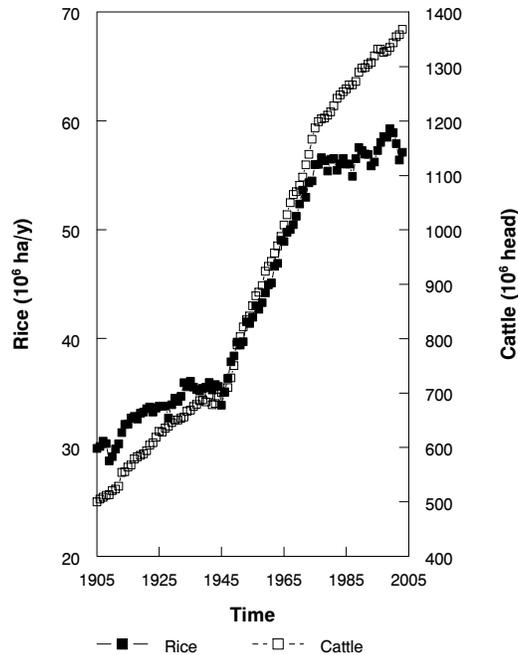


Figure 7. Global population of domestic cattle and hectares of rice harvested. These are proportional to the emissions from rice and cattle, however the emission factors that describe the average amount of methane emitted per hectare of rice or per head of cattle is not constant. Therefore these data cannot be directly translated into methane emissions.

### 3.2 Nitrous Oxide

We can consider the nitrous oxide budget in a manner similar to the discussion of methane in the last section. Fig 8 shows the globally averaged concentrations from the same locations as the methane data. Unlike the case of methane, there is no decrease in the trend of  $N_2O$ . The source de-convolution in Fig 9 also shows an increasing emission from human activities, assuming again that the natural sources have not systematically increased or decreased. This latter assumption seems reasonable based on Table 2 that shows the major sources of  $N_2O$ . The trend of the anthropogenic source parallels the increasing use of nitrogen based fertilizers for agriculture, and may therefore be the primary explanation for the trend of anthropogenic sources shown in Fig. 9

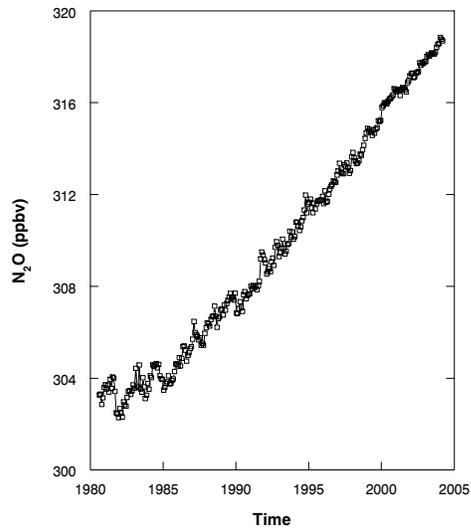


Figure 8. The global average concentration of nitrous oxide.

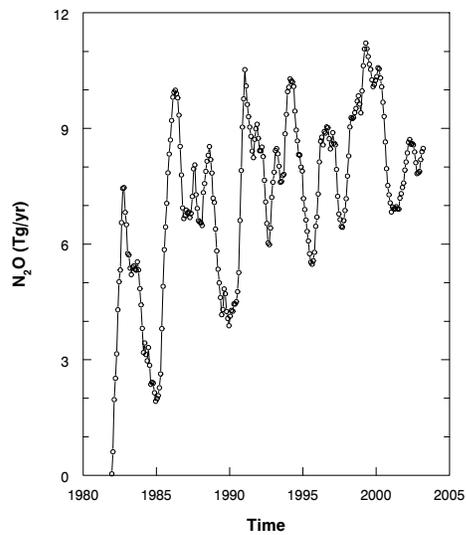


Figure 9. The time series of estimated emissions of nitrous oxide from human activities calculated in the same manner as for methane shown in Fig. 6. It is assumed that natural sources have not changed, and especially that there are no systematic increases or decreases in natural emissions during this period.

### *3.3 The Increasing Role of Nitrous Oxide*

We have seen so far that methane and nitrous oxide are the most significant non-CO<sub>2</sub> greenhouse gases at present and likely to remain so in the future. It is also apparent that methane has increased much more during the last century compared with nitrous oxide, which gives it a greater excess radiative forcing at present than N<sub>2</sub>O. But we have also seen that methane trends are decreasing rapidly, while N<sub>2</sub>O continues to increase unabated. We can construct a measure of the relative importance of the two gases by looking at the year by year changes in the ratio of the excess radiative forcing due to the two gases:

$$R = \Delta \text{RF} (\text{N}_2\text{O}) / \Delta \text{RF} (\text{CH}_4)$$

Where  $\Delta \text{RF}$  is the radiative forcing caused by human activities as defined in Eqn. 2 earlier, except that now it is time dependent over the years when we have measurements of both methane and nitrous oxide. The results of this calculation are shown in Fig 10 below. We can see that the importance of N<sub>2</sub>O has risen from a low of about 30% as effective as CH<sub>4</sub> to nearly 40% in 20 years. This trend of increasing importance of N<sub>2</sub>O is likely to continue based on all the qualitative indicators including past trends and the nature of the sources of the two gases. To some extent it shows that the potential of methane to increase is reaching natural limits but for nitrous oxide such limits may be far off since it is a more recent emission from human activities.

The result in Fig. 10 is partly due to the inter-relationship between methane and nitrous oxide emissions from agriculture, and particularly rice agriculture. Agricultural practices using less organic fertilizers and more nitrogenous fertilizers in China and with reduced flooding during the growing cycle of rice would simultaneously decrease methane emissions while increasing nitrous oxide emissions.

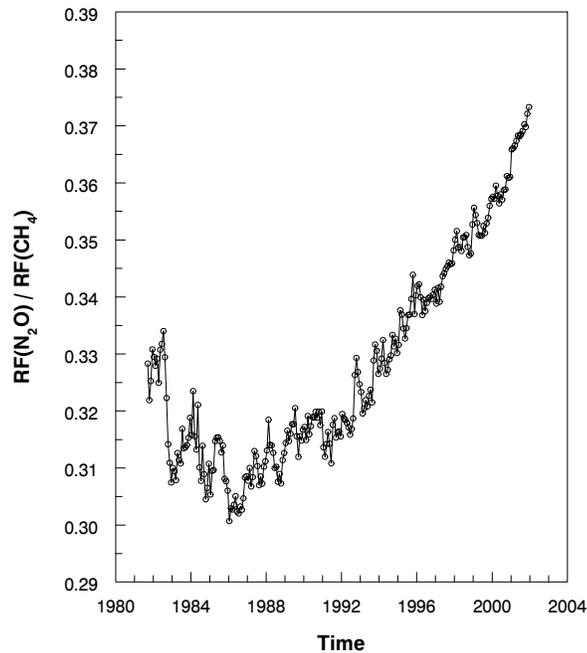


Figure 10. The changes in the radiative forcing from anthropogenic nitrous oxide relative to that for methane. In recent years the importance of nitrous oxide is rising rapidly relative to methane. This trend is expected to continue since there is remaining potential for continued increases of nitrous oxide that is greater than the potential for methane.

#### 4. Conclusions

We have seen that the Global Warming Potential (GWP) is not an indicator of the actual importance of a gas in causing global warming either at present or in the future. The index was not intended to do that, but rather to screen for gases that may be useful for controlling future global warming. Yet the mere existence of large GWP values has sometimes been taken as a measure of the importance of a gas in global warming. This is not the case. The amount that may be or is emitted into the atmosphere is also significant.

Among the many non-CO<sub>2</sub> greenhouse gases, methane and nitrous oxide stand out as the most important both at present and probably into the future. The rate of increase of methane has slowed down significantly in the last decade; and it has been slowing down since the inception of

global measurements some 20 years ago. These changes are caused by various complex social and economic factors which have not yet been fully quantified, but are the focus of current research. At the same time, nitrous oxide trends have been driven steadily, likely by increasing nitrogen fertilizer use. The importance of N<sub>2</sub>O in present radiative forcing, relative to methane, is rising rapidly since the role of methane is more or less steady. This tendency may accelerate if methane trends continue to fall. Although it has been accepted for some time now that CO<sub>2</sub> will remain the main cause of future global warming, it is apparent that the main non-CO<sub>2</sub> greenhouse gas of the future is likely to be nitrous oxide with diminishing contributions from methane.

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