

Variations of Carbon Dioxide and Methane in the Atmosphere and their Global Cycles

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ABSTRACT

Systematic measurements of the atmospheric CO₂ and CH₄ concentrations were initiated late in the 1950s and early in the 1980s, respectively, in association with global climate change due to human activities. These measurements have established that the atmospheric CO₂ and CH₄ concentrations show seasonal cycles with high values in cold seasons and low values in warm seasons, long-term increase and interannual variations with periods of a few or several years. In this article, our present knowledge of these temporal variations is described on the basis of the results from systematic CO₂ and CH₄ measurements made so far at various locations around the world. The causes of the variations are also discussed in terms of the results of measurements of CO₂ and CH₄ concentrations, O₂/N₂ ratios and $\delta^{13}\text{C}$ values in CO₂ and CH₄ in the atmosphere, as well as of analyses of these observation data with global carbon cycle models or photochemical models. In addition, our current understanding of the global cycles of CO₂ and CH₄ is discussed.

Key words : carbon dioxide, global cycle, greenhouse effect, human activity, methane

1. INTRODUCTION

Concentrations of atmospheric carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) have increased steadily for the last 200 years due to human activities such as energy production/consumption, deforestation and food production (Neftel *et al.*, 1985 ; Etheridge *et al.*, 1992, 1996 ; Nakazawa *et al.*, 1993a, b ; Machida, *et al.*, 1994, 1995). For example, the increase of the atmospheric CO₂ concentration by fossil fuel combustion and deforestation amounted to over 80 ppmv, and the current CH₄ concentrations are more than double pre-industrial levels of approximately 700 ppbv due to rice farming, ruminants, landfills, fossil fuel production and biomass burning. The atmospheric concentrations of chlorofluorocarbons (CFCs) have also increased as a result of the fact that people, especially in developed countries, have used them in great quantities for their convenience in an affluent life style (Elkins *et al.*, 1996). The increase of these trace gases will enhance the greenhouse effect of the Earth's atmosphere and bring about an additional warming of the surface-troposphere system, which is one of the greatest concerns in the world at the present time. To understand so-called "global warming", it is indispensable to elucidate the global cycles of greenhouse gases, as this is necessary for predicting future levels of their atmospheric concentrations as well as for limiting or reducing their emissions into the atmosphere. Therefore, substantial efforts have been devoted to establishing a worldwide close-knit network of stations for background monitoring of relevant gases and their isotopes, as well as to developing global carbon cycle models and photochemical models (Keeling *et al.*,

1989a ; Tans *et al.*, 1990 ; Fung *et al.*, 1991 ; Siegenthaler & Joos, 1992 ; Law & Pyle, 1993). However, there are still substantial uncertainties in our understanding of sources and sinks of the respective constituents.

In this article, temporal variations of atmospheric CO₂ and CH₄ concentrations and their causes will be discussed on the basis of the results from comprehensive studies made so far, including our own research programs. Current knowledge and understanding of the global cycles of CO₂ and CH₄ will also be discussed.

2. CARBON DIOXIDE

2.1 Concentration Variations of CO₂ in the Atmosphere

Systematic measurements of the atmospheric CO₂ concentration were initiated for the first time by C.D. Keeling at the South Pole in 1957 and on Mauna Loa, Hawaii, in 1958 (Keeling *et al.*, 1976a, b). The number of the monitoring stations has increased substantially for the last 40 years, and over 50 stations are currently operating around the world. To examine characteristic variations of the atmospheric CO₂ concentration, the results of our aircraft measurements in the troposphere over Japan are shown in Fig.1. It is evident from this figure that the CO₂ concentration varies seasonally, superimposed on the long-term increase. The CO₂ concentration also shows interannual variations with periods of a few or several years. The seasonal cycle of the atmospheric CO₂ concentration reaches a minimum in summer due to photosynthetic CO₂ fixation and a maximum in spring due to release of biospheric CO₂ through respiration of living plants and oxidation of soil organic matter. The role of the terrestrial biosphere in the seasonal cycle of atmo-

spheric CO₂ was discussed by Nakazawa *et al.* (1993c, 1997) in terms of $\delta^{13}\text{C}$ in CO₂. The seasonal CO₂ cycle is much more enhanced in the northern hemisphere than in the southern hemisphere (Nakazawa *et al.*, 1997), reflecting different masses of land biota between both hemispheres. CO₂ exchange between the atmosphere and the oceans is also partly responsible for the seasonal cycle of atmospheric CO₂, which is more effective in the southern hemisphere than in the northern hemisphere (Keeling *et al.*, 1989a).

It is well known that the interannual variations of atmospheric CO₂ concentration are closely related with the ENSO event in the tropical Pacific Ocean, and that the atmospheric CO₂ concentration increases and decreases when the ENSO event occurs and terminates, respectively, with a phase delay of a few or several months which is dependent on location. Therefore, it has been thought that the interannual CO₂ variations could be attributed to an imbalance of the CO₂ exchange between the atmosphere and the oceans. However, the release of CO₂ from the eastern tropical Pacific Ocean is expected to decrease in ENSO years, since upwelling of intermediate and deep ocean waters rich in CO₂ is much reduced when the ENSO event occurs. A detailed inspection of the atmospheric CO₂ concentration data also revealed that the interannual variations were sometime observed independent of the appearance of the ENSO event. Therefore, it was recently suggested that the interannual CO₂ variations are produced primarily by an imbalance of the CO₂ exchange between the atmo-

sphere and the terrestrial biosphere due to climate change in association with the ENSO event, volcanic eruptions and other factors (Keeling *et al.*, 1989b, 1995; Nakazawa *et al.*, 1993c, 1997; Keeling *et al.*, 1996). Keeling *et al.* (1995) also pointed out that terrestrial biospheric CO₂ is released into the atmosphere and the oceans absorb atmospheric CO₂ when the ENSO event occurs, the former being stronger than the latter in magnitude.

Figure 1 shows that the CO₂ concentration has increased at an average rate of about 1.5 ppmv/year in the troposphere over Japan for the last 18 years, and that yearly mean values of the CO₂ concentration were approximately 337 and 362 ppmv for 1979 and 1996, respectively. A similar secular CO₂ increase was also observed in the stratosphere (Nakazawa *et al.*, 1995). Longer data records of the CO₂ concentration at Mauna Loa and the South Pole indicate that the rate of CO₂ increase was about 0.7 ppmv/year around 1960 and then increased with time to a recent value of 1.5 ppmv/year. These data also show that yearly mean CO₂ concentrations were 315 and 356 ppmv for 1958 and 1992, respectively. The concentration difference of 41 ppmv corresponds to 87 GtC. On the other hand, the amount of carbon released into the atmosphere by fossil fuel combustion and cement production for this period is estimated to be 156 GtC (Boden *et al.* 1992). Therefore, the average airborne fraction of CO₂ from these sources is calculated to be about 56%.

It is indispensable for understanding the global

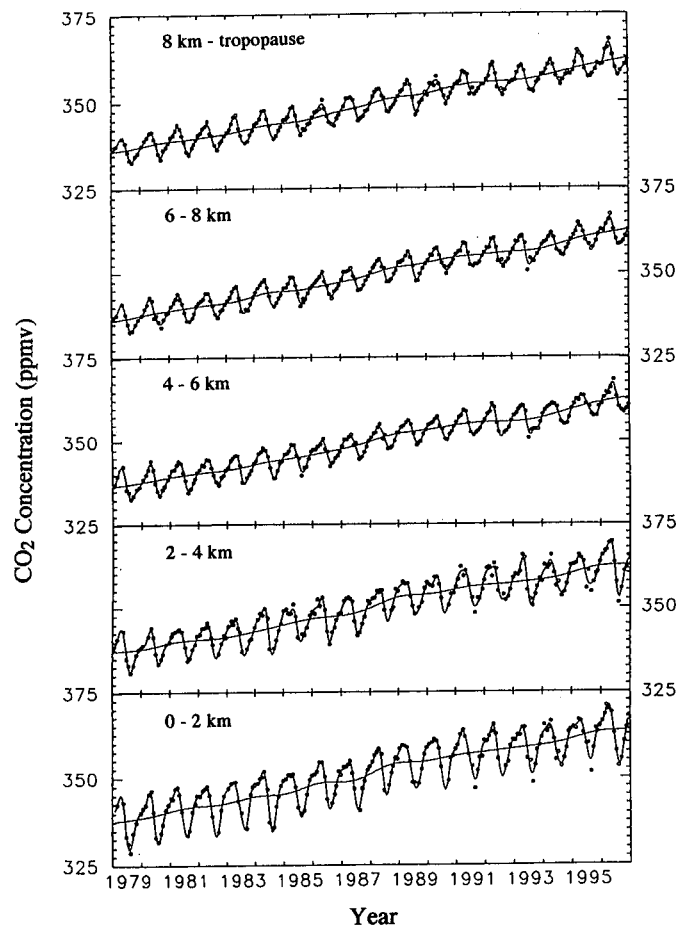


Fig. 1 Variations of the tropospheric CO₂ concentration over Japan.

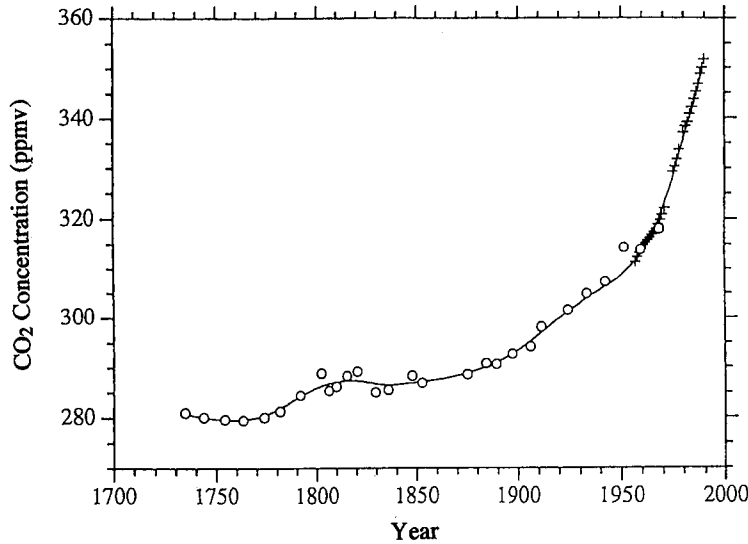


Fig. 2 Atmospheric CO₂ concentrations for the last 250 years deduced from an Antarctic ice core, H 15. Yearly mean CO₂ concentrations from direct measurements at the South Pole are also plotted by pluses.

carbon cycle to clarify the variations of the atmospheric CO₂ concentration in the past. Figure 2 shows the CO₂ concentrations during the last 250 years which were deduced by analyzing an Antarctic ice core, H15 (Nakazawa *et al.*, 1993a). Also shown are yearly mean values of the CO₂ concentration from systematic measurements at the South Pole. As seen from this figure, the CO₂ concentration was approximately 280 ppmv in the 1700s, which is regarded as pre-industrial levels, and began to increase around 1800, with a rapid trend after the middle of this century. Taking

account of a recent global mean CO₂ concentration of about 360 ppmv, it is pointed out that the atmospheric CO₂ concentration has been increased by 80 ppmv due to human activities. A concentration hump around 1800 was also found in the results from Antarctic ice cores, Mizuho (our unpublished data) and Law Dome (Etheridge *et al.*, 1996). Since air temperature was relatively high in this period, a large amount of CO₂ may have been released into the atmosphere from the terrestrial biosphere through respiration of living plants and oxidation of organic matter in soil. The CO₂

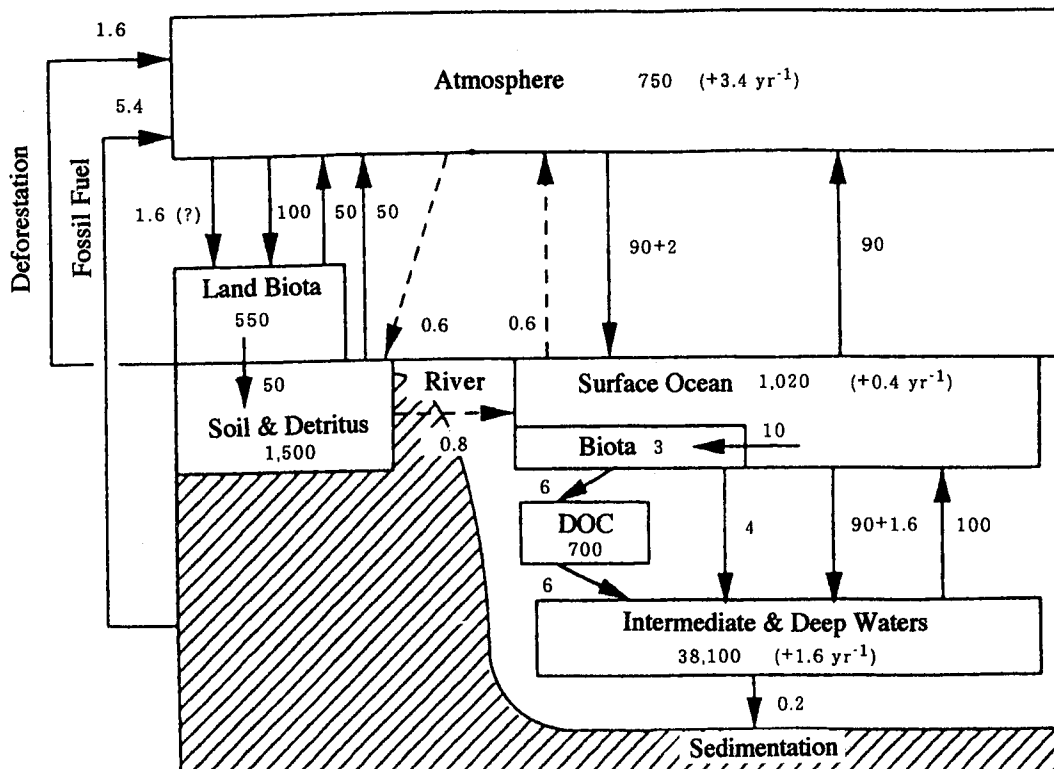


Fig. 3 Global carbon cycle in the 1980s. The sizes of the reservoirs and the fluxes are represented in GtC and GtC/year, respectively.

concentrations deduced from the H15 ice core are in excellent agreement with those from the Siple ice core (Neftel *et al.*, 1985), except for around 1800.

2.2 Global Carbon Cycle and Budget of Anthropogenic CO₂

Major carbon reservoirs on the Earth's surface are the atmosphere, the oceans and the terrestrial biosphere. Present knowledge of the global carbon cycle in the 1980s is illustrated in Fig.3 (Siegenthaler & Sarmiento, 1993; IPCC, 1990, 1995). It can be seen from this figure that CO₂ was released into the atmosphere at a rate of 5.4 GtC/year by fossil fuel combustion and at 1.6 GtC/year by deforestation especially in the tropical region, that the atmospheric CO₂ concentration increased at 3.4 GtC/year, and that the oceans absorbed CO₂ at 2 GtC/year. By summing these fluxes, it was found that there is an imbalance of 1.6 GtC/year for the anthropogenic CO₂ budget. Possible causes of such an imbalance are attributable to (1) underestimation of ocean uptake of anthropogenic CO₂, (2) overestimation of biospheric CO₂ released by deforestation and (3) the terrestrial biosphere acting as a net CO₂ sink due to re-growth of forests at northern middle and high latitudes, climate effects, and nitrogen and CO₂ fertilization. In Fig.3, the imbalance of 1.6 GtC/year is speculatively ascribed to uptake by the terrestrial biosphere.

The causes of the secular increase of the atmospheric CO₂ concentration have been examined extensively from various facets. Figure 4 shows total emissions of CO₂ estimated by analyzing past CO₂ concentration variations, given in Fig.2, by a deconvolution

calculation with a box-diffusion model (Siegenthaler and Oeschger, 1987). Also shown in this figure are fossil fuel CO₂, calculated ocean uptake of CO₂ and non-fossil fuel CO₂ obtained by subtracting fossil fuel CO₂ from total CO₂ emissions. It is obvious that non-fossil fuel CO₂ exceeds fossil fuel CO₂ in the 18th and 19th centuries and the situation is reversed in this century. Deforestation and changes in land use in Europe and North America may be responsible for the release of non-fossil fuel CO₂ before the 19th century, except for around 1800 when the release of biospheric CO₂ is thought to have been enhanced by climate effects, as mentioned before. On the other hand, the recent net flux of non-fossil fuel CO₂ is negative, which implies that the terrestrial biosphere absorbs CO₂ somewhere in the world, exceeding CO₂ released by deforestation in the tropics.

Carbon isotopic ratio, $\delta^{13}\text{C}$, of atmospheric CO₂ is expected to provide us with valuable information for elucidating the global carbon cycle, since the CO₂ exchange between the atmosphere and the terrestrial biosphere can be separated from that between the atmosphere and the oceans on the basis of the different isotopic fractionations of CO₂ in these exchange processes (Keeling *et al.*, 1989b; Nakazawa *et al.*, 1993c, 1997). Figure 5 show the results obtained by analyzing the atmospheric $\delta^{13}\text{C}$ data measured by the CSIRO (Commonwealth Scientific and Industrial Research Organization) at Cape Grim, Tasmania (Francey *et al.*, 1995) and by Tohoku University between 55° N and 39° S in the western Pacific region (Nakazawa *et al.*, 1997), in the light of

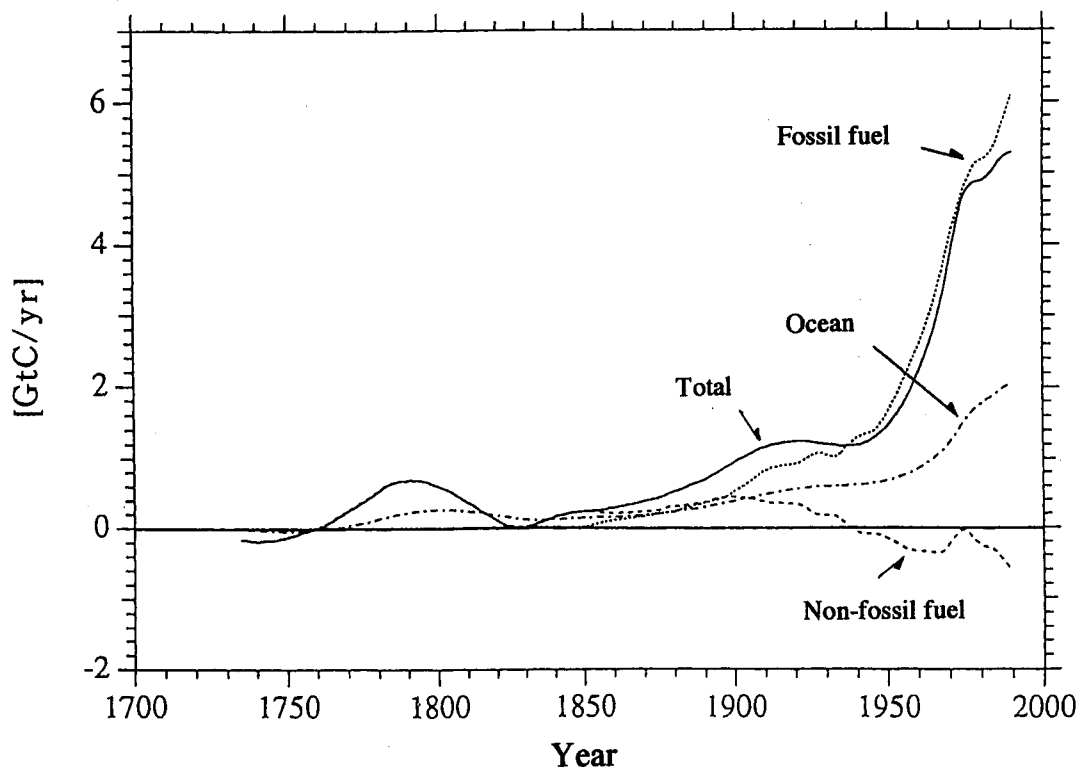


Fig. 4 Total emissions of CO₂ deduced from a box-diffusion model and the CO₂ concentration data shown in Fig.2. CO₂ emissions from fossil fuel combustion, non-fossil fuel CO₂ (total-fossil fuel) and the calculated CO₂ uptake by the oceans are also shown. The net release of non-fossil fuel CO₂ into the atmosphere and ocean CO₂ uptake are expressed in positive values.

the global budget of ¹³C. The results derived from the CSIRO data indicate the fossil fuel combustion of 5.7 GtC/year, the atmospheric increase of 2.9 GtC/year, the ocean uptake of 1.2 GtC/year and the terrestrial biospheric net sink of 1.6 GtC/year for an average budget of anthropogenic CO₂ for the period 1982-1993. On the other hand, corresponding values from the Tohoku data for the period 1984-1990 are 5.7, 3.5, 1.2 and 1.0 GtC/year, respectively. The ocean uptake of anthropogenic CO₂ deduced from the two data sets is 1.2 GtC/year, which is somewhat smaller than the average value of 2.0 GtC/year estimated by global carbon cycle models for the 1980s, and consequently it is suggested that the terrestrial biosphere acts as a net sink for anthropogenic CO₂. If the release of CO₂ by deforestation in the tropics is assumed to be 1.6 GtC/year, the CSIRO and Tohoku data imply that the terrestrial biosphere absorbed CO₂ at the respective rates of 3.2 and 2.6 GtC/year.

Keeling *et al.* (1989a) pointed out, by analyzing their atmospheric CO₂ concentration and δ¹³C data with a 3-dimensional atmospheric transport model, that the terrestrial biosphere acted as a net source (0.3 GtC/year) in 1960 and changed its role to a net sink (0.5 GtC/year) in 1984, reflecting enhanced CO₂ uptake by forests at northern middle and high latitudes due to the CO₂ fertilization effect. Tans *et al.* (1990) suggested, by simulating an average latitudinal CO₂ distribution for the period 1981-1987 with a 3-dimensional atmospheric transport model, that the ocean uptake of anthropogenic CO₂ was only 0.3-0.8 GtC/

year and the remaining CO₂ of 1.5-2.0 GtC/year was absorbed by boreal forests. We also analyzed our data of the CO₂ concentration and δ¹³C in the western Pacific during the period 1984-1990, using a 2-dimensional atmospheric transport model (Morimoto *et al.*, 1997). From this analysis, the uptake of anthropogenic CO₂ by the oceans and the terrestrial biosphere were estimated to be 1.5 and 0.8 GtC/year, respectively. These values are slightly different from those shown in Fig.5. The results also suggested that the terrestrial biosphere at northern middle and high latitudes absorbed CO₂ exceeding the emissions from deforestation in the tropics.

Atmospheric O₂ is affected by fossil fuel combustion, deforestation and biospheric fixation of atmospheric CO₂, while O₂ does not participate in the CO₂ exchange between the atmosphere and the oceans. From this point of view, R.F. Keeling (Keeling & Shertz, 1992; Keeling *et al.*, 1996) has developed a high precision technique for measuring the O₂ concentration in the atmosphere and then begun its systematic measurements at several places around the world. An example of their results is shown in Fig.6. The O₂ concentration is given by $\delta(O_2/N_2) = (R/R_s - 1) \times 10^6$, where R and R_s are the O₂/N₂ ratios of the sample and standard air, respectively, and 1 ppmv of the atmospheric O₂ concentration is equivalent to 4.8 per meg. As seen from this figure, the atmospheric O₂ concentration decreased secularly, corresponding to the CO₂ increase. If the observed decrease of the atmospheric O₂ concentration is steeper than that expected from

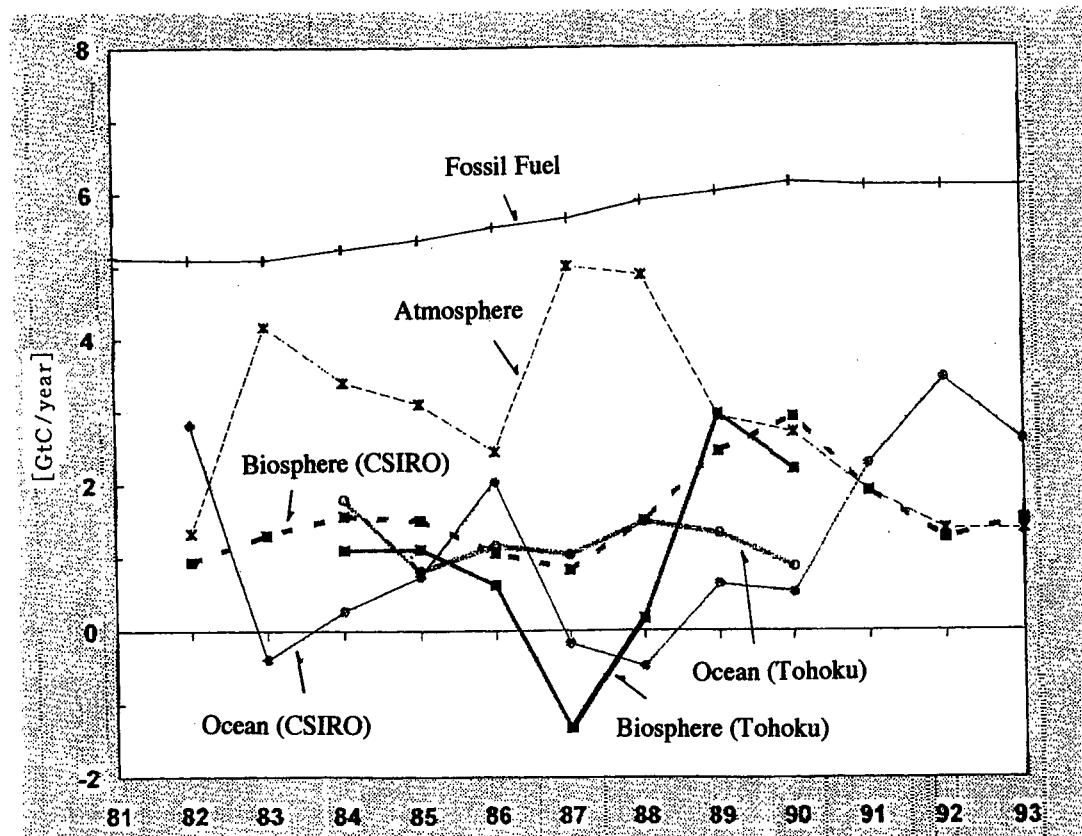


Fig. 5 Budgets of anthropogenic CO₂ estimated from the δ¹³C values of atmospheric CO₂ measured by CSIRO and Tohoku University. Net absorption of CO₂ by the oceans and the terrestrial biosphere are given by positive values.

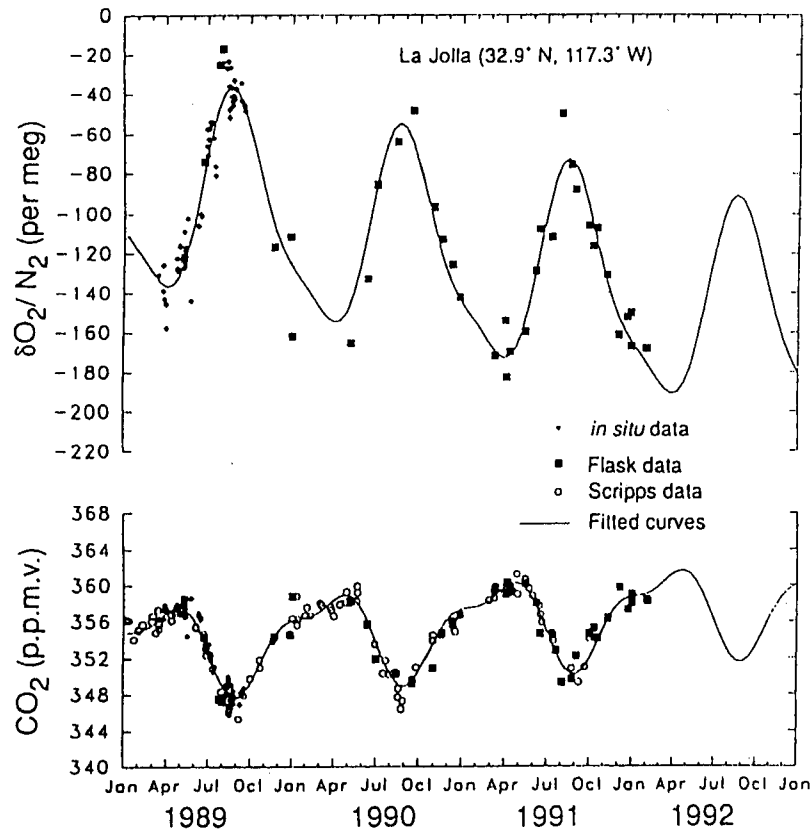


Fig. 6 Measured values of the O_2/N_2 ratio and the CO_2 concentration in the atmosphere in La Jolla, California.

fossil fuel combustion, then it would be suggested that the terrestrial biosphere acts as a net CO_2 sink, and vice versa. By substituting the observed values of the O_2 concentration decrease and the CO_2 concentration increase and other necessary parameters into the budget equations for CO_2 and O_2 , it was derived for the global budget of anthropogenic CO_2 around 1990 that the net release of CO_2 from the terrestrial biosphere was 0.24 GtC/year and the ocean uptake of CO_2 was 3.0 GtC/year. With respect to the phenomenon that the secular increase of the atmospheric CO_2 concentration was almost stagnant from 1991 to 1994, Keeling *et al.* (1996) pointed out from their O_2 measurements that such a stagnation can be ascribed to CO_2 fixation of 2.0 GtC/year by the terrestrial biosphere at northern middle and high latitudes, in addition to the ocean uptake of 1.7 GtC/year. They also suggested that tropical forests did not act as a strong CO_2 source at least for this period.

3. METHANE

3.1 Concentration Variations of CH_4 in the Atmosphere

Systematic measurements of the atmospheric CH_4 concentration were started early in the 1980s. Figure 7 shows the variations of the atmospheric CH_4 concentration obtained from the NOAA/CMDL (National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory) global sampling network (Dlugokencky *et al.*, 1994a). The CH_4 concentration increases secularly, accompanied by the

seasonal cycle and interannual variations, which is similar to the CO_2 concentration. The seasonal cycle of the CH_4 concentration is produced mainly by the seasonality of CH_4 destruction by OH radicals as well as of CH_4 emissions from various sources (Fung *et al.*, 1991). In general, the atmospheric CH_4 concentration decreases in summer when the reaction of CH_4 with OH is activated and increases in cold seasons when CH_4 emissions take precedence over the chemical destruction of CH_4 by OH. However, in the northern hemisphere, the seasonal CH_4 cycle depends largely on location, since CH_4 sources with seasonally-different strengths are distributed unevenly on the ground surface. On the other hand, the cycle is almost similar throughout the southern hemisphere where there are no strong CH_4 sources.

The causes of the interannual variations of the CH_4 concentration are not yet understood well. However, it may be thought that the variations are produced by changes in magnitude of CH_4 sources and sinks, as well as in the atmospheric transport, in association with climate changes due to the ENSO event, volcanic eruptions and other factors. For example, to interpret an observational fact that the CH_4 concentration increased in the southern hemisphere and decreased in the northern hemisphere in 1988, Steele *et al.* (1992) inferred that the northern hemispheric air with high CH_4 concentrations was transported to the southern hemisphere with low CH_4 concentrations and vice versa, due to the enhancement of air exchange between both hemispheres by the La Nina event. It was also observed that the CH_4 concentration in-

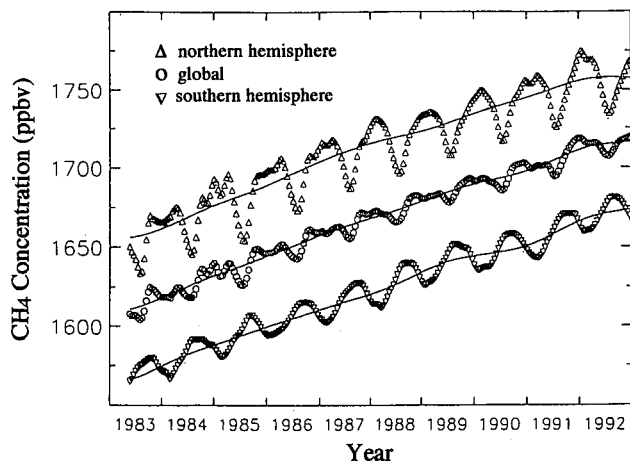


Fig. 7 Variations of northern and southern hemispherical and global average CH₄ concentrations.

creased rapidly from 1990 to 1991 and slowly from 1992 to 1993. With respect to the rapid CH₄ increase in 1990–1991, Tans *et al.* (1996) suggested that solar UV was absorbed or scattered by SO₂ and sulfuric acid, originating from the eruption of Mt. Pinatubo in June 1991, in the stratosphere and that subsequently O (¹D), which is indispensable for producing OH from atmospheric water vapor, decreased. Regarding the stagnation of the CH₄ increase in 1992–1993, Dlugokencky *et al.* (1994a, b) pointed out the possibility of reduced emissions of fossil fuel CH₄ in Russia as well as of biogenic CH₄ from wetlands in relation to low temperatures after the eruption of Mt. Pinatubo, and Lowe *et al.* (1994) suggested that CH₄ from biomass burning was decreased in the southern hemisphere, in addition to the reduced emissions of fossil fuel CH₄ in the northern hemisphere. Bekki *et al.* (1994) reported that the increase of tropospheric OH due to stratospheric O₃ reduction in 1991–1992 was also responsible for the stagnation of the CH₄ increase for this period. We also analyzed our CH₄ concentration data between 55° N and 69° S during the period 1988–1994 (Sugawara *et al.*, 1994), using a 2-dimensional photochemical-atmospheric transport model. The results indicated that not only the enhancement of the chemical CH₄ destruction due to the tropospheric OH increase but also the reduction of CH₄ emissions would be significant for the rapid decrease of the CH₄ growth rate in 1992. From continuous measurements of the CO₂ and CH₄ concentrations at Syowa Station, Antarctica, Aoki and Nakazawa (1994) found that the growth rates of the two components were opposite in phase with each other. This may imply that sources and/or sinks of CH₄ were affected by climate changes such as droughts and abnormally high or low temperatures.

As seen from Fig.7, the atmospheric CH₄ concentration increased by about 100 ppbv for 10 years from 1983 to 1992. To examine the secular increase of the CH₄ concentration over a long time in the past, our results obtained by analyzing the H15 ice core are shown in Fig.8 (Machida *et al.*, 1994). It is obvious from this figure that the atmospheric CH₄ concentra-

tion was approximately 700 ppbv in the pre-industrial era and then increased with time, showing an especially rapid trend after the middle of this century. Taking account of the observational fact that the globally averaged atmospheric CH₄ concentration was about 1750 ppbv in 1995, the increase of the CH₄ concentration due to human activities amounts to approximately 1000ppbv. Our analyses of an Antarctic ice core, Mizuho, and a Greenland ice core, Site-J, revealed that pre-industrial levels of the atmospheric CH₄ concentration were higher by about 50 ppbv in the northern polar region than in the southern polar region (Nakazawa *et al.*, 1993b). Since the recent differences between yearly mean CH₄ concentrations at northern and southern high latitudes are about 140 ppbv, it is suggested that the north-south CH₄ gradient has been extended about 3 times by human activities.

It is obvious from systematic CH₄ measurements that the secular increase of the atmospheric CH₄ concentration has been decelerated since the mid-1980s (Aoki *et al.*, 1992 ; Steele *et al.*, 1992 ; Dlugokencky *et al.*, 1994a, b ; Sugawara *et al.*, 1994). Such a phenomenon is clearly found in Fig.7. Steele *et al.* (1992) and Dlugokencky *et al.* (1994a) attributed the cause to the reduced emissions of fossil fuel CH₄, considering their observational fact that the deceleration of the CH₄ increase was especially remarkable at northern middle and high latitudes. In addition, Mardonich and Granier (1992) reported, from their analyses of total O₃ during 1979–1989, that the decrease of stratospheric O₃ may have affected the chemical reaction of CH₄ with OH. We also analyzed the NOAA/CMDL CH₄ data during the period 1983–1993 with a 2-dimensional photochemical-atmospheric transport model (Saeki *et al.*, 1998). From this analysis, it was found that global emissions of CH₄ were almost constant during the period, but the CH₄ emissions decreased secularly at northern high and middle latitudes and increased at northern low latitudes.

3.2 Sources and Sinks of CH₄

The global budget of CH₄ is expressed by $dM/dt = -kM + p$, where M is the total weight of atmospheric

CH_4 , p is the release rate of CH_4 into the atmosphere, k is the 1st-order loss rate of CH_4 in the atmosphere (a reciprocal of the average lifetime of CH_4 , τ). By substituting 11.1 years and our data taken at latitudes 55°N – 69°S over the period 1988–1994 for τ , M and dM/dt , p is calculated to be $477 \text{ TgCH}_4/\text{year}$. Differentiating the above equation with respect to t , we obtain $d^2M/dt^2 + kdM/dt = -Mdk/dt + dp/dt$. By assuming that dk/dt is equal to 0 (i.e., constant destruction rate), dp/dt is found to be $-3.2 \text{ TgCH}_4/\text{year}^2$.

Quantitative estimation of CH_4 emissions from various sources, chemical destruction of CH_4 by OH and CH_4 absorption by soil have been made by many investigators. The Intergovernmental Panel on Climate Change (IPCC) has estimated the strength of the respective CH_4 sources and sinks four times, on the basis of these available studies (IPCC, 1990, 1992, 1995, 1996). However, the results are not in agreement with each other. The estimates of CH_4 sources and sinks by IPCC (1995) are presented in Table 1 for reference. The values estimated for the atmospheric CH_4 increase, the total sinks and the total sources are 37, 552 and 535 $\text{TgCH}_4/\text{year}$, respectively. It is seen from this table that uncertainties of the estimates for the respective sinks and sources are significantly large.

In order to estimate the strength of the CH_4 sources precisely, measurements of carbon isotopes of atmospheric CH_4 and analyses of the atmospheric CH_4 concentration and carbon isotope data with atmospheric transport-chemical models would be very useful. Radioactive carbon (^{14}C) with a half-life of 5730 years is not included in fossil fuel CH_4 , while the ^{14}C concentrations of non-fossil CH_4 originating in rice paddies, ruminants, biomass burning and others are almost similar to those of present atmospheric CH_4 . $\delta^{13}\text{C}$ in CH_4 is also dependent on its origin; the approximate values are -60 , -41 and -27‰ for CH_4 from biogenic sources, fossil fuel and biomass burning, respectively. Taking this into account, several investigators estimated the contributions of the respective sources to atmospheric CH_4 , on the basis of

their measurements of the ^{14}C concentration and $\delta^{13}\text{C}$ of atmospheric CH_4 . For example, Quay *et al.* (1991) found to be 16 and 11% for the respective contributions of CH_4 from fossil fuel and biomass burning.

Fung *et al.* (1991) calculated atmospheric CH_4 concentrations using a 3-dimensional atmospheric transport model under several source scenarios, and then selected the best scenario by comparing the calculated results with those observed at the NOAA/CMDL flask sampling network from 1984 to 1987. Quay *et al.* (1991) also found that their observed $\delta^{13}\text{C}$ values of atmospheric CH_4 agreed well with those calculated by the same model with the selected source scenario. We also derived the latitudinal distribution of CH_4 emissions by analyzing the NOAA/CMDL CH_4 concentration data for the period 1983–1993 with a 2-dimensional atmospheric transport model (Saeki *et al.*, 1997). The average total emission and sink of CH_4 over this period were found to be 559 and 528 $\text{TgCH}_4/\text{year}$, respectively. The results also showed that about 80% of total emissions occur in the northern hemisphere and emissions at latitudes 30° – 90°N amounted to 50% of the total.

4. SUMMARY

Many of recent studies on the global carbon cycle suggest that the terrestrial biosphere does not act as a strong net source of atmospheric CO_2 . Indeed, in IPCC (1995), CO_2 from deforestation is compensated by the biospheric uptake due to the re-growth of forests, nitrogen and CO_2 fertilization, and the climate effects. However, quantitative estimates of CO_2 uptake for the respective processes are still insufficient. Further studies are needed not only to examine possible processes of biospheric uptake but also to estimate their fluxes with high precision. For a better understanding of the global carbon cycle, it is necessary (1) to establish a worldwide close-knit network of stations for background monitoring of the CO_2 concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO_2 , and the O_2 concentration, (2) to re-evaluate the CO_2 release from and uptake by the terrestrial biosphere on the basis of

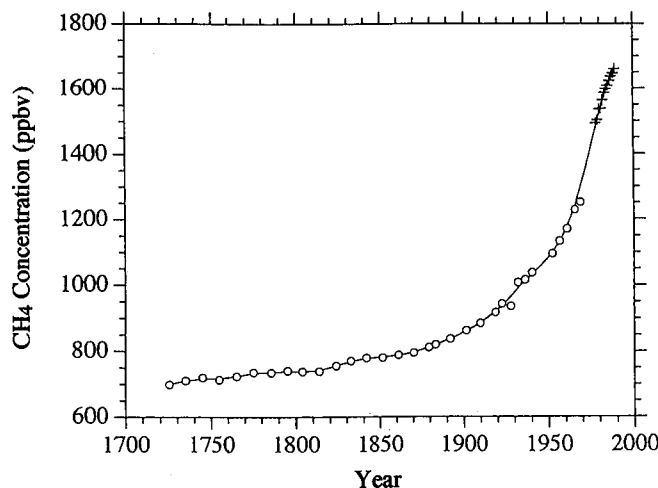


Fig. 8 The same as in Fig.2, but for the CH_4 concentration. Pluses represent yearly mean CH_4 concentrations at Cape Grim, Tasmania.

Table 1 Sources and sinks of CH₄ and their estimated strength (TgCH₄/year)

	Strength	Total
Atmospheric increase	37 (35-40)	37 (35-40)
Atmospheric removal (lifetime=9.4yr)		
Tropospheric OH	445 (360-530)	
Stratosphere	40 (32-48)	
Soils	30 (15-45)	
Total sinks		515 (430-600)
Implied total sources		552 (465-640)
Sources	Strength	Total
Natural		
Wetlands	115 (55-150)	
Termites	20 (10-50)	
Oceans	10 ⁷ (5-50)	
Other	15 (10-40)	
Anthropogenic		
Fossil fuel-related		375 (300-450)
Natural gas	40 (25-50)	
Coal mines	30 (15-45)	
Petroleum industry	15 (5-30)	
Coal combustion	? (1-30)	
Biospheric carbon		275 (200-350)
Enteric fermentation	85 (65-100)	
Rice paddies	60 (20-100)	
Biomass burning	40 (20-80)	
Landfills	40 (20-70)	
Animal waste	25 (20-30)	
Domestic sewage	25 (15-80)	
Total sources		535 (410-660)

analyses of relevant data, (3) to re-examine the absorption processes of CO₂ by the oceans, (4) and to develop sophisticated global carbon cycle models which are constrained not only by the CO₂ concentration but also by $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO₂ and the O₂ concentration and are also coupled with climate models.

Our present knowledge of the global cycle of CH₄ is also still insufficient in spite of much research done so far. In order to increase our quantitative understanding of the global CH₄ budget, further studies are required especially for the establishment of a comprehensive station network for monitoring the atmospheric CH₄ concentration and $\delta^{13}\text{C}$, the development of global CH₄ cycle models, the re-evaluation of CH₄ emissions from various sources using statistical methods and basic data, measurements of $\delta^{13}\text{C}$ of the respective sources, the determination of precise fractionation factors for the reactions of CH₄ with OH and Cl as well as for the soil absorption process of CH₄, and the elucidation of the OH radical field by observational and theoretical bases.

REFERENCES

- Aoki, S., T.Nakazawa, S.Murayama and S.Kawaguchi (1992) Measurements of atmospheric methane at Japanese Antarctic station, Syowa. *Tellus*, 44B : 273-281.
- Aoki, S. and T.Nakazawa (1994) *Relationship between the atmospheric CO₂ and CH₄ concentrations at Syowa Station, Antarctica. Proceedings of the NIPR Symposium on Polar Meteorology and Glaciology*, 8 : 14-18.
- Bekki, S., L.S. Law and J.A. Pyle (1994) Effect of ozone depletion on atmospheric CH₄ and CO concentrations. *Nature*, 371 : 595-597.
- Boden, T.A., R.J. Sepanski and F.W. Stoss (1992) *TREND*

'91: A compendium of data on global change-Highlights. ORNL/CDIAC-049 Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge.

- Dlugokencky, E.L., L.P. Steele, P.M. Lang and K.A. Masarie (1994a) The growth rate and distribution of atmospheric methane. *J. Geophys. Res.*, 99 : 17021-17043.
- Dlugokencky E.J., K.A. Masarie, P.M. Lang, P.P. Tans, L. P. Steele and E.G. Nisbet (1994b) A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992. *Geophys. Res. Lett.* 21 : 45-48.
- Elkins, J.W., J.H. Butler, T.M. Thompson, S.A. Montzka, R.C. Myers, J.M. Lobert, S.A. Yvon, P.R. Wamsley, F.L. Moore, J.M. Gilligan, D.F. Hurst, A.D. Clarke, T.H. Swanson, C.M. Volk, L.T. Lock, L.S. Geller, G.S. Dutton, R.M. Dunn, M.F. Dacorleto, T.J. Baring and Hayden A. H. (1996) *Nitrous Oxide and Halocompounds. CMDL Summary Report 1994-1995* (eds. D.J. Hofmann, J.T. Peterson and R.M. Rosson), NOAA, Boulder, USA, 84-111.
- Etheridge, D.M., G.I. Pearman and P.J. Fraser (1992) Changing in the tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core. *Tellus*, 44B : 282-294.
- Etheridge, D.M., L.P. Steele, R.L. Langenfelds, R.J. Francey, J.M. Barnola and V.I. Morgan (1996) Natural and anthropogenic changes in atmospheric CO₂ over the last 1000 years from air in Antarctic ice and firn. *J. Geophys. Res.*, 101 : 4115-4128.
- Francey, R.J., P.P. Tans, C.E. Allison, I.G. Enting, J.W.C. White and M.Trolier (1995) Changes in oceanic and terrestrial carbon uptake since 1982. *Nature*, 373 : 326-330.
- Fung, I., J.John, J.Lerner, E.Matthews, M.Prather, L.P. Steele and P.J. Fraser (1991) Three-dimensional model synthesis of the global methane cycle. *J.Geophys. Res.*, 96 : 13033-13065.
- IPCC (1990) *Climate Change : The IPCC Scientific Assessment* (eds. J.T. Houghton, G.J. Jenkins & J.J. Ephraums), Cambridge University Press, Cambridge, UK.
- IPCC (1992) *Climate Change 1992 : The supplementary Report to the IPCC Scientific Assessment* (eds. J.T. Houghton, B.A. Callander & S.K. Varney), Cambridge University Press, Cambridge, UK.
- IPCC (1995) *Climate Change 1994 : Radiative Forcing of Climate Change and an Evaluation of the IPCC 1992 IS92 Emission Scenarios* (eds. J.T. Houghton, L.G. Meria Filho, J.Bruce, H.Lee, B.A. Callander, E.Haites, N.Harris and K.Maskell), Cambridge University Press, Cambridge, UK.
- IPCC (1996) *Climate Change 1995 : The Science of Climate Change* (eds. J.T. Houghton, L.G. Meira Filho, B.A. Callander, N.Harris, A.Kattenberg and K.Maskell), Cambridge University Press, Cambridge, UK.
- Keeling, C.D., R.B. Bacastow, A.E. Bainbridge, C.A. Ekdahl, P.R. Guenther, L.S. Waterman and J.F.S. Chin (1976a) Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. *Tellus*, 28 : 538-551.
- Keeling, C.D., J.A. Adams, C.A. Ekdahl and P.R. Guenther (1976b) Atmospheric carbon dioxide variations at the South Pole. *Tellus*, 28 : 552-564.
- Keeling, C.D., S.C. Piper and M.Heimann (1989a) A three-dimensional model of atmospheric CO₂ transport based on observed winds : 4. mean annual gradients and inter-annual variations. *AGU Monograph*, vol.55, American Geophysical Union, Washington, pp.305-362.
- Keeling, C.D., R.B. Bacastow, A.F. Carter, S.C. Piper, T.P.

- Whorf, M., Heimann, W.G., Mook and H. Roeloffzen (1989b) A three-dimensional model of atmospheric CO₂ transport based on observed winds: 1. Analysis of observed data. *AGU Monograph*, vol.55, American Geophysical Union, Washington, pp.165-236.
- Keeling, C.D., T.P. Whorf, M. Wahlen & J. Van der Plicht (1995) Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. *Nature*, 375 : 666-670.
- Keeling, R.F. and S.R. Shertz (1992) Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature*, 358 : 723-727.
- Keeling, R.F., S.C. Piper and M. Heimann (1996) Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration. *Nature*, 381 : 218-221.
- Law, K.S. and J.A. Pyle (1993) Modelling trace gas budgets in the troposphere 2. CH₄ and CO. *J. Geophys. Res.*, 98 : 18401-18412.
- Lowe, D.C., C.A.M. Brenninkmeier, G.W. Brailsford, K.R. Lassey and A.J. Gornes (1994) Concentration and ¹³C records of atmospheric methane in New Zealand and Antarctica; evidence for changes in methane sources. *J. Geophys. Res.*, 99 : 16913-16925.
- Machida, T., T. Nakazawa, M. Tanaka, Y. Fujii, S. Aoki and O. Watanabe (1994) *Atmospheric CH₄ and N₂O concentrations during the last 250 years deduced from HI5 ice core, Antarctica*. Proceedings of International Symposium of Global Cycle of Atmospheric Greenhouse Gases, 113-116.
- Machida, T., T. Nakazawa, Y. Fujii, S. Aoki and O. Watanabe (1995) Increase in the atmospheric nitrous oxide concentration during the last 250 years. *Geophys. Res. Lett.*, 21 : 2921-2924.
- Madronich, S. and C. Granier (1992) Impact of recent total ozone changes on tropospheric ozone photodissociation, hydroxyl radicals, and methane trends. *Geophys. Res. Lett.*, 19 : 465-467.
- Morimoto, S., T. Nakazawa, K. Higuchi and S. Aoki (1997) *Sources and sinks of atmospheric carbon dioxide deduced from its surface concentration and carbon isotopic data using a two-dimensional atmospheric transport model*. Proceedings of the 5th International Conference on Analysis and Evaluation of Atmospheric CO₂ Data, Present and Past, Cairns, September 8-12, 1997.
- Nakazawa, T., T. Machida, M. Tanaka, Y. Fujii, S. Aoki & O. Watanabe (1993a) *Atmospheric CO₂ concentrations and carbon isotopic ratios for the last 250 years deduced from an Antarctic ice core, HI5*. Proceedings of the 4th International Conference on Analysis and Evaluation of Atmospheric CO₂ Data, Present and Past, 193-196.
- Nakazawa, T., T. Machida, M. Tanaka, Y. Fujii, S. Aoki & O. Watanabe (1993b) Differences of the atmospheric CH₄ concentration between the Arctic and Antarctic regions in pre-industrial/pre-agricultural era. *Geophys. Res. Lett.*, 20 : 943-946.
- Nakazawa, T., S. Morimoto, S. Aoki & M. Tanaka (1993c) Time and space variations of the carbon isotopic ratio of tropospheric carbon dioxide over Japan. *Tellus*, 45B : 258-274.
- Nakazawa, T., H. Honda, T. Machida, S. Sugawara, S. Murayama, G. Hashida, S. Morimoto and T. Itoh (1995) Measurements of the stratospheric carbon dioxide concentration over Japan using a balloon-borne cryogenic sampler. *Geophys. Res. Lett.*, 22 : 1229-1232.
- Nakazawa, T., S. Morimoto, S. Aoki and M. Tanaka (1997) Temporal and spatial variations of the carbon isotopic ratio of atmospheric carbon dioxide in the western Pacific region. *J. Geophys. Res.*, 102 : 1271-1285.
- Neftel, A., E. Moor, H. Oeschger and B. Stauffer (1985) Evidence from polar ice cores for the increase in the past two centuries. *Nature*, 315 : 45-47.
- Quay, P.D., S.L. King, J. Stutsman, D.O. Wilbur, L.P. Steele, I. Fung, R.G. Gammon, T.A. Brown, G.W. Farwell, P.M. Grootes and F.H. Schmidt (1991) Carbon isotopic composition of atmospheric CH₄: Fossil and biomass burning source strengths. *Global Biogeochem. Cycles*, 5 : 25-47.
- Saeki, T., T. Nakazawa, M. Tanaka and K. Higuchi (1998) Methane emissions deduced from a two-dimensional atmospheric transport model and surface concentration data. *J. Meteorol. Soc. Japan*, 76, 307-324.
- Siegenthaler, U. and H. Oeschger (1987) Biospheric CO₂ emissions during the past 200 years reconstructed by deconvolution of ice core data. *Tellus*, 39B : 140-154.
- Siegenthaler, U. and F. Joos (1992) Use of a simple model for studying oceanic tracer distributions and the global carbon cycle. *Tellus*, 44B : 186-207.
- Siegenthaler, U. and J.L. Sarmiento (1993) Atmospheric carbon dioxide and the ocean. *Nature*, 365 : 119-125.
- Steele, L.P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin and K.A. Masarie (1992) Slowing down of the global accumulation of atmospheric methane during the 1980s. *Nature*, 358 : 313-316.
- Sugawara, S., T. Nakazawa, G. Hashida, C. Sakai and M. Tanaka (1994) *Variations of atmospheric methane concentration over the western Pacific Ocean*. Proceedings of International Symposium of Global Cycles of Atmospheric Greenhouse Gases, 121-128.
- Tans, P.P., I.Y. Fung and T. Takahashi (1990) Observational constraints on the global atmospheric CO₂ budget. *Science*, 247 : 1431-1438.
- Tans, P.P., P.S. Bakwin, T.J. Conway, R.W. Dissly, E.J. Dlugokencky, L.S. Geller, D.W. Guenther, D.F. Hurst, D. R. Kitzis, P.M. Lang, K.A. Masarie, J.W. Miller, P. Novelli, C. Prostko-bell, M. Ramone, K.W. Thoning, M. Troleir, L.S. Waterman, H. Zhang and C. Zhao (1996) *Carbon cycle. CMDL Summary Report 1994-1995* (eds. D.J. Hofmann, J.T. Peterson and R.M. Rosson), NOAA, Boulder, USA, 29-49.

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