Modeling the Sudden Decrease in CH_4 Growth Rate in 1992①

Zhang Renjian(张仁健) and Wang Mingxing(王明星)

State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029

(Received March 24, 1998; Revised November 11, 1998)

ABSTRACT

A two-dimensional global chemistry model is developed to study the distribution and long-term trends of methane. The model contains 34 species and 104 chemical and photochemical reactions. Using the model, the long-term trends of CH_4, CO and OH in atmosphere are simulated, comparison between the model and observations shows that the simulation is successful.

Experiments are done to investigate the causes of dramatic decrease in the growth rate of CH_4 in 1992 such as OH increase due to stratospheric ozone depletion, decrease of temperature in the troposphere due to Mount Pinatubo eruption and descendent of CH_4 sources fluxes. A new explanation is proposed and verified by this model that the decrease of CO emission plays an important role for the abnormal growth rate of CH_4 in 1992. We find that the decreases of CH_4 and CO emissions are the main reasons for the sudden decrease of growth rate of CH_4 in 1992, which account for 73% and 27% respectively.

Key words: Two-dimensional global chemistry model, Methane, Growth rate, OH

1. Introduction

Methane (CH_4) is an important greenhouse gas in atmosphere. The main removal process of CH_4 in atmosphere is reacted with OH which is determined by the abundance of methane, carbon monoxide (CO) and nitrous oxides (NO_x) whose emissions have increased greatly because of human activities since industry revolution (Crutzen, 1995).

During the past 150 years, the CH_4 concentration (volume fraction) increased from 0.7×10^{-6} before industry revolution to 1.7×10^{-6} in the 1990s. But its growth rate is not constant. Steel et al. (1992) believed that the growth rate of CH_4 decreased from 13.3×10^{-9}/a in 1983 to 9.5×10^{-9}/a in 1990. Another research by Dlugokencky et al. (1994) showed that the increasing rate of CH_4 was 11.6×10^{-9}/a in the Northern Hemisphere and 11.1×10^{-9}/a in the Southern Hemisphere from 1983 to 1991, but it decreased sharply in 1992.

In this paper, using a two-dimensional global chemistry transport model set up by ourselves (Zhang, 1997), we try to simulate the long-term trend of methane and investigate the causes of dramatic decrease in methane growth rate in 1992.

①This work is supported by the State Key Program for basic research "Climate Dynamics and Climate Prediction Theory" (Pandeng-yu-21).

2. The global two-dimensional model

2.1 *Model structure*

The behavior of an atmospheric gas is governed by the continuity equation

$$\frac{\partial \bar{C}}{\partial t}+\frac{\partial(\rho v \bar{C}\cos\varphi)}{\rho\cos\varphi\partial y}+\frac{\partial(\rho w \bar{C})}{\rho\partial z}=S+L\bar{C}+\frac{1}{\rho\cos\varphi}\frac{\partial}{\partial y}(\rho K_{yy}\cos\varphi\frac{\partial \bar{C}}{\partial y})+\frac{1}{\rho}\frac{\partial}{\partial z}(\rho K_{zz}\frac{\partial \bar{C}}{\partial z}), \quad (1)$$

where C is the volume mixing ratio, S is the chemical production rate, L is the chemical loss term, ρ is the air density, φ is latitute, y, z are northward and upward directions, $y=r\Delta\varphi$, r is radius of the earth. K_{yy} and K_{zz} are the horizontal and vertical diffusion coefficients respectively from Hidalgo et al. (1977).

This model is from 90°S to 90°N with a resolution of 5° and up to 20 km with a resolution of 1 km. The constituents are advected by residual circulation which is shown to equal the diabatic circulation and is calculated from the diabatic rate (Stordal, 1985).

Two-dimensional tracer equations are solved by the use of Peaceman-Rachford method (Su Yucheng, et al., 1989; Wang et al., 1992). Each time step is divided into two steps to solve equation (1). In the first step, the chemical loss term, advection term and diffusion term along y direction are treated as implicit while chemical production term, advection term and diffusion term along z direction are treated as explicit. In the second step, the chemical loss term, advection term and diffusion term along z direction are treated as implicit, while chemical production term, advection term and diffusion term along y direction are treated as explicit. First-order upstream scheme is used for the advection term. The time step is 8 hours.

The water vapor and temperature fields are input monthly obtained from the data of European Center Medium-Range Weather Forecasts (ECMWF) in 1990.

2.2 *Model chemistry*

The model includes 34 species and 104 chemical and photochemical reactions. There are five fixed species: N_2, O_2, H_2, CO_2 and H_2O. Concentrations of N_2, O_2, H_2, and CO_2 are 0.78, 0.21, 0.56×10^{-6} and 340×10^{-6} respectively. Water vapor is fixed input data from ECMWF. Photochemical steady state is assumed for the species with short chemical lifetimes compared to time steps, which are: $O(^3P)$, $O(^1D)$, H, OH, HO_2, N, NO_3, HCO, CH_2O, CH_3, CH_3O, CH_3O_2, CH_3OOH. Other species such as CH_4, N_2O, CO, CH_3CL, $CFCL_3$, CCL_4, CF_2CL_2, CH_3CCL_3, O_3, $NO_x(NO+NO_2)$, H_2O_2, HNO_2, HNO_3, HNO_4, N_2O_5 are treated as long life species. The photochemical reactions and the photochemical reaction rates data are from Hough (1991), Law and Pyle (1993), Kanakidou et al.(1991), Brasseur et al. 1990, and Wang et al. (1992). The photolysis rate are calculated at the middle of each month using data from WMO (1986) and DeMore et al.(1987) .The dry and wet depositions included in the model are from Law and Pyle (1993).

2.3 *Emissions*

The sources of CH_4 are divided into two parts: seasonal sources (such as wetlands, rice paddies and biomass burning) and non-seasonal sources (ruminants, coal mining, natural gas production and transportation, landfill, termites and ocean et al.). For CO and NO_x, all sources are non-seasonal except that the source of biomass burning is sea-

sonal. All sources of CH_4, CO and NO_x are parameterized as function of latitude and time (month and year) according to Law and Pyle (1993).

3. Model calculation and results

3.1 *Long-term trends of* CH_4

Long time before industry revolution, methane concentration kept stable between $500-750\times10^{-9}$, so it can be regarded as quasi-steady state.

With annual emission of 280 Tg for CH_4, 320 Tg for CO, and 20 Tg(N) for NO_x, after long time integration, the modeled composition of atmosphere can be regarded as steady state before industry revolution. With this composition in 1840 as initial condition and parameterized emission scenario, we run the model from 1840 to 2050. The model results are as follows:

In 1840, annual emission of methane is 280 Tg, absorption by soil is 30 Tg, the upper flux from the troposphere is 16.7 Tg, reaction with OH is 233.3 Tg, total amount in atmosphere is 2136.9 Tg, and the global average concentration is 760.1×10^{-9}. The OH concentration is 7.17×10^5 molecule / cm^3. In 1991, methane annual emission is 530.1 Tg, absorption by soil is 30 Tg, the upper flux from troposphere is 36.4 Tg, reaction with OH is 467.5 Tg, total amount in atmosphere is 4531.7 Tg, and the global average concentration is 1611.9×10^{-9}. The OH concentration is 5.79×10^5 molecule / cm^3. In 2020, the concentration of CH_4 and OH will be 2090.7×10^{-9} and 5.47×10^5 molecule / cm^3. Table 1 is the simulation of CH_4, CO, O_3 and OH in 1840, 1991 and 2020, respectively.

Table 1. Simulation of CH_4, CO, O_3 and OH in 1840, 1991 and 2020

Time	CH_4 (10^{-9})	CO(10^{-9})	O_3 (10^{-9})	OH(10^5 molecule / cm^3)
1840	760.1	26.9	39.0	7.17
1991	1611.9	75.7	51.7	5.79
2020	2090.7	104.6	57.8	5.47

Methane concentration increases with the increase of emission mostly from human activities. CO concentration increases because of increase of CO emission from human activities and oxidation of methane. The ozone increases because of increase of NO_x emission from human activities that will make OH rise. Also, increasing CH_4 and CO will consume more OH. The total result is that OH decreases with time. Fig.1 gives the long-term trends of CH_4 and OH. The modeled CH_4 agrees well with that deduced from air bubbles trapped in ice core from Law Dome of Antarctica and observed CH_4 at Cape Grim, Tasmania (IPCC, 1994).

Table 2 is the modeled global averaged OH concentration at different time. In 1991, OH decreased by 19% compared with 1840, and it will continue to decrease.

Table 2. Modeled global averaged OH at different time (Unit: 10^5 molecule / cm^3)

Year	N.H.	Divided by OH in 1840	S.H.	Divided by OH in 1840	Global	Divided by OH in 1840
1840	7.28	1	7.08	1	7.17	1
1991	5.81	0.80	5.77	0.82	5.79	0.81
2020	5.47	0.75	5.47	0.77	5.47	0.76

Fig. 2 is the model calculated CH_4 and observation (James, 1992) of CH_4 at ground level in 1991. There is not much change in middle and high latitudes of the Southern Hemisphere, from 40°S to north, CH_4 increases and reaches maximum at 60°N, then it will decrease to north pole.

Annual increase of CH_4 is 37.9 Tg in 1991, the growth rate is 0.84%. According to IPCC(1994), the present annual increase of CH_4 is 37 Tg(35–40 Tg). Modeled growth rate of CO is 1.03–1.06%, which is in good agreement with observation (Crutzen, 1995).

Fig. 3 is the simulation of CH_4 concentration at ground in 35°N–40°N and observation of methane at Minqin(38°N), Gangsu Province from 1985 to 1988. The seasonal behavior of simulation agrees well with observation. The observed CH_4 reaches minimum in July and reaches maximum in December, while modeled CH_4 reaches minimum in June and reaches maximum in December. Reversely, OH reaches maximum in June

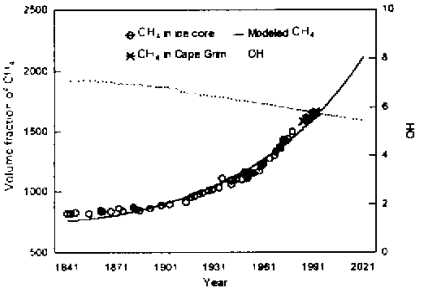

Fig. 1. Long-term trends of CH_4 and OH (in 10^5 molecule / cm^3).

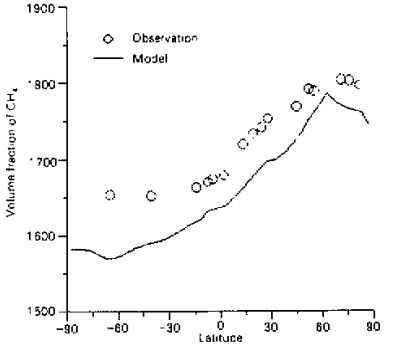

Fig. 2. Modeled result and observation (James, 1992) of CH_4 at ground in 1991.

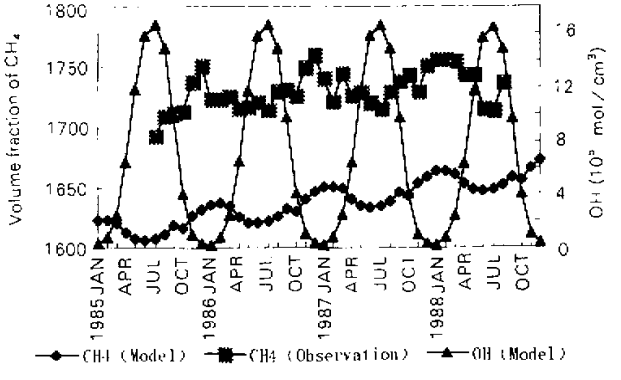

Fig. 3. Calculated CH_4 at 37.5°N and observation at Minqin(38°N) from 1985 to 1988.

and reaches minimum in December.

3.2 *Causes of decrease of methane growth rate in* 1992

For 1983–1991, the average rate of change in CH_4 mixing ratio in the Northern and Southern Hemispheres observed by Dlugokencky et al. (1994) is $11.6 \pm 0.2 \times 10^{-9}$/a in Northern Hemisphere and $11.1 \pm 0.2 \times 10^{-9}$/a in Southern Hemisphere. But in 1992, the growth rates of methane are $1.8 \pm 1.6 \times 10^{-9}$/a in Northern Hemisphere and $11.1 \pm 0.2 \times 10^{-9}$/a in the Southern Hemisphere. That is to say, in 1992, the annual increase of CH_4 decreased by 9.8×10^{-9}/a in the Northern Hemisphere and 3.4×10^{-9}/a in the Southern Hemisphere.

Presently, there are several explanations about the sudden decrease in methane growth rate in 1992:

1) Effects of OH change due to stratospheric ozone depletion

Ozone depletion in the stratospheric during 1992 was larger than that in previous years and hence caused enhanced UV penetration into the troposphere which resulted in increase in OH concentration. According to Bekki et al.(1994), the averaged ozone column decreased by about 10% in the Northern Hemisphere from mid-1991 to the beginning of 1993. So In 1992, the averaged ozone column decreased by about 6% in the stratosphere.

2) Effects of change in atmospheric temperature due to Mount Pinatubo eruption

Observations have demonstrated that the eruption of Mt. Pinatubo reduced temperature in the troposphere by more than 0.7 K during 1992(McCormick et al., 1995). A lowering of temperature changes the chemical reaction rates and decreases water vapor concentrations. For example, a decrease of 0.7 K in atmosphere will cause a decrease of 1.35% for reaction rate of CH_4 and OH, and a decrease of 4.7% for H_2O concentration at 298K.

3) Effects of change in CH_4 sources fluxes

Reduction in gas and coal production in the former Soviet Union may result in the reduction of methane emission in 1992. There is some evidence that biomass burning in the tropics was less intensive in 1992 than in previous years. It's difficult to estimate the possible reduction worldwide. The cooling of the troposphere due to the Mt Pinatubo eruption could have reduced methane emission from natural wetlands, as Dlugokencky et al. (1994) pointed out. In a word, both social and natural elements can reduce CH_4 emissions and then result in decrease in growth rate of CH_4 in 1992.

CO, with which about 60% of OH radicals in the troposphere react, increased by about 1% during 30 years before 1987 (Zander, et al., 1989). But recently, observation by Novelli et al.(1994) showed a pronounced decrease in CO at an average rate of about 7×10^{-9}/a (~ 6%) in the Northern Hemisphere and 4×10^{-9}/a (~ 7%) in the Southern Hemisphere from 1990 to 1993. Observation by Khalil and Rasmussen(1994) showed a decrease in CO concentration at an average rate of about 2.3×10^{-9}/a (~ 5.2%) in the Southern Hemisphere and 1.3×10^{-9}/yr(~ 1.4%) in the Northern Hemisphere from 1987 to 1992. Which is the reason that CO did not increase but decrease in recent years? Does it have influence on the change of growth rate of methane in 1992? In the following, experiments are done to investigate the reasons of sudden decrease of methane growth rate while considering the change of CO concentration (Table 3).

Table 3. Experiments that may result in change in CH_4 growth rate

Experiments(In 1992)	Hemisphere	Growth rate in 1992	Change of growth rate ($\times 10^{-9}$)
Observation	NH.	1.8	-9.8
	SH.	7.7	-3.4
Exp. A (in 1992, Total emission of 533.9 Tg) Model runs as usual, emission increases by 3.85 Tg in 1992 more than in 1991	NH.	14.40	+0.18
	SH.	13.49	+0.18
Exp. B(in 1992, Total emission of 530.1 Tg) Emission in 1992 is same as in 1991	NH.	13.16	-1.24
	SH.	12.82	-0.67
Exp. C(A decrease of 0.7 °C of troposphere temperature)	NH.	17.02	2.62
	SH.	15.64	2.15
Exp. D (stratospheric ozone decreases by 6 %)	NH.	11.90	-2.50
	SH.	11.56	-1.93
Exp. E(Exp. C+ Exp. D)	NH.	14.55	0.15
	SH.	13.71	0.22
Exp.F(Total emission of 506.2 Tg in 1992) Reduction of 21.4 Tg in 30°N-60°N and 6.3 Tg in 0-30°S	NH.	4.40	-10.00
	S.H.	9.91	-3.58
Exp. G(Total emission of 533.9 Tg in 1992) No reduction of CH_4; Reduction of CO emission of 50 Tg	NH.	13.28	-1.12
	SH.	12.69	-0.80
Exp. H(Total emission of 510.9 Tg in 1992) CH_4 : Reduction of 19.3 Tg in 30°N-60°N and 4.4 Tg in S.H. (0-30°S); CO: emission of 50 Tg	NH.	4.45	-9.95
	SH.	9.90	-3.60
Exp. I(Total emission of 533.9 Tg in 1992) No reduction of CH_4 ;Reduction of CO emission of 100 Tg	NH.	12.13	-2.27
	S.H.	11.88	-1.61
Exp. J(Total emission of 514.2 Tg in 1992) CH_4 : Reduction of 17.2 Tg in 30°N-60°N and 2.5 Tg in 0-30°S, CO: Decrease of emission of 100 Tg	NH.	4.48	-9.92
	SH.	9.87	-3.62
Exp. K(Total emission of 514.2 Tg in 1992) a) Stratospheric ozone decreases by 6 %;b)A decrease of 0.7 °C of tropospheric temperature; c) Reduction of 17.2 Tg of CH_4 in 30°N-60°N and 2.5 Tg in 0-30°S; d)Decrease of emission of CO of 100 Tg.	NH.	4.64	-9.76
	SH.	10.09	-3.40

Exp. A: If no changes, the emission of CH_4 continues to increase as the given scenario, the growth rate of CH_4 has very small increase in 1992.

Exp. B: If the emission of CH_4 in 1992 is the same as 1991, the CH_4 growth rate will decrease 1.24×10^{-9} in the Northern Hemisphere and 0.67×10^{-9} in Southern Hemisphere in 1992.

Exp. C: If the temperature in 1992 decreases by 0.7 °C as that McCormick et al.(1995) pointed out, the growth rate of CH_4 will increase in 1992.

Exp. D: If stratospheric ozone decreases by 6% in 1992 according to Bekki et al.(1994), the growth rate of CH_4 will decrease by 2.50×10^{-9} in the Northern Hemisphere and 1.93×10^{-9} in the Southern Hemisphere.

Exp. E: With both stratospheric ozone depletion and cooling of troposphere, there is little influence on the change of CH_4 growth rate (<3%).

Exp. F With decrease of 21.4 Tg emission of CH_4 , the decrease in growth rate of

CH_4 in 1992 will agree well with sudden decrease of CH_4 growth rates observed by Dlugokencky et al.(1994).

Exp. G: Reduction of CO emission of 50 Tg will result in decrease in CH_4 growth rate in 1992 (which accounts for 14% of the observations). Also, CO concentration decreases by 3.35×10^{-9} in the Northern Hemisphere and 1.49×10^{-9} in the Southern Hemisphere which agrees well with observation by Khalil and Rasmussen (1994).

Exp. H: With reduction of CO emission of 50 Tg, and reduction of 19.3 Tg in 30°N–60°N and 4.4 Tg in 0–30°S for CH_4 , the CH_4 growth rate in 1992 will decrease as observations. The CO concentration will decrease by 3.35×10^{-9} in the Northern Hemisphere and 1.49×10^{-9} in the Southern Hemisphere which is in the CO change range observed by Khalil and Rasmussen(1994)..

Exp. I: Reduction of CO emission of 100 Tg will result in decrease in CH_4 growth rate in 1992 (which account for 27% of the observations). The CO concentration will decrease by 8.02×10^{-9} in the Northern Hemisphere and 3.74×10^{-9} in the Southern Hemisphere which agrees well with observation by Novelli(1994).

Exp. J: With reduction of CO emission of 100 Tg, and reduction of 19.3 Tg in 30°N–60°N and 4.4 Tg in 0–30°S for CH_4, the CH_4 growth rate in 1992 will decrease as observed results. The CO concentration will decrease by 8.02×10^{-9} in the Northern Hemisphere and 3.74×10^{-9} in the Southern Hemisphere which agrees well with observation by Novelli(1994).

Exp. K: a) Stratospheric ozone decrease by 6%; b) A decrease of 0.7 °C of troposphere temperature ; c)Reduction of 17.2 Tg of CH_4 in 30°N–60°N and 2.5 Tg in 0°–30°S; d) Decrease of CO emission of 100 Tg . This scenario will result in both decrease in CH_4 growth rate in 1992 and decrease of CO concentration at the same time.

From above experiments, we find that the decrease of emission of CH_4 is the main reason of sudden decrease in growth rate of CH_4 in 1992 (about 73%), another important reason is decrease of emission of CO (about 27%). The decrease in CH_4 growth rate due to ozone depletion in the stratosphere, which is 2.50×10^{-9} in the Northern Hemisphere and 1.93×10^{-9} in the Southern Hemisphere is almost offset by the increase in CH_4 growth rate due to cooling of the atmosphere after the Mt. Pinatubo eruption, which is 2.62×10^{-9} in the Northern Hemisphere and 2.15×10^{-9} in the Southern Hemisphere.

4. Conclusion

Using this two-dimensional model, we simulate the long-term trends of CH_4 and OH. Then we do several sensitivity experiments to study the reason which may result in dramatic decrease in the growth rate of methane in 1992.The main results are as follows.

1) The calculated global averaged concentration of CH_4 pre-industry revolution is 760×10^{-9}, its emission is 280 Tg per year. In 1991, the concentration of CH_4 is 1611.9×10^{-9}, with emission of 530.1 Tg per year. This result is in good agreement with IPCC (1994). With the given scenario, in 2020, the concentration of CH_4 will be 2090.7×10^{-9}, with emission of 766.2 Tg per year. From 1840 to 1991, the concentration of OH changed from 7.17×10^5 molecule / cm^3 to 5.79×10^5 molecule / $cm^3$and 75.7×10^{-9}, and will be 5.47×10^5 molecule / cm^3 in 2020.

2) The calculated annual growth rate of methane in 1991 is 37.9 Tg or 0.84%.

3) The decrease in CH_4 growth rate due to ozone depletion in the stratosphere is almost offset by the increase in CH_4 growth rate due to cooling of the atmosphere after the Mt. Pinatubo eruption.

4) Besides two reasons mentioned above, the decrease in the growth rate of methane in 1992 has two main reasons: one is the direct decrease of methane emission of 17.2 Tg in the Northern Hemisphere(30°N–60°N) and 2.5 Tg in the Southern Hemisphere (0–30°S), another is the decrease of CO emission of 100 Tg.

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