Study on Atmospheric Components in Northern China

Renjian Zhang Lixin Ren Mingxing Wang Yongfu Xu

Institute of Atmosphere Physics

Chinese Academy of Science,Beijing,100029,China

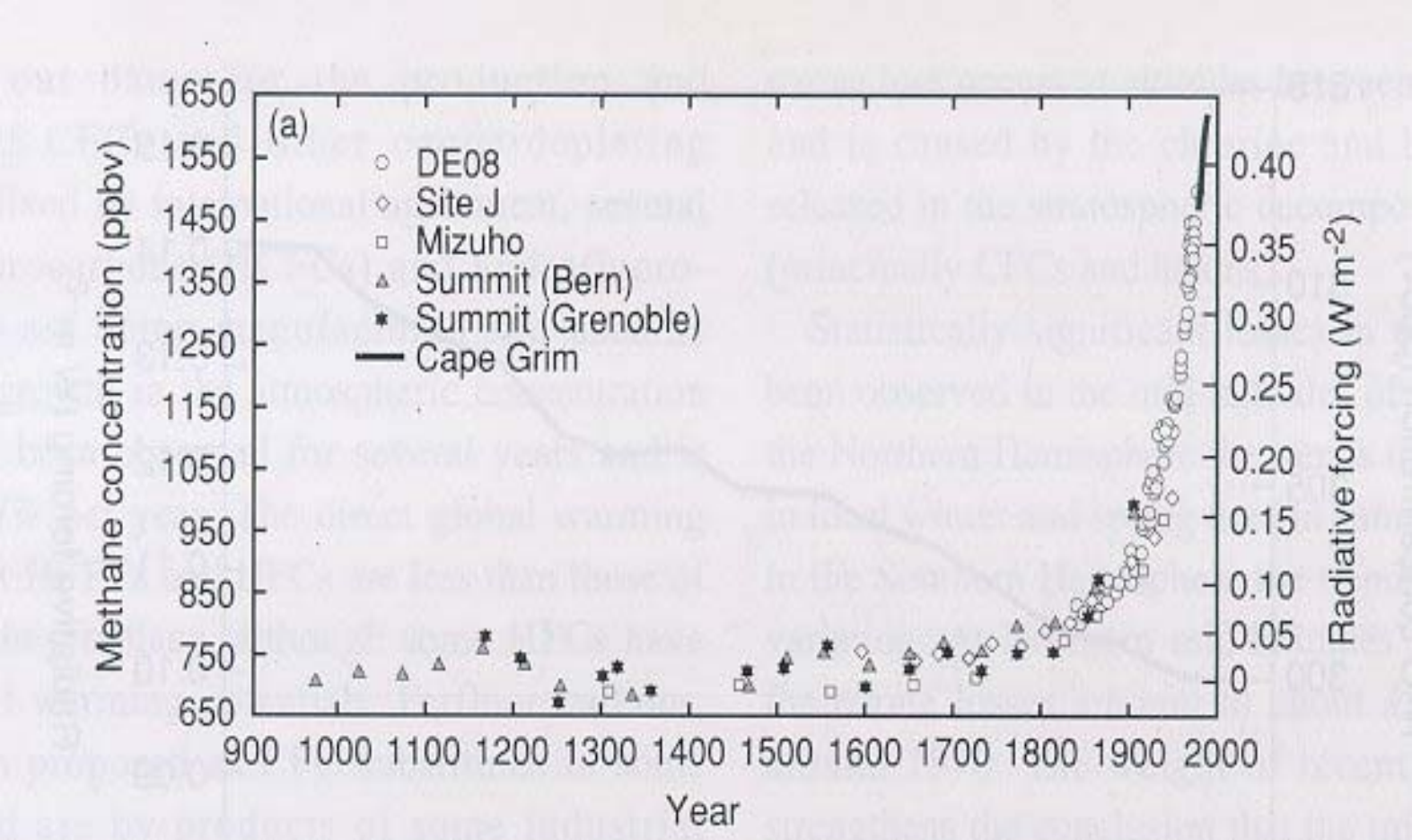
Report Content

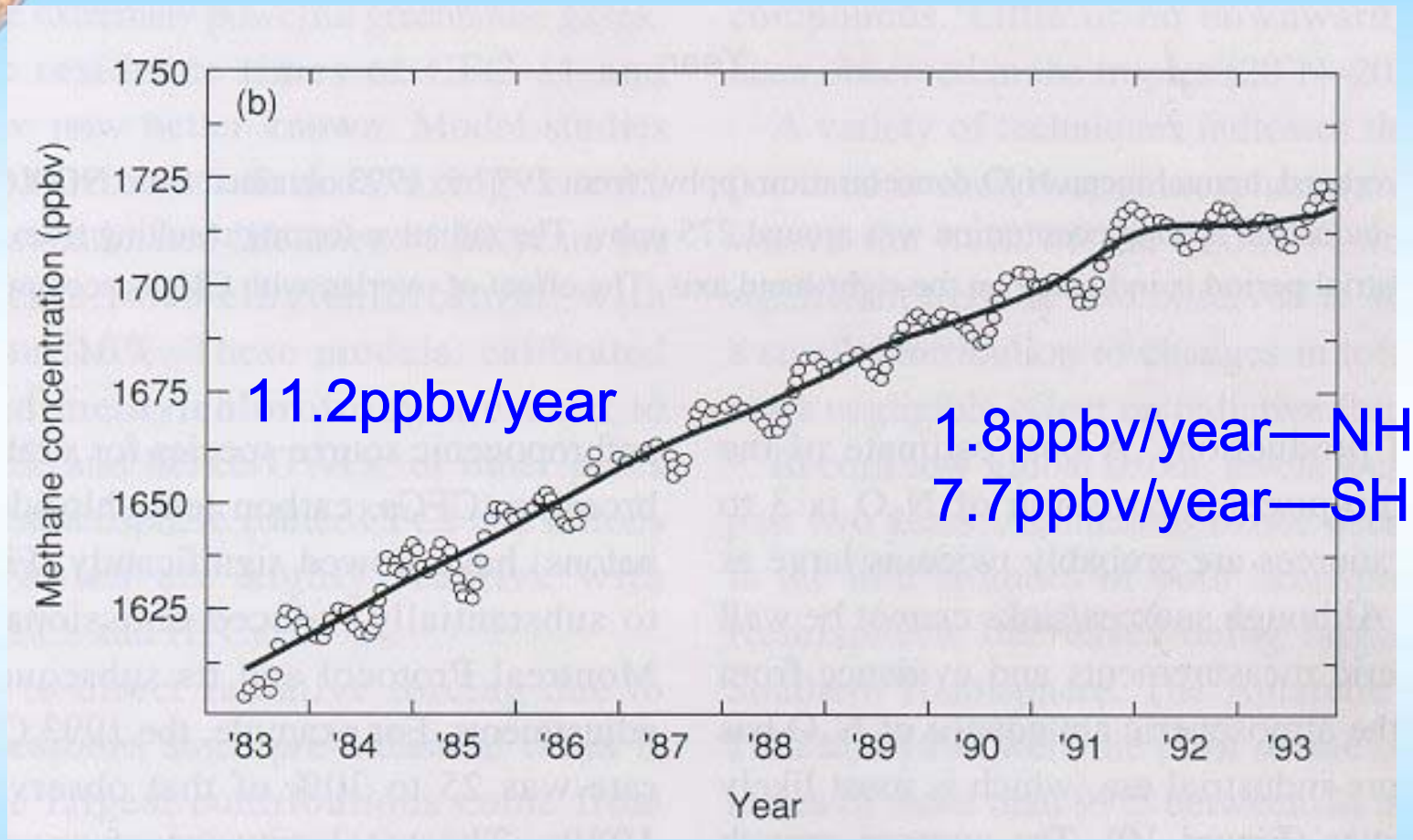
1. Simulation of CH_4 and CO at Minqin

2. Recent Observation of Dust Aerosols

CH_4 in ice core from Antarctica and surface station over the last 1000 years

(IPCC 1994)





（Many of these factors contributor to the observed CH_4 in 1992,but it is not clear what their relative contributions are.IPCC 1995）

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.

This model is by Zhang R.J.,(1999,2000,2001)

Global 2-D Atmospheric Chemistry Model

Diabatic rates → **Residual circulation**

Peaceman-Rachford method

Meteorological data ECMWF

Emissions of CO, CH_4,NOx → **2-D Model**

GACM

- **emissions**
- **transport**
- **diffusion**
- **dry deposition**
- **wet deposition**
- **chemical process**

34 Species

104 reactions

Long-term trends of CH_4,CO,OH

Experiments are done to study…

Chemical mechenism

Chemical species:

Fixed species(5): N_2 O_2 H_2 CO_2 H_2O

Transportation species(16) :

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

Short life-time species(13):

$O(^3P)$, $O(^1D)$, H, OH, HO_2, N, NO_3, HCO, CH_2O, CH_3, CH_3O, CH_3O_2, CH_3OOH

Chemical and photo reaction

Two body reaction and three body reaction	81
Photo reaction	23

Number	Reaction	Reaction rate (cm^3 $molecules^{-1}$ s^{-1})
1	$O(^1D)+N_2 \rightarrow O(^3P)+N_2$	$1.8\times10^{-11}exp(107/T)$
2	$O(^1D)+O_2 \rightarrow O(^3P)+O_2$	$3.2\times10^{-11}exp(67/T)$
3	$O(^1D)+N_2O \rightarrow N_2+O_2$	4.9×10^{-11}
4	$O(^1D)+N_2O \rightarrow NO+NO$	6.7×10^{-11}
5	$O(^1D)+H_2O \rightarrow 2OH$	2.2×10^{-10}
6	$O(^1D)+CH_4 \rightarrow OH+CH_3$	1.4×10^{-10}
7	$O(^1D)+CH_4 \rightarrow H_2+CH_2O$	1.4×10^{-11}
8	$O(^1D)+H_2 \rightarrow OH+H$	1.1×10^{-10}
9	$O(^1D)+O_3 \rightarrow O_2+O_2$	1.2×10^{-10}
10	$O(^1D)+O_3 \rightarrow O_2+2O(^3P)$	1.2×10^{-10}
11	$O(^1D)+CCL_4 \rightarrow 4CL$	3.3×10^{-10}
12	$O(^1D)+CF_2CL_2 \rightarrow 2CL$	1.4×10^{-10}
13	$O(^1D)+CFCL_3 \rightarrow 3CL$	2.3×10^{-10}
14	$O(^3P)+OH \rightarrow O_2+H$	$2.2\times10^{-11}exp(117/T)$
15	$O(^3P)+O_3 \rightarrow O_2+O_2$	$8.0\times10^{-12}exp(-2060/T)$
16	$O(^3P)+HO_2 \rightarrow OH+O_2$	$3.0\times10^{-11}exp(200/T)$
17	$O(^3P)+H_2O_2 \rightarrow OH+HO_2$	$1.4\times10^{-12}exp(-2000/T)$
18	$O(^3P)+NO_2 \rightarrow NO+O_2$	$6.5\times10^{-12}exp(120/T)$
19	$O(^3P)+NO_3 \rightarrow O_2+NO_2$	1.0×10^{-11}
20	$CH_3+O(^3P) \rightarrow CH_2O+H$	1.4×10^{-10}
21	$CH_3O_2+NO \rightarrow CH_3O+NO_2$	$4.2\times10^{-12}exp(180/T)$
22	$OH+OH \rightarrow H_2O+O(^3P)$	$4.2\times10^{-12}exp(-242/T)$
23	$OH+H_2O_2 \rightarrow H2O+HO_2$	$3.1\times10^{-12}exp(-187/T)$
24	$OH+HO_2 \rightarrow H_2O+O_2$	$4.6\times10^{-11}exp(230/T)$
25	$OH+CH_3CL \rightarrow H_2O+CLO$	$1.8\times10^{-12}exp(-1112/T)$
26	$OH+CH_3CCL_3 \rightarrow H_2O+[3CL]$	$5.4\times10^{-12}exp(-1820/T)$
27	$OH+CO \rightarrow CO_2+H$	$1.5\times10^{-13}\times(1+0.6P_{atm})$
28	$OH+CH_4 \rightarrow CH_3+H_2O$	$2.3\times10^{-12}exp(-1700/T)$
29	$CH_3O_2+ CH_3O_2 \rightarrow 2CH_3O+O_2$	1.5×10^{-13}
30	$O(^3P)+CH_3 \rightarrow HCO+OH$	$3.4\times10^{-11}exp(-1600/T)$

30	$O(^3P)+CH_3 \rightarrow HCO+OH$	$3.4\times10^{-11}exp(-1600/T)$
31	$OH+CH_2O \rightarrow H_2O+CHO$	1.0×10^{-11}
32	$OH+O_3 \rightarrow HO_2+O_2$	$1.6\times10^{-12}exp(-940/T)$
33	$O_3+H \rightarrow OH+O_2$	$1.4\times10^{-10}exp(-470/T)$
34	$O_3+HO_2 \rightarrow OH+O_2+O_2$	$1.4\times10^{-14}exp(-580/T)$
35	$O_3+N \rightarrow NO+O_2$	1.0×10^{-15}
36	$O_3+NO \rightarrow NO_2+O_2$	$1.8\times10^{-12}exp(-1370/T)$
37	$O_3+NO_2 \rightarrow NO_3+O_2$	$1.2\times10^{-13}exp(-2450/T)$
38	$HO_2+H \rightarrow H2O+O(^3P)$	1.6×10^{-12}
39	$HO_2+HO_2 \rightarrow H_2O_2+O_2$	$2.2\times10^{-13}exp(600/T)$
40	$HO_2+NO \rightarrow NO_2+OH$	$3.7\times10^{-12}exp(240/T)$
41	$HO_2+NO_2 \rightarrow HO_2NO_2$	2.2×10^{-12}
42	$N_2O_5+H_2O \rightarrow 2HNO_3$	5.0×10^{-12}
43	$N+O_2 \rightarrow NO+O(^3P)$	$4.4\times10^{-12}exp(-3220/T)$
44	$NO+NO_3 \rightarrow NO_2+NO_2$	$1.3\times10^{-11}exp(250/T)$
45	$N+NO \rightarrow N_2+O(^3P)$	3.4×10^{-11}
46	$N+NO_2 \rightarrow N_2O+O(^3P)$	$2.1\times10^{-11}exp(-580/T)$
47	$OH+HNO_4 \rightarrow H_2O+NO_2+O_2$	$1.3\times10^{-12}exp(-380/T)$
48	$O(^3P)+CH_4 \rightarrow CH_3+OH$	$3.5\times10^{-11}EXP(-4550/T)$
49	$CH_3O_2+HO_2 \rightarrow CH_3OOH+O_2$	$3.3\times10^{-13}exp(800/T)$
50	$CH_3O+O_2 \rightarrow CH_2O+HO_2$	$3.9\times10^{-14}exp(-900/T)$
51	$CH_3O_2+O(^3P) \rightarrow CH_3O+O_2$	3.0×10^{-11}
52	$HCO+O_2 \rightarrow CO+HO_2$	$3.5\times10^{-12}exp(140/T)$
53	$OH+H_2 \rightarrow H_2O+H$	$5.5\times10^{-12}exp(-2000/T)$
54	$O(^3P)+HNO_4 \rightarrow OH+NO_2+O_2$	$7.8\times10^{-11}exp(-3400/T)$
55	$OH+HNO_2 \rightarrow H_2O+NO_2$	6.6×10^{-12}
56	$O(^1D)+CO_2 \rightarrow O(^3P)+CO_2$	$7.4\times10^{-11}exp(117/T)$
57	$O(^1D)+CH_3CL \rightarrow CL+CH_2O$	4.0×10^{-10}
58	$O(^1D)+CH_3CCL_3 \rightarrow 3CL+CH_2O$	4.0×10^{-10}
59	$O(^3P)+CH_2O \rightarrow OH+CHO$	$3.0\times10^{-11}exp(-1500/T)$
60	$OH+HNO_3 \rightarrow H_2O+NO_3$	3.2×10^{-13}
61	$OH+HNO_4 \rightarrow H_2O+O_2+NO_2$	$1.3\times10^{-12}exp(380/T)$
62	$H+HO_2 \rightarrow 2OH$	7.3×10^{-11}
63	$H+HO_2 \rightarrow H_2+O_2$	6.5×10^{-12}
64	$OH+CH_3OOH \rightarrow CH_3O_2+H_2O$	$1.7\times10^{-12}exp(220/T)$
65	$OH+CH_3OOH \rightarrow CH_2O+OH+H_2O$	$2.9\times10^{-12}exp(190/T)-K_{64}$
66	$CH_2O+NO_3 \rightarrow CO+HO_2+HNO_3$	6.0×10^{-16}
67	$OH+HNO_3 \rightarrow H_2O+NO_3$	$9.4\times10^{-15}exp(778/T)$
68	$O(^3P)+O(^3P)+M \rightarrow O_2+M$	$4.7\times10^{-33}(300/T)^2[M]$

Table 3. Photochemical reaction in the 2-D model (s^{-1})

Number	Reaction
1	$O_2 \rightarrow 2O(^3P)$
2	$O_3 \rightarrow O_2+O(^1D)$
3	$O_3 \rightarrow O_2+O(^3P)$
4	$H_2O \rightarrow OH+H$
5	$HO_2 \rightarrow OH+O(^3P)$
6	$H_2O_2 \rightarrow 2OH$
7	$NO \rightarrow N+O(^3P)$
8	$NO_2 \rightarrow NO+O(^3P)$
9	$NO_3 \rightarrow NO+O_2$
10	$NO_3 \rightarrow NO_2+O(^3P)$
11	$N_2O \rightarrow N_2+O(^1D)$
12	$N_2O_5 \rightarrow NO_2+NO_3$
13	$HNO_2 \rightarrow OH+NO$
14	$HNO_3 \rightarrow OH+NO_2$
15	$HNO_4 \rightarrow HO_2+NO_2$
16	$CCL_4 \rightarrow 4CL$
17	$CCL_3F \rightarrow 3CL$
18	$CF_2CL_2 \rightarrow 2CL$
19	$CH_3CL \rightarrow CH_3+CL$
20	$CH_3CL_3 \rightarrow 3CL$
21	$CH_2O \rightarrow CO+H$
22	$CH_2O \rightarrow CO+H_{2F}$
23	$CH_3OOH \rightarrow CH_3O+OH$

Differential scheme

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

$$\frac{\partial \bar{C}}{\partial t}+\frac{\partial(\rho v\bar{C}\cos\phi)}{\rho\cos\phi\,\partial y}+\frac{\partial(\rho w\bar{C})}{\rho\,\partial z}=S+LC+\frac{1}{\rho\cos\phi}\frac{\partial}{\partial y}\left(\rho K_{yy}\cos\phi\frac{\partial\bar{C}}{\partial y}\right)+\frac{1}{\rho}\frac{\partial}{\partial z}\left(\rho K_{zz}\frac{\partial\bar{C}}{\partial z}\right) \qquad (6)$$

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

Two-dimensional tracer equations are solved by the use of Peaceman-Rachford method (Su Yucheng et al., 1989; Wang Suren et al., 1992). First-order up stream scheme is used to treat the advection term. The time step is 8 hours.

Time step=4×2=8hour

More detail about the model:

1. Zhang Renjian and Mingxing Wang, Modeling the sudden decrease in CH_4 growth rate in 1992, Advances in Atmospheric Sciences, 16(2), 242-250, 1999.
2. Zhang Renjian, Wang Mingxing, and Zeng Qingcun, Global two-dimensional chemical model and its simulation of composition of atmosphere, Adv. Atmos.Sci., 17(1), 72-82,2000.
3. Zhang Renjian, Wang Mingxing and Renlixin, Long-term trends of carbon monoxide inferred using a 2-d Model, Chemosphere, 3(2),123-132,2001.

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.

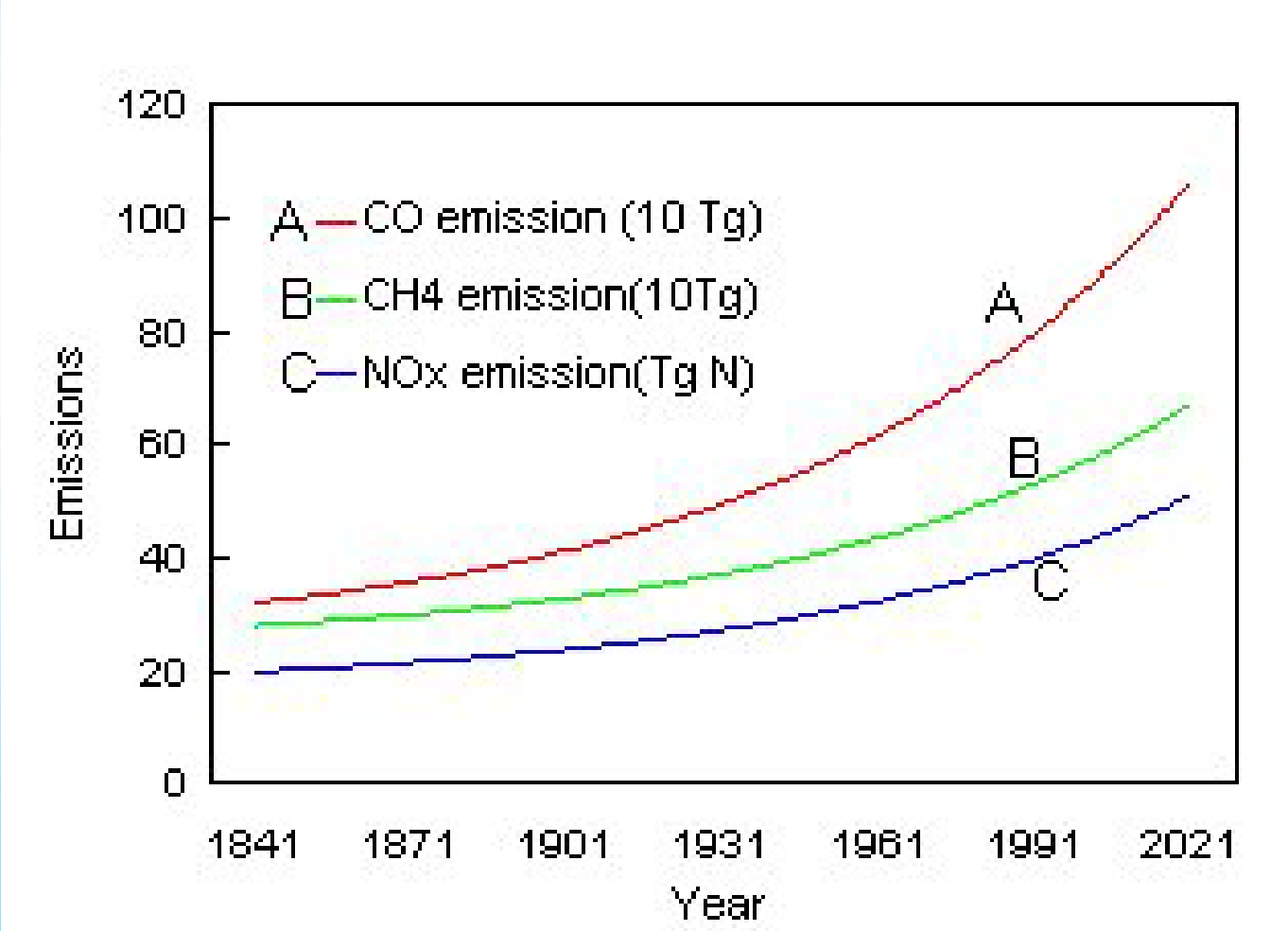
1.Simulation of CH_4, CO at Minqin inferred by 2D Global Chemical model

工业革命以来排放源的长期变化

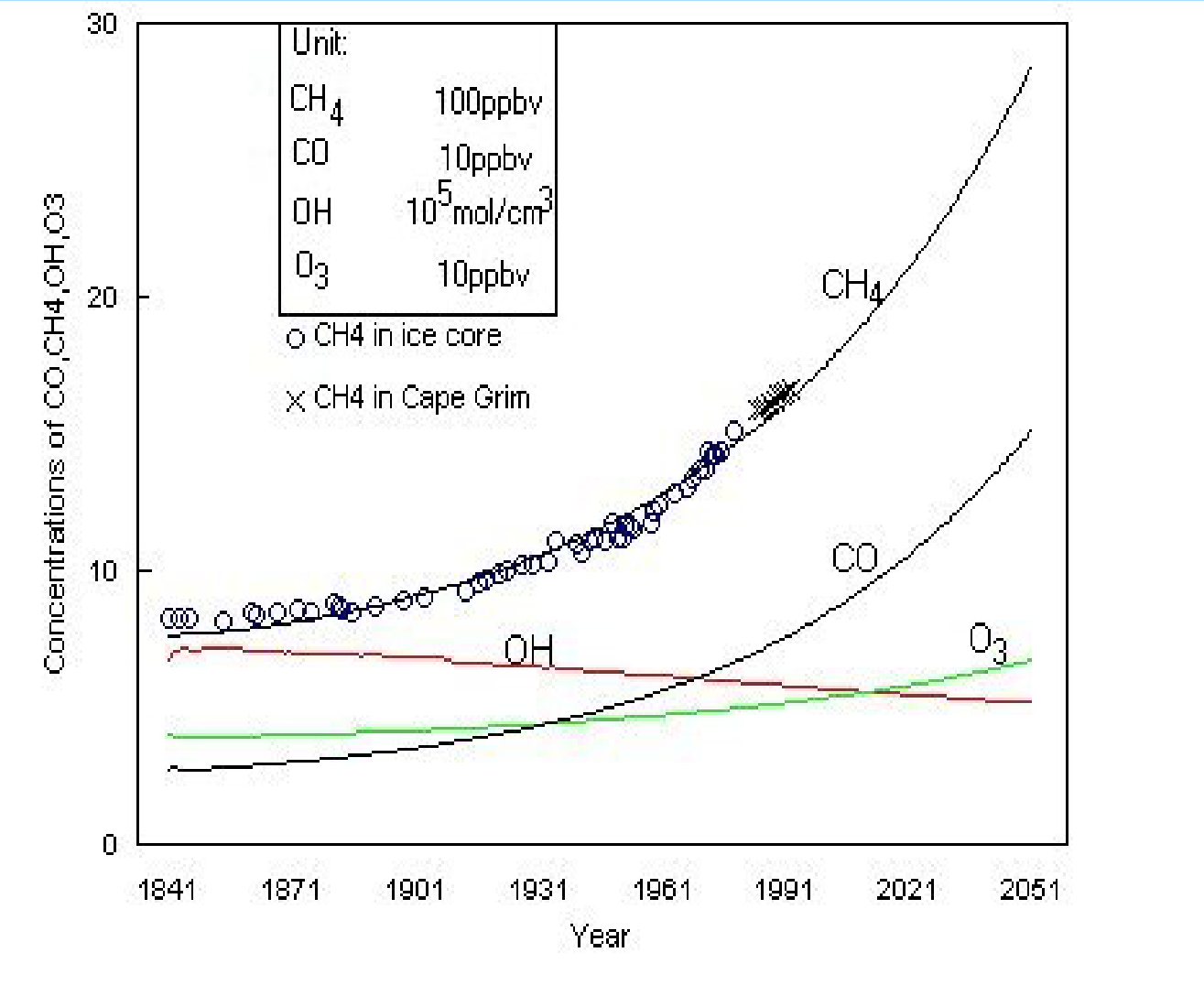
CH_4 $S_{year}=280+39.225(e^{(0.0132324*(year-1840)}-1)$

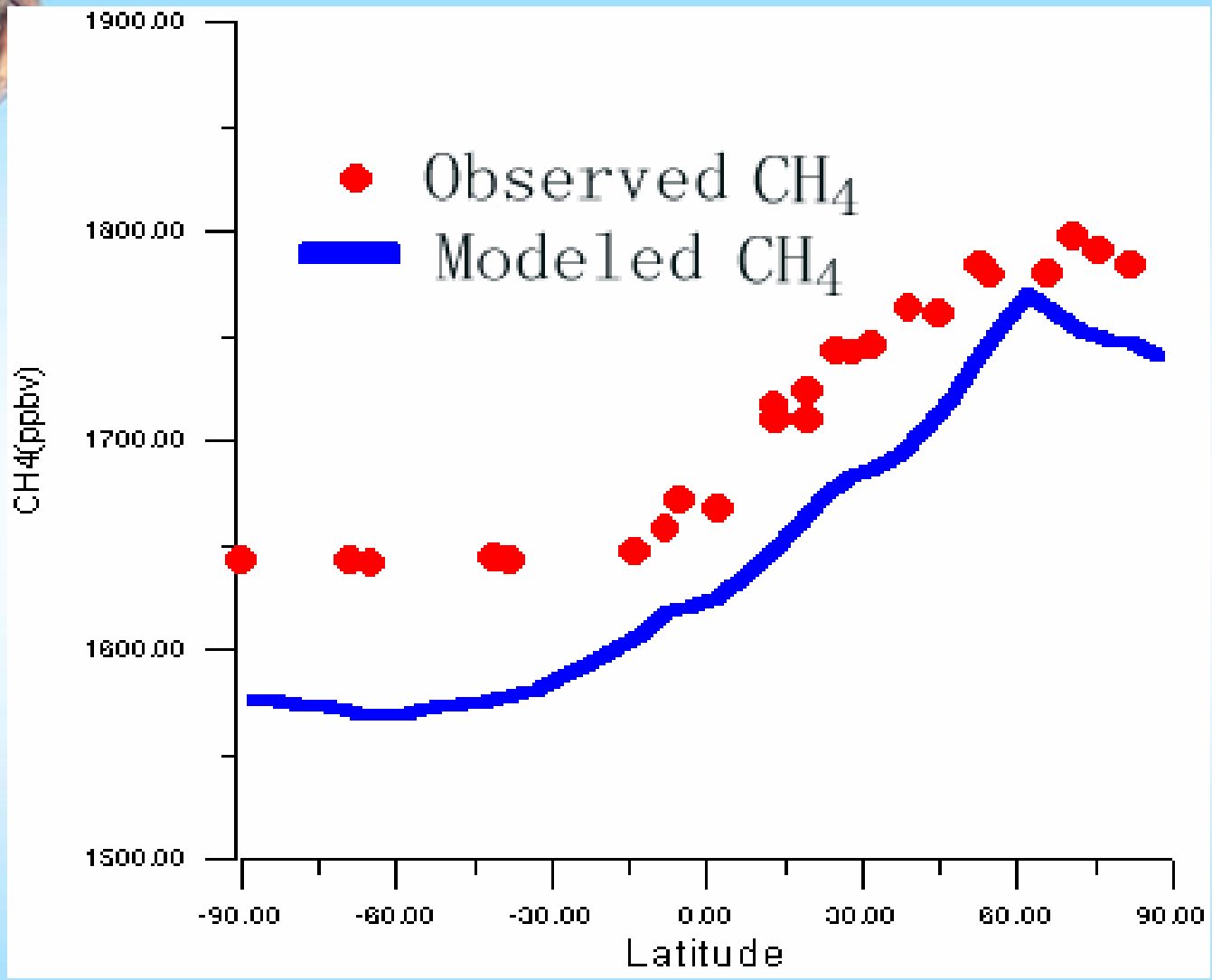
CO $S_{year}=320+76.8(e^{(0.01312*(year-1840)}-1)$

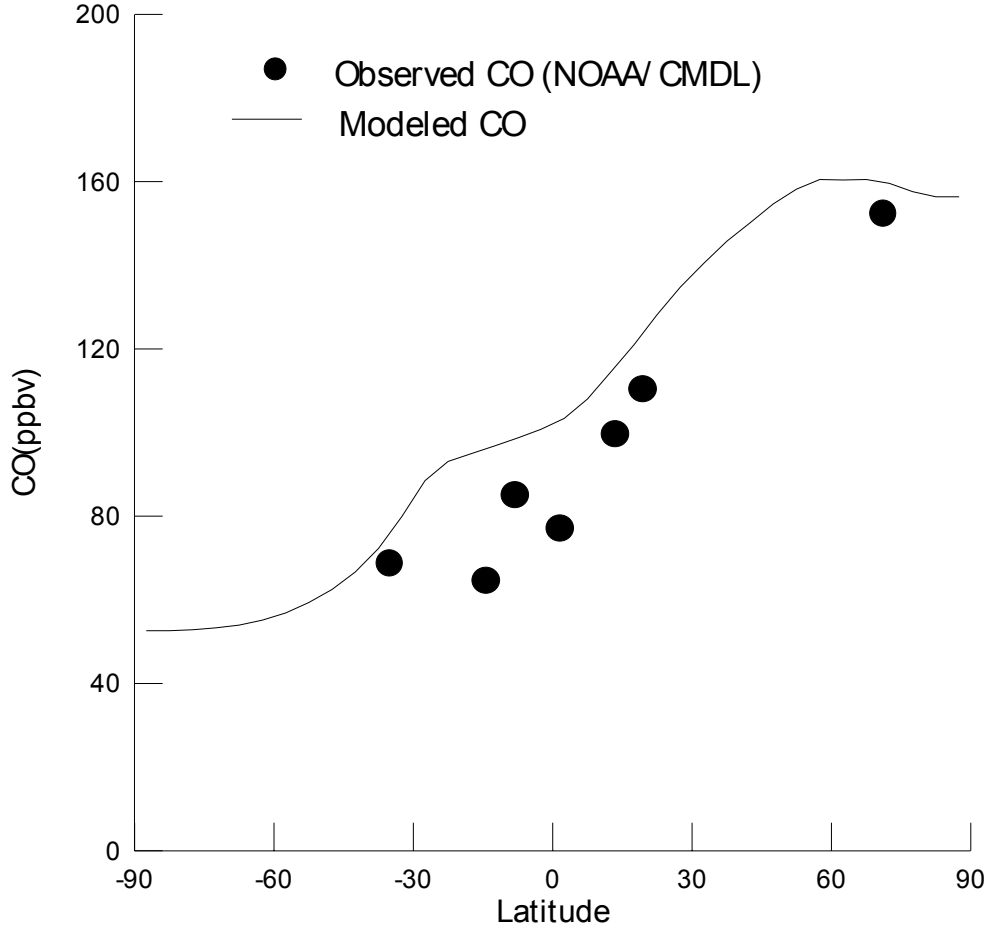
NO_x $S_{year}=20+3.2(e^{(0.01312*(year-1840)}-1)$



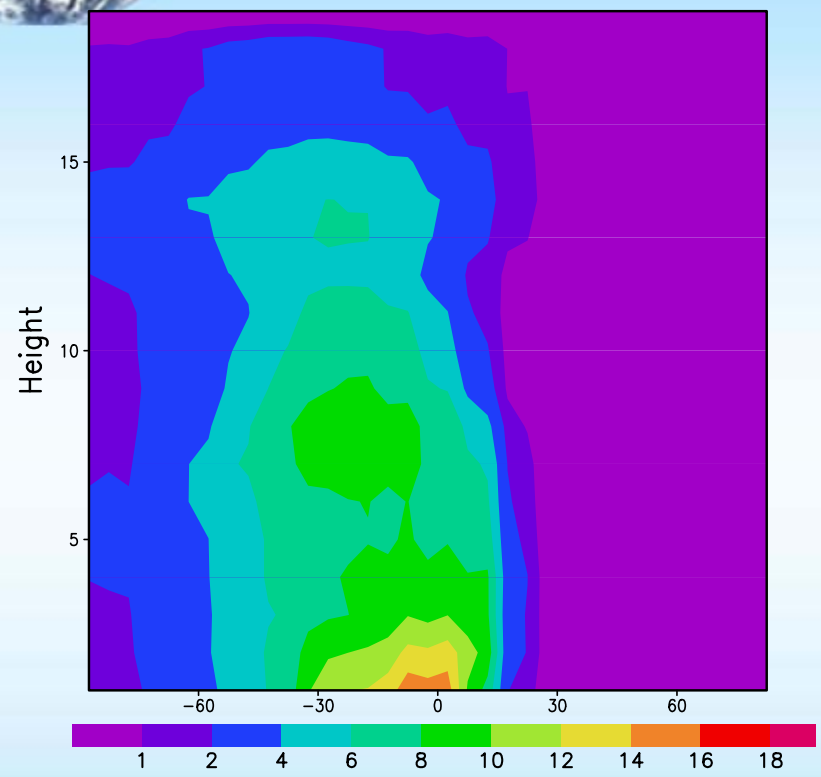
Modeled long-term trends of CH_4, CO, OH and O_3

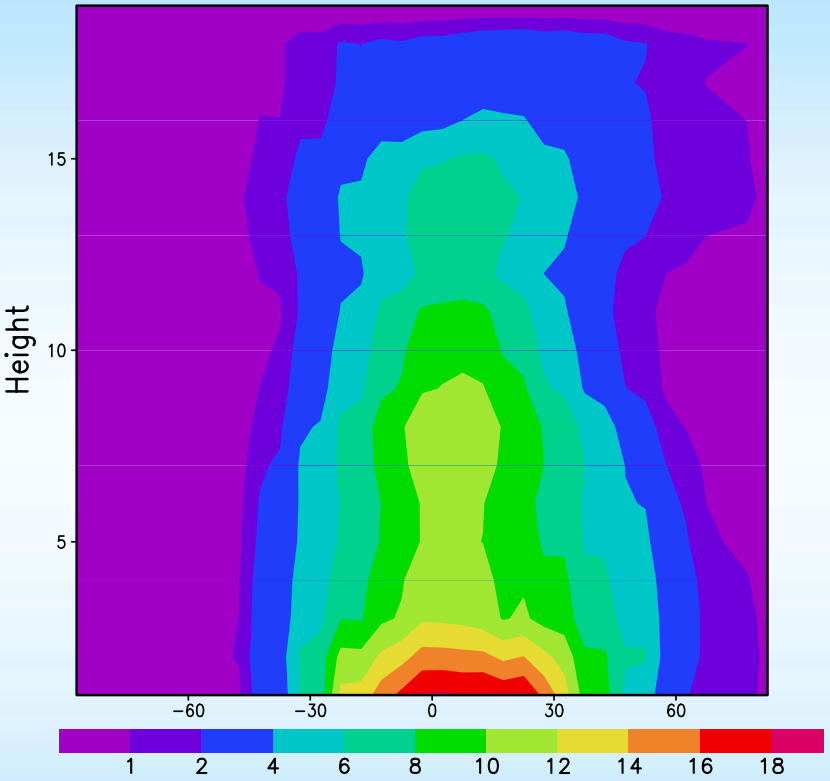



Observed CH_4
Modeled CH_4
1900.00
1800.00
1700.00
1600.00
1500.00
CH4(ppbv)
-90.00
-60.00
-30.00
0.00
30.00
60.00
90.00
Latitude

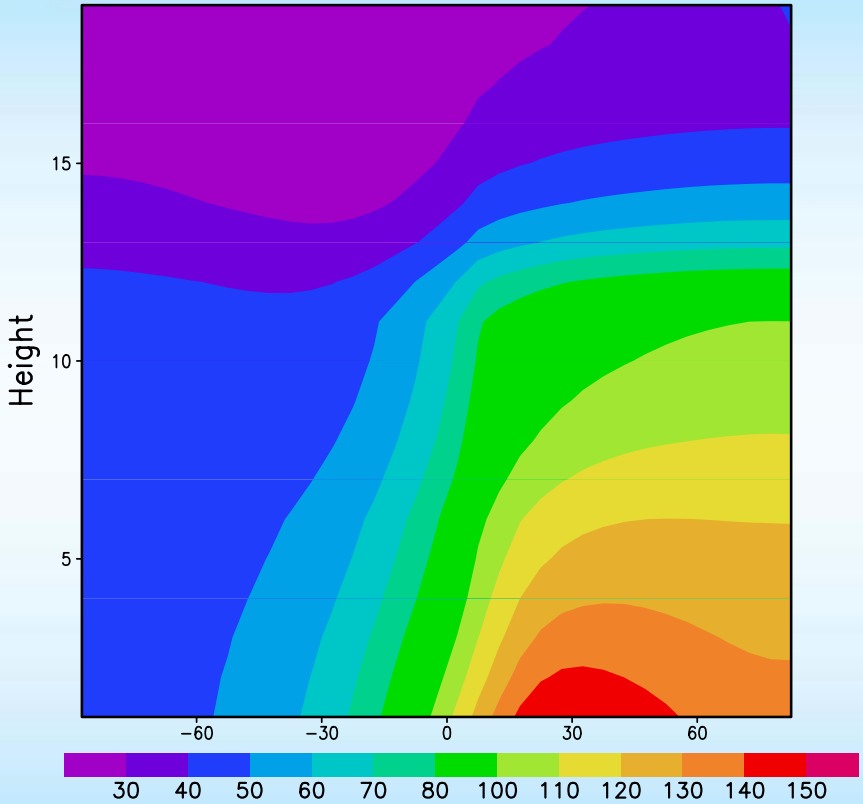


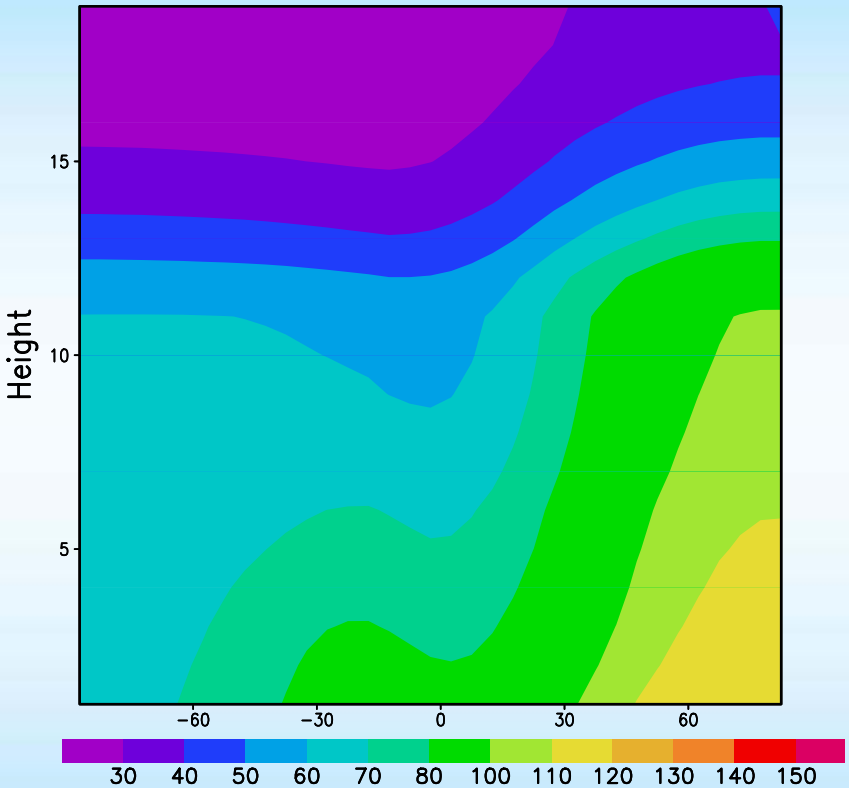
Latitudinal distribution of ground CO in 1990



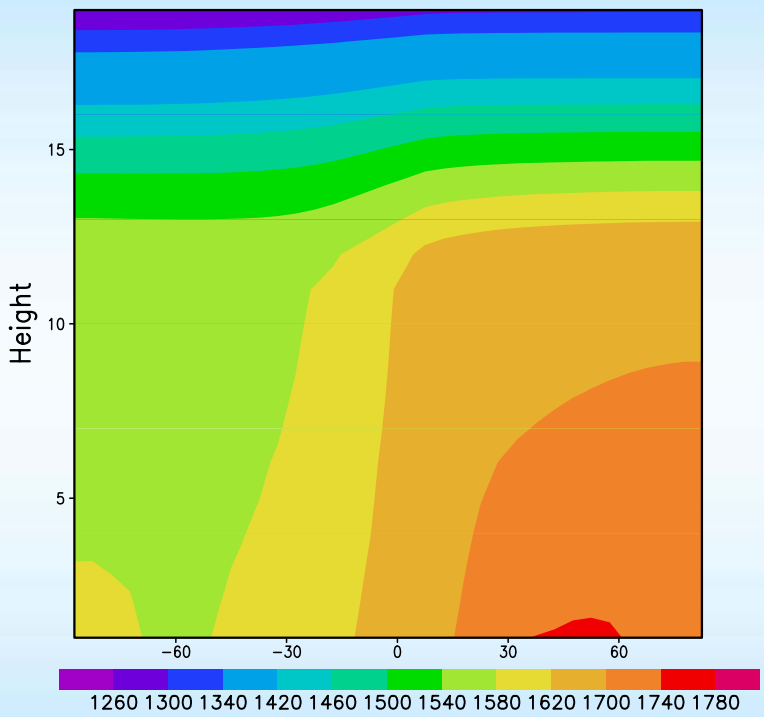


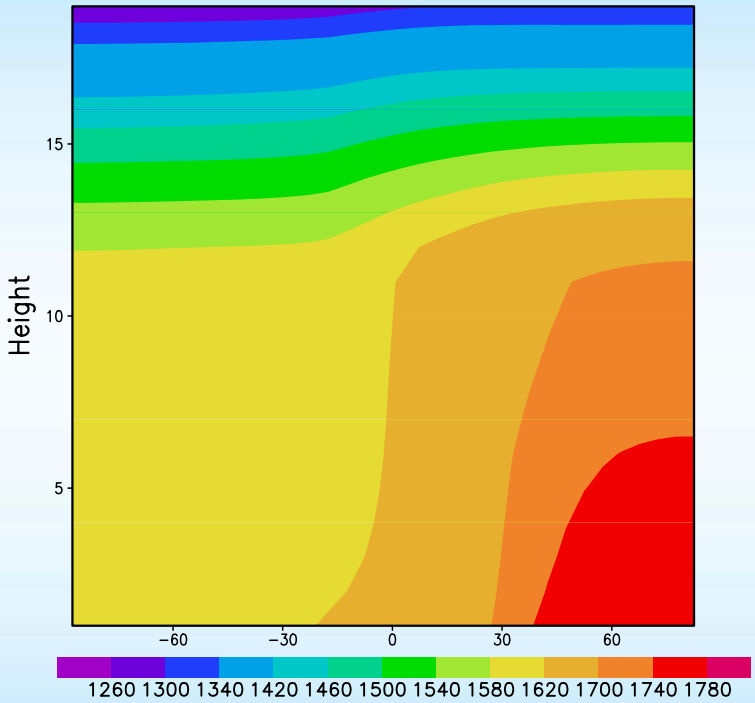
The distribution of OH in 1991(Jan. And Jul.) (Unit: ppbv)





The distribution of CO in 1991(Jan. And Jul.) (Unit: ppbv)





The distribution of CH_4 in 1991(Jan. And Jul.) (Unit: ppbv)

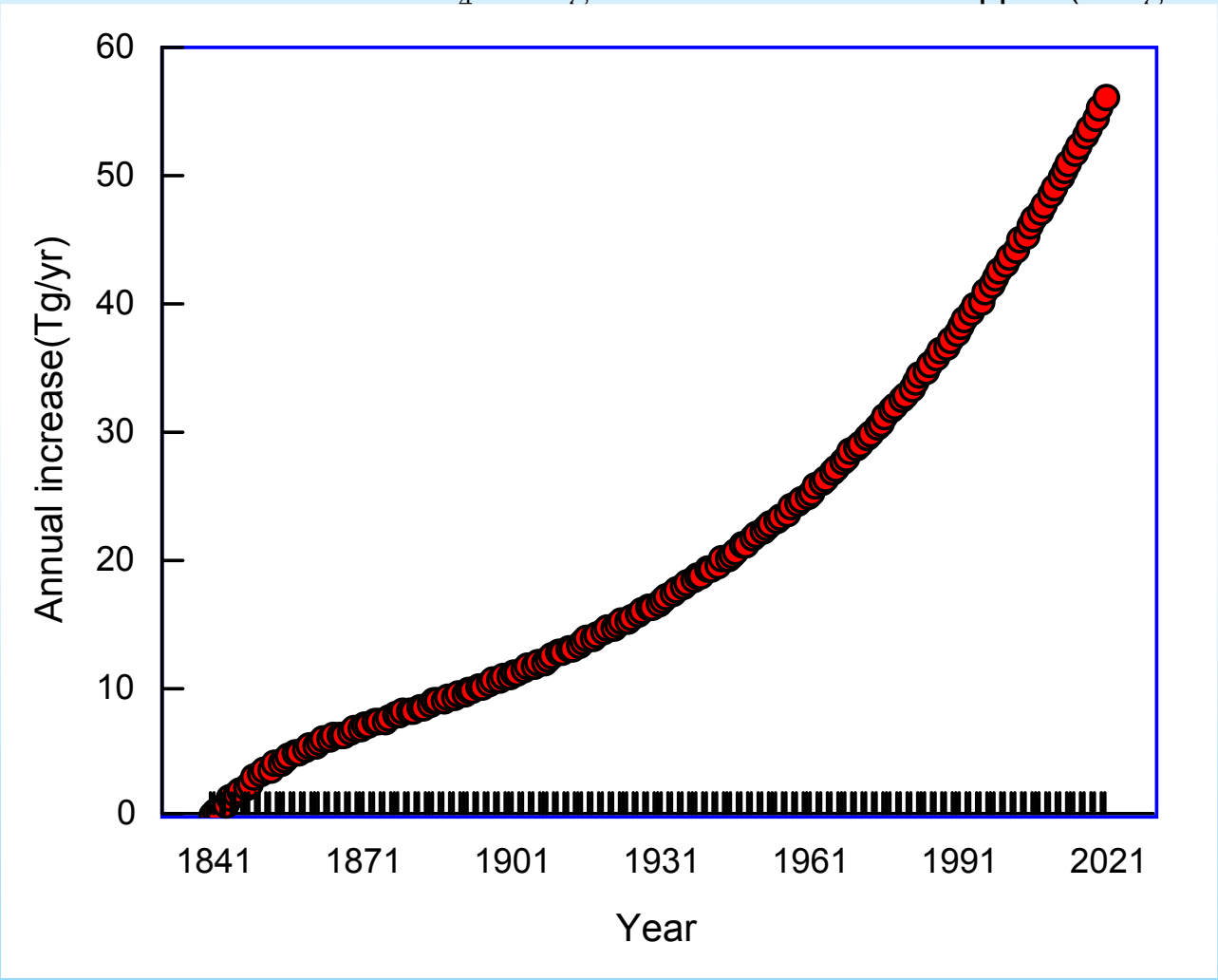
Annual growth rate(Tg/yr)

Modeled increase of CH_4 is 37.9Tg/yr in 1990, or 0.84%/yr, 13ppbv/yr.

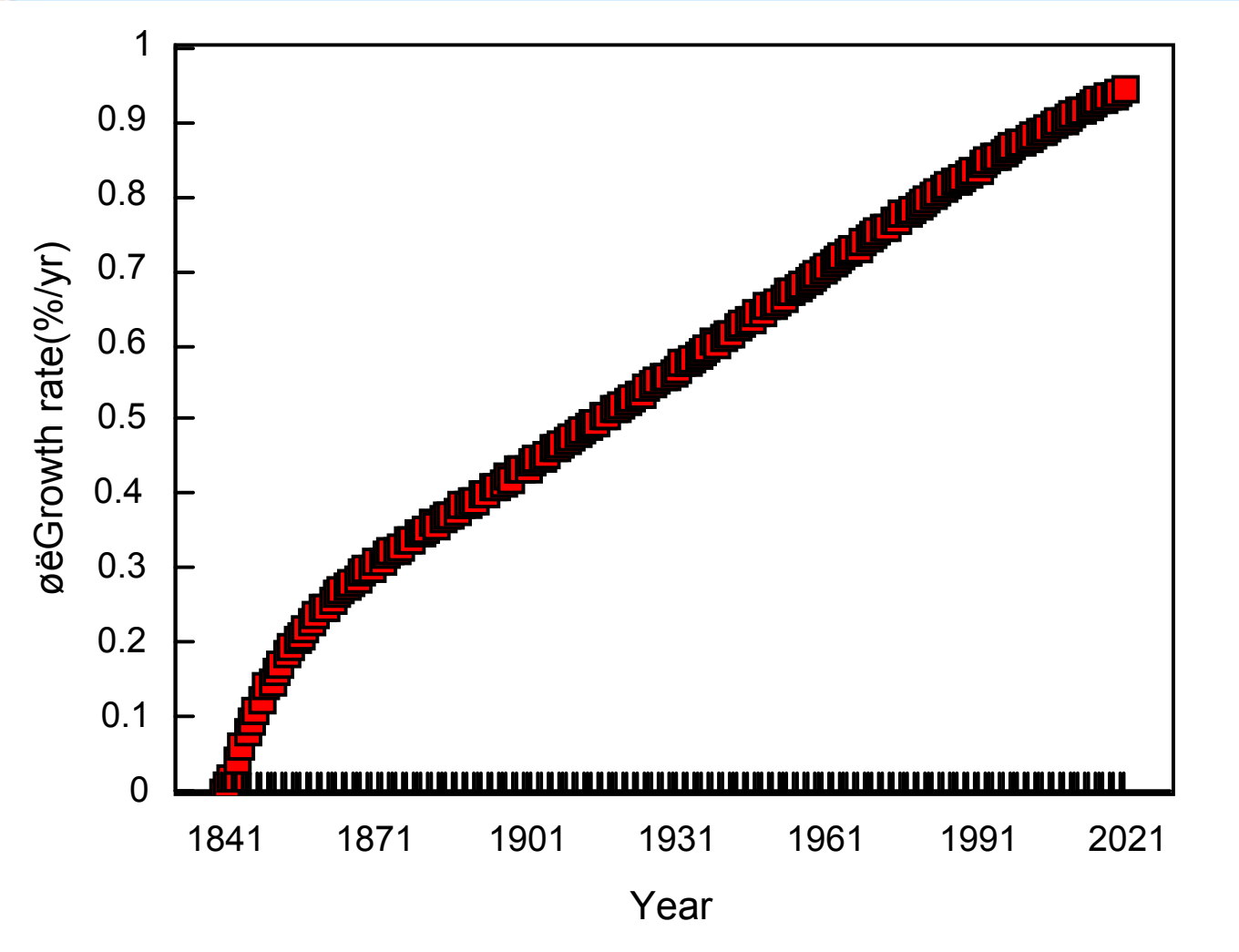
According to IPCC (1994), atmospheric increase of CH_4 from 1980 to 1990 was about ~35-40 Tg/yr

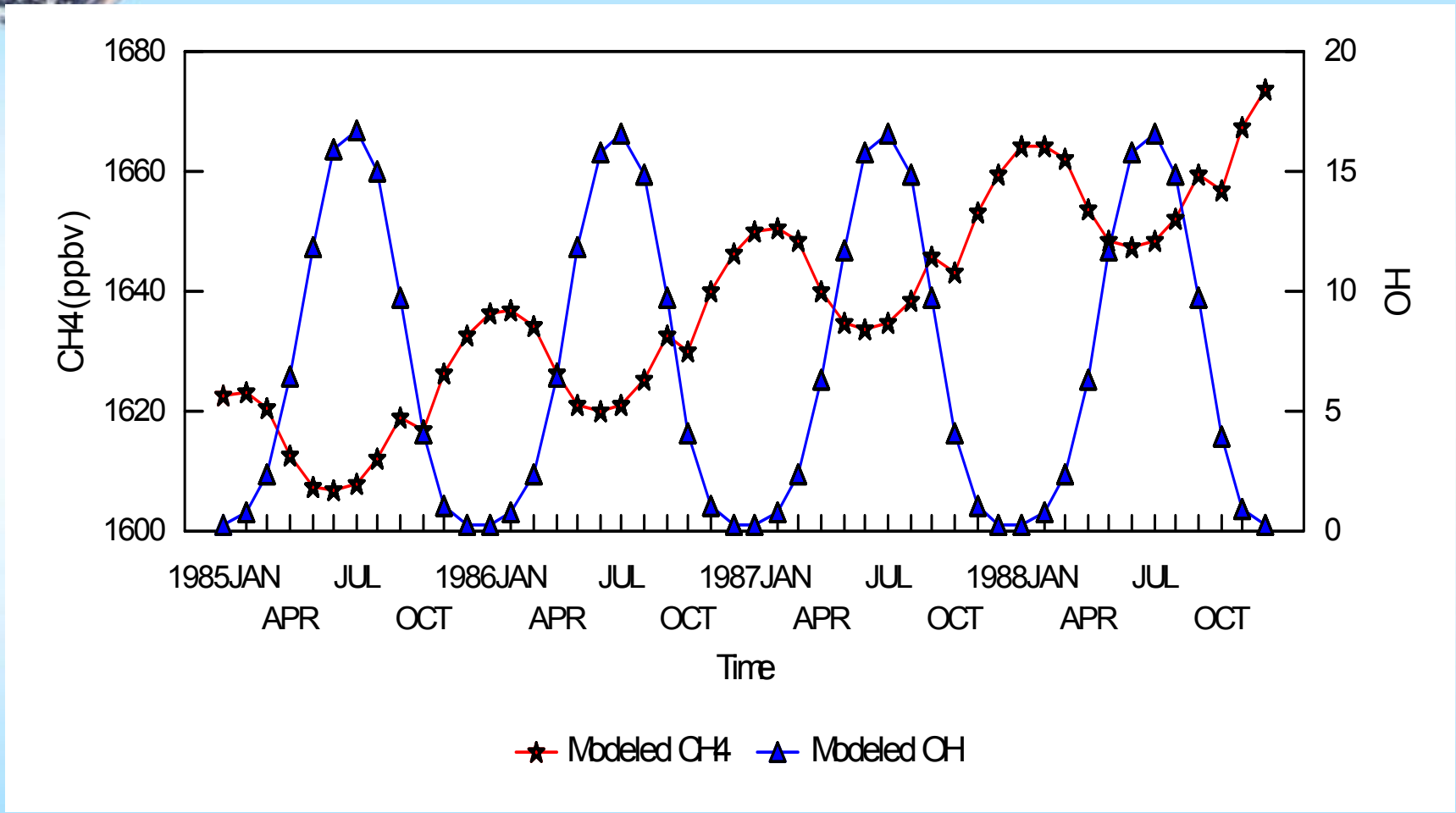
The calculated annual increase of global CH_4 mixing ratio during 1983-1991 is ~12.1-13.3ppbv.

The observed annual increase of CH_4 during 1983-1991 is 11.1-11.6ppbv (Dlugokencky et.al., 1994)



Modeled annual growth rate of CH_4(%/yr)





Modeled CH_4 and OH at Minqin(OH:10^5molecule/cm^3)

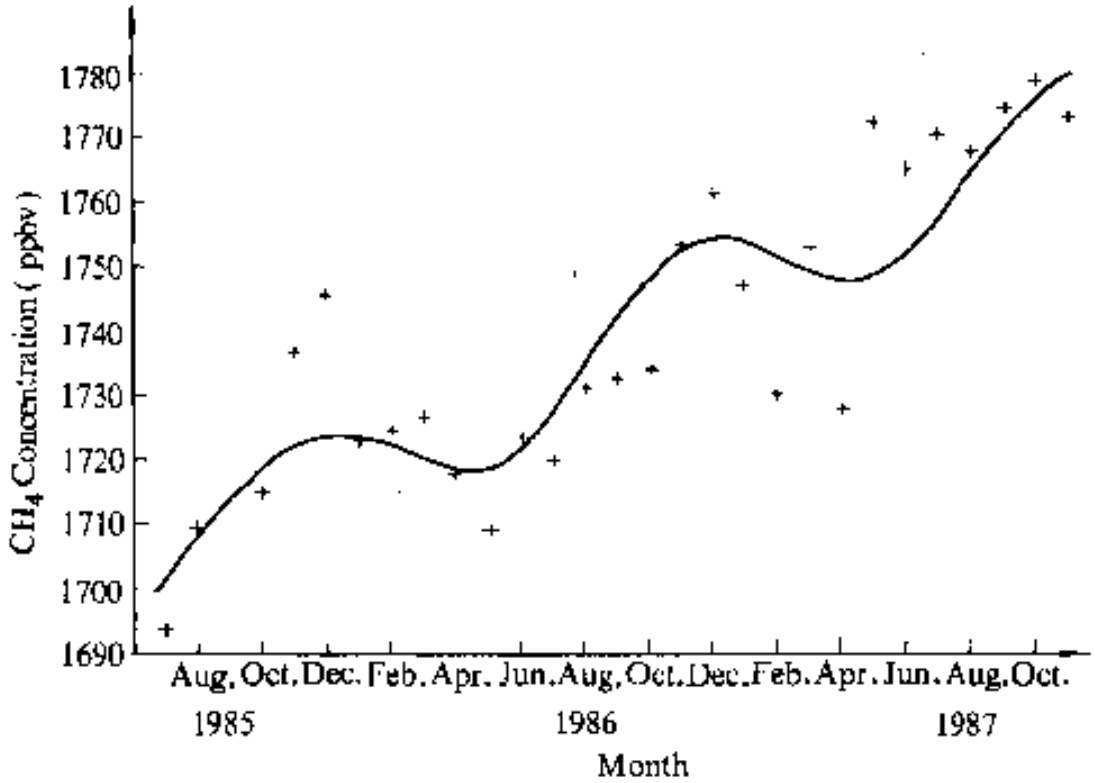
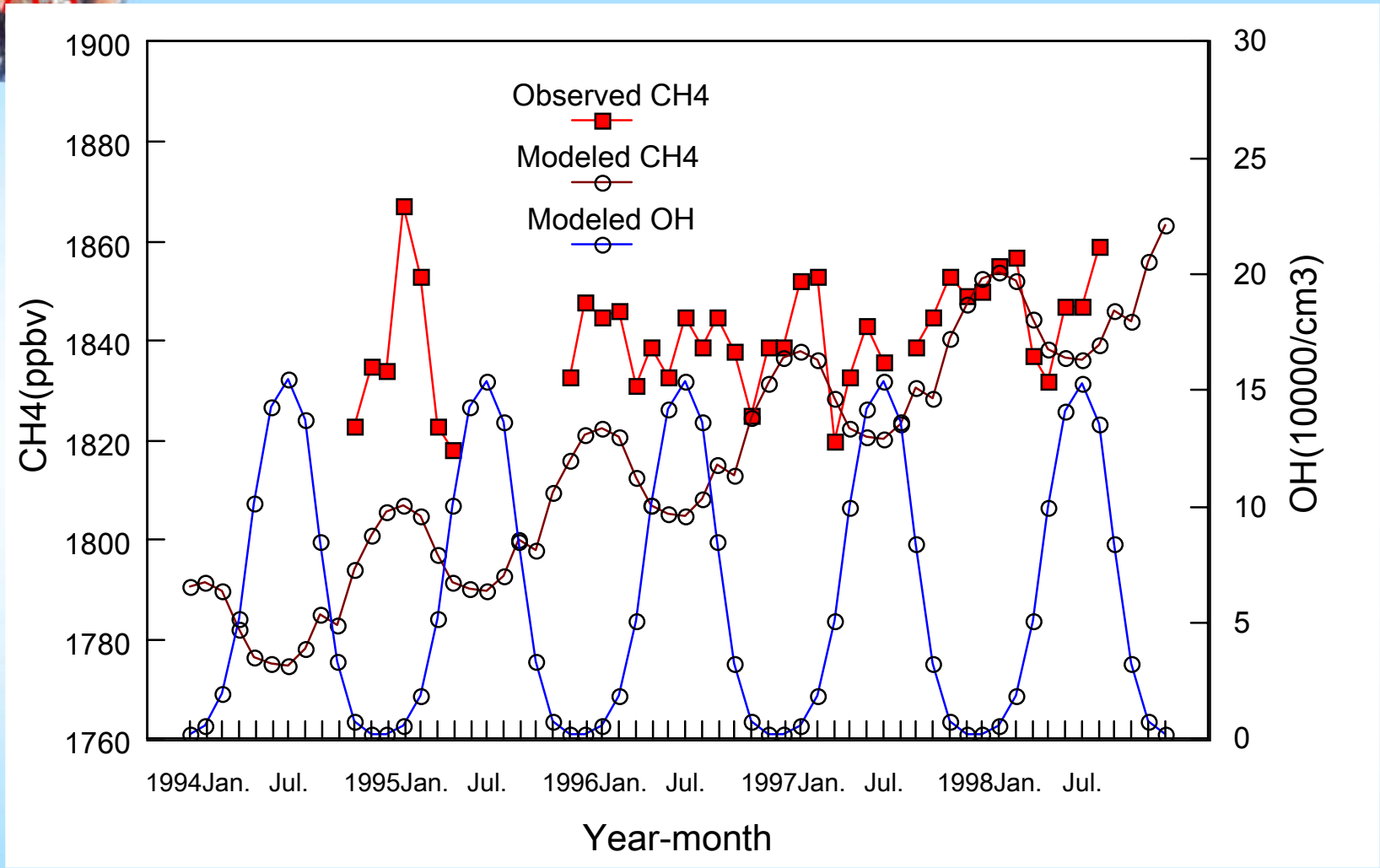


Fig. 1. Measured and fitted monthly mean concentrations of atmospheric methane.

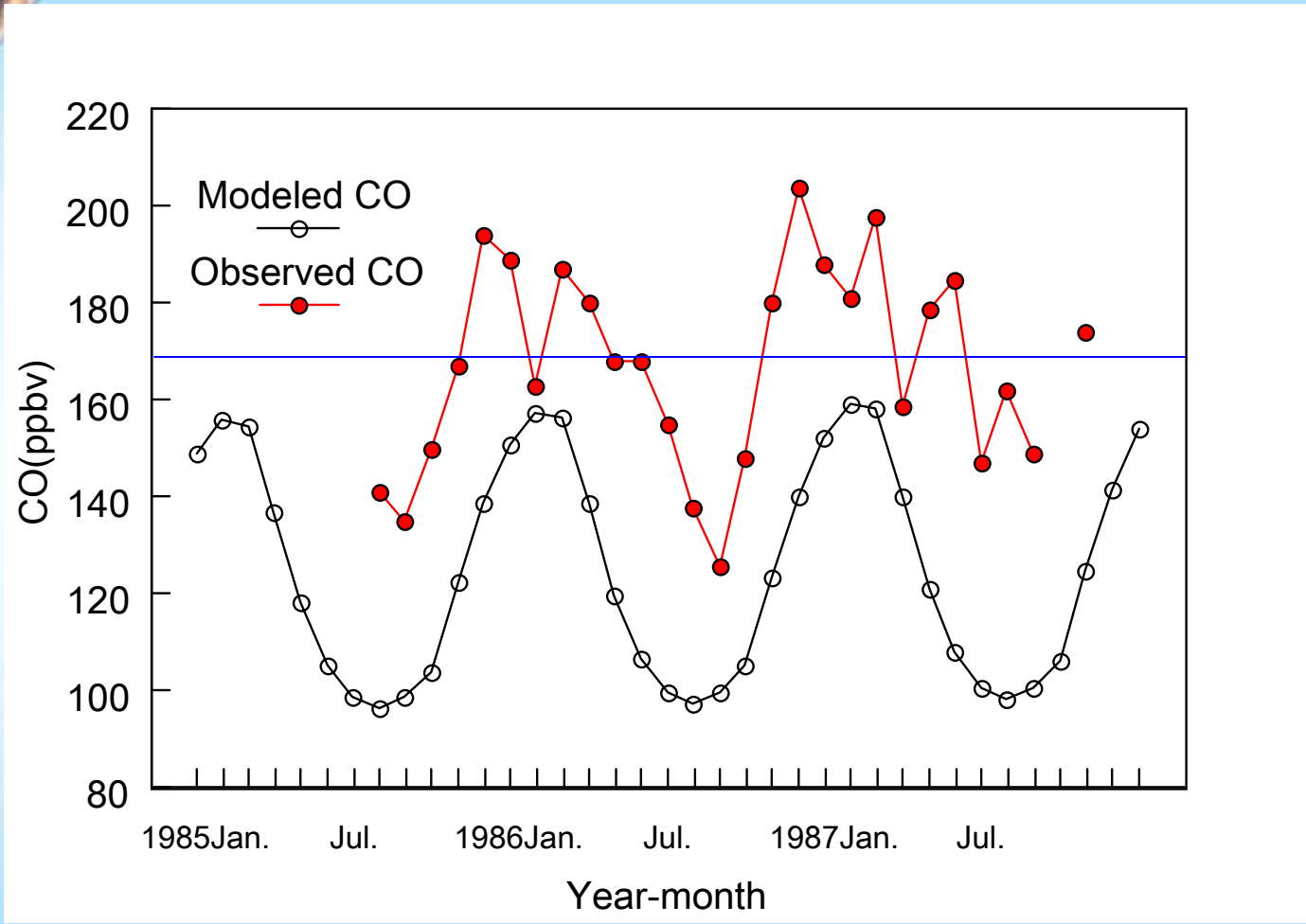
According to Wang et al.(1990), CH_4 increased by 1.6% during 1985-1987

Modeled seasonal variation of ground CH_4(35—40°N) at Minqin(38°37′N, 103° 5′E)China during 1994-1998



According to CH_4 data by Prof. Ren and Khalil, CH_4 increased by 0.16% during 1996-1998

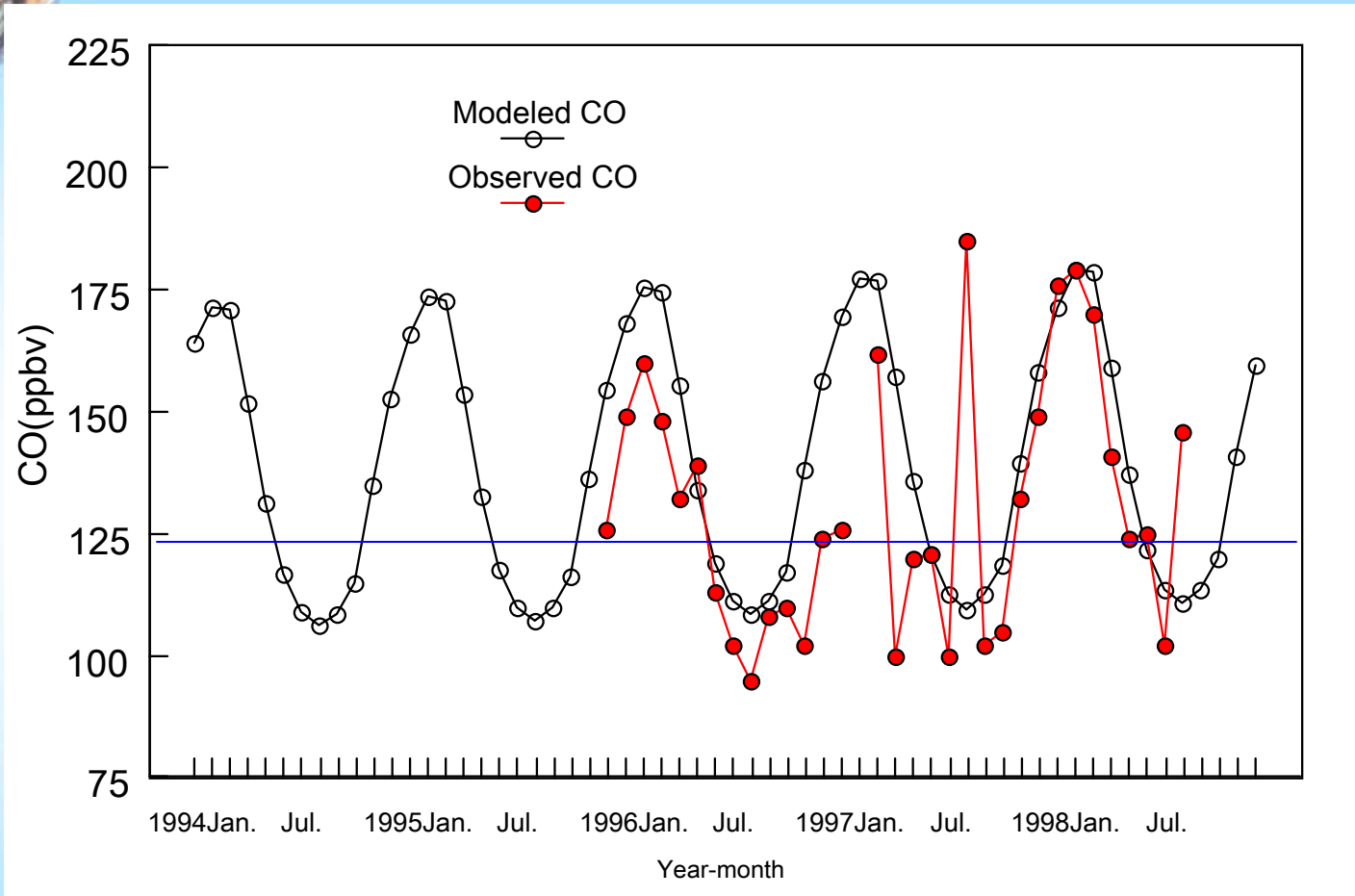
Modeled seasonal variation of ground CO(35—40N) at Minqin(38°37′N, 103° 5′E)China during 1985-1988



Averaged CO =169ppbv

CO data is from Prof. Lixin Ren and M.A.K.Khalil in CAS-DOE Joint research

Modeled seasonal variation of ground CO(35—40N) at Minqin(38°37′N, 103° 5′E)China during 1996-1998



Averaged CO =125ppbv, decreased by 25%

CO data is from Prof. Lixin Ren and M.A.K.Khalil in CAS-DOE Joint research

Summary

1. The annual growth rate of CH_4 at Minqin is 1.6% in 1987 and 0.16 in 1997. It shows that the increase growth rate of CH_4 has been much slower down in 1990s. It imply that the real emission and sink condition of CH_4 in 1980s and 1990s are different.
2. The averaged concentration of CO is 169.4 ppbv during 1986-1987 and 125.4 ppbv during 1996-1998. CO concentration in 1986-1987 is 25% lower than that in 1996-1997 at Minqin.
3. The modeled seasonal variation trends of CH_4 and CO are compared with observations. The maximum and minimum of CH_4 and CO reverse that of OH as the sink of OH is mainly reacted with CH_4 and CO. The modeled seasonal variations of CH_4 and CO agree well with observation data at the baseline station of minqin, Ganshu province, China. Both CH_4 and CO have high concentration in winter time and low concentration in summer time at Minqin. Modeled results shows that OH radical have low concentration in winter time and high concentration in summer time at Minqin.

4. Possible cause for the Change of CH_4 and CO in 1980s and 1990s:

CO emission ↓	CO ↓	OH ↑	CH_4 ↓
IF 300Tg	35ppbv		6 ppbv

And Slower increase growth rate of CH4 emission

OK!

Recent observation of aerosol/dust storms in Beijing

Renjian Zhang

Institute of Atmospheric Physics,

Chinese Academy of Science, Beijing, 100029 P.R. China

Zrj@mail.iap.ac.cn

Why do we research dust aerosols?

A) Effect on climate and environment
B) Traffic, airport,farmland
C) Economical loss
D) People's health and life
E) etc.

New Features of Dust storm in China

In recent years

- **Frequency being increasing**

In 2000 15 times
In 2001 18 times
In 2002 17 times

Influencing wider area

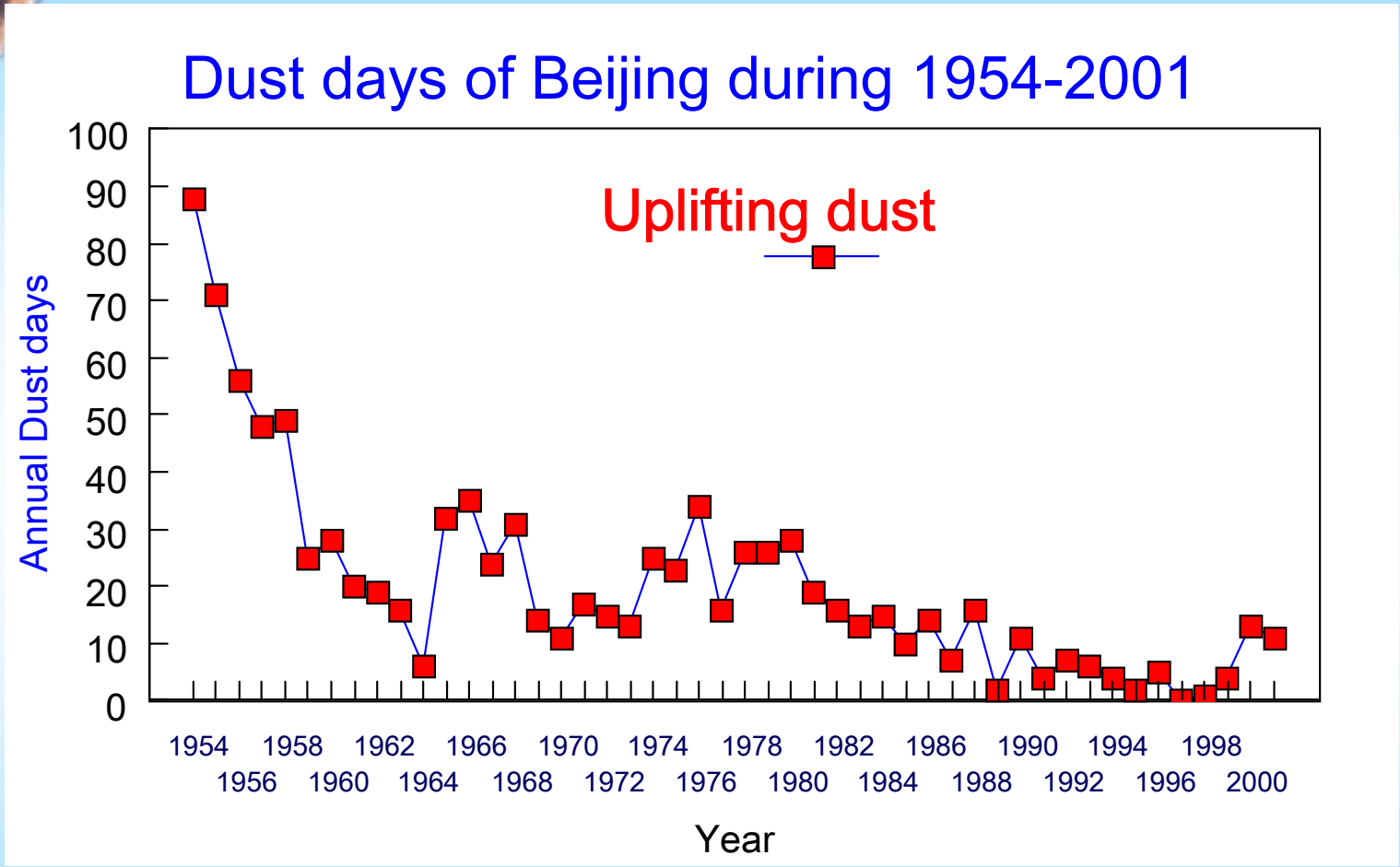
6 April,2000 2-3rd of China

- **Dust storm being much severer**

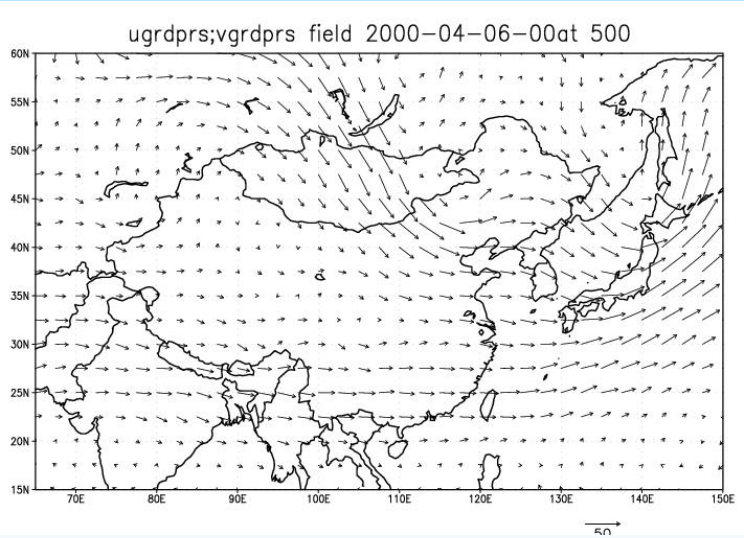
6 April,2000 3900μg/m^3

- **Period of dust being much longer**

In 2001,first dust occurred on 1 Jan.
In 2002 The last occurred on 11 November 1 year!


Dust days of Beijing during 1954-2001
Uplifting dust
Annual Dust days
100
90
80
70
60
50
40
30
20
10
0
1954
1956
1958
1960
1962
1964
1966
1968
1970
1972
1974
1976
1978
1980
1982
1984
1986
1988
1990
1992
1994
1996
1998
2000
Year

Possible Causes



- **La nina Year**

  Strong wind occurred frequently

- **Weather condition:**

  —— A stable ridge in West Asia

  ——A stable and deep trough in East China sea

- **Climate analysis**

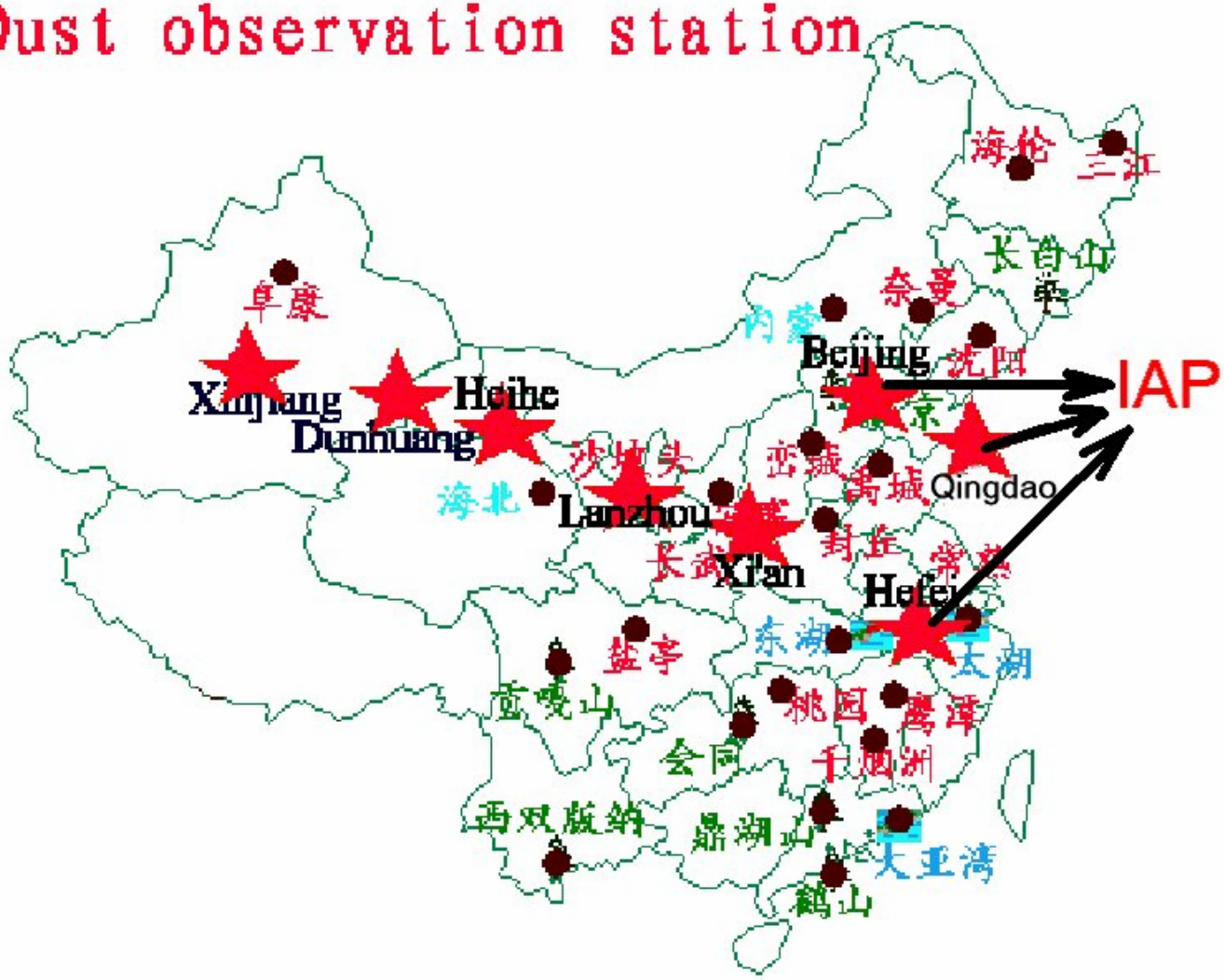
  Rainfall in In 2000 spring is 50-90% less than in 1999

  Temperature is 1-2℃ higher (some place 3-4℃)

- **Human activities and land use**

  Dust areas are increasing

Dust observation station



8-stage-Cascade (PIXE)

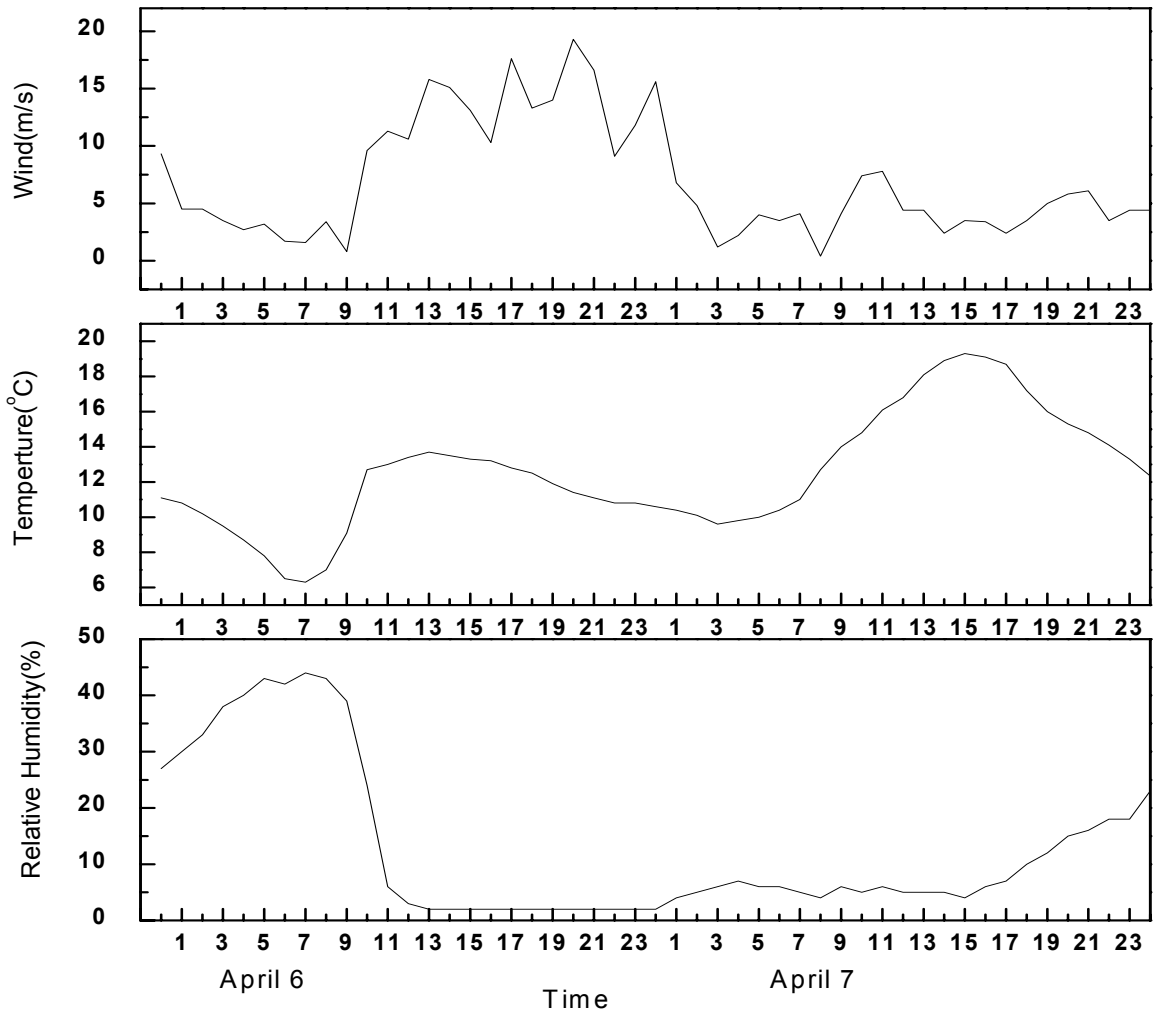
IAP CAS

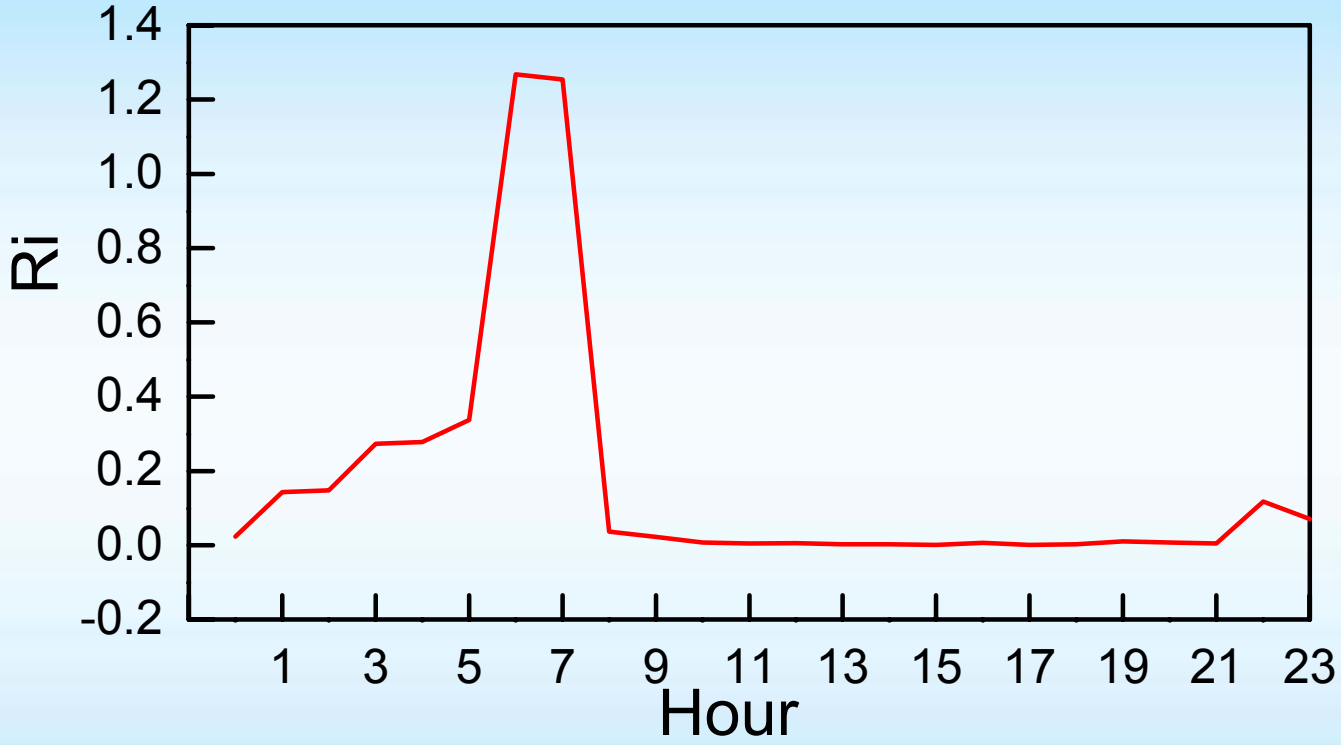
OPC

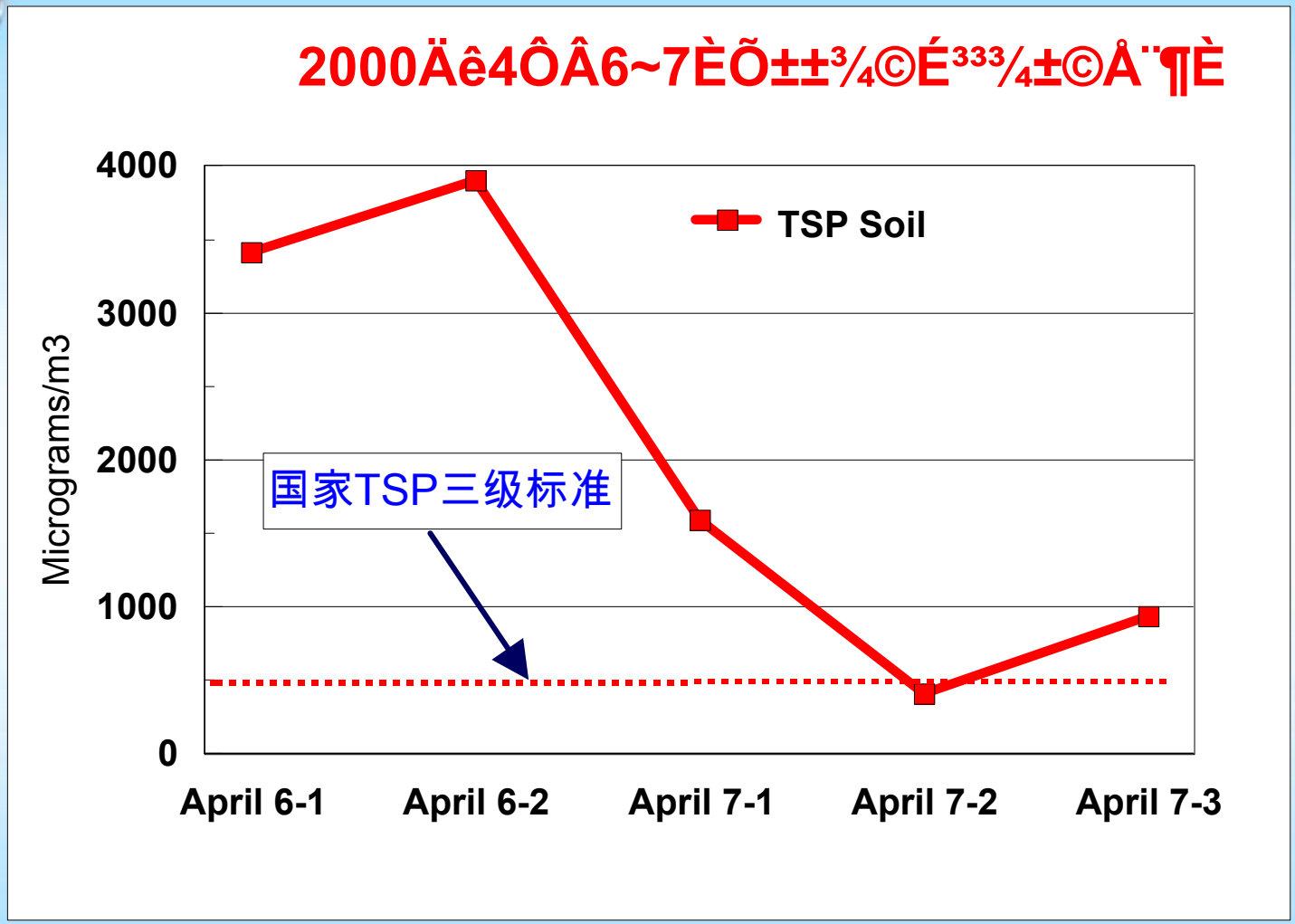
In spring 2000, 9 dust events attacked Beijing:

- March 3
- March 17
- March 22-23
- March 27
- April 3
- April 6 The severest!
- April 9
- April 25
- April 29

325m Meteorological Tower

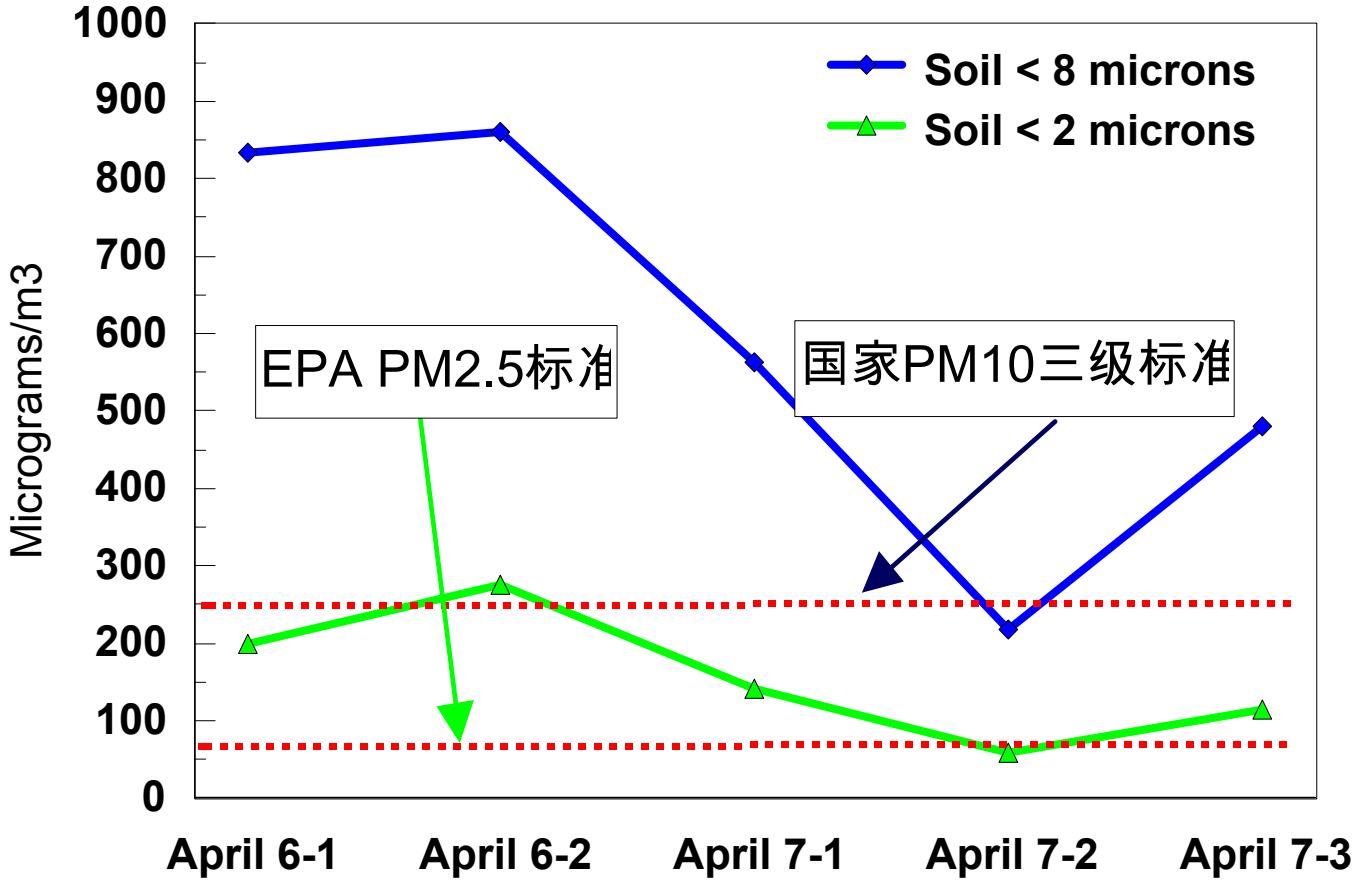

Wind(m/s)
20
15
10
5
0
1 3 5 7 9 11 13 15 17 19 21 23 1 3 5 7 9 11 13 15 17 19 21 23
Temperture(°C)
20
18
16
14
12
10
8
6
1 3 5 7 9 11 13 15 17 19 21 23 1 3 5 7 9 11 13 15 17 19 21 23
Relative Humidity(%)
50
40
30
20
10
0
1 3 5 7 9 11 13 15 17 19 21 23 1 3 5 7 9 11 13 15 17 19 21 23
April 6
April 7
Time

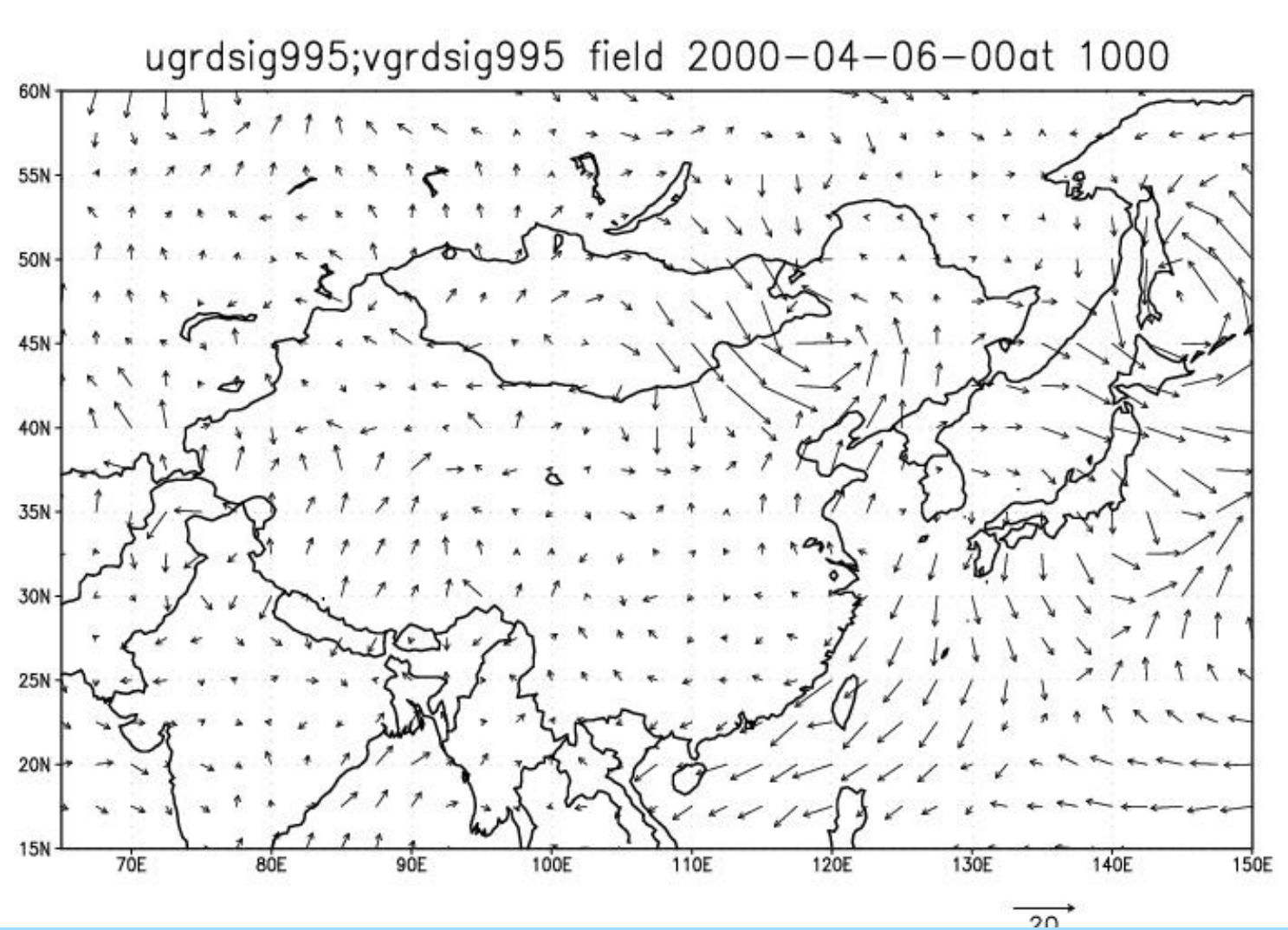

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
Ri
1
3
5
7
9
11
13
15
17
19
21
23
Hour

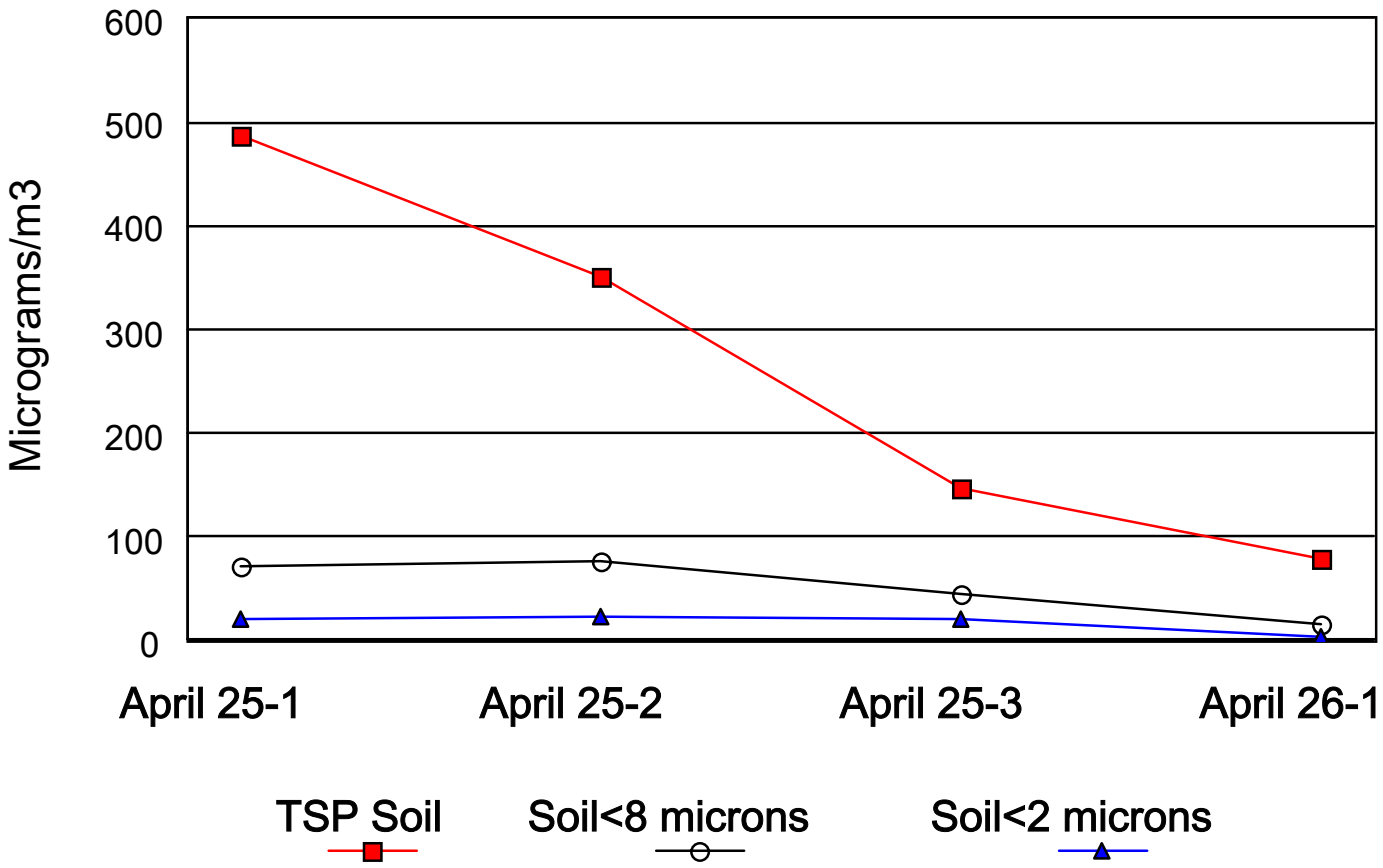


$$C=2.2[Al]+2.49[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti]$$

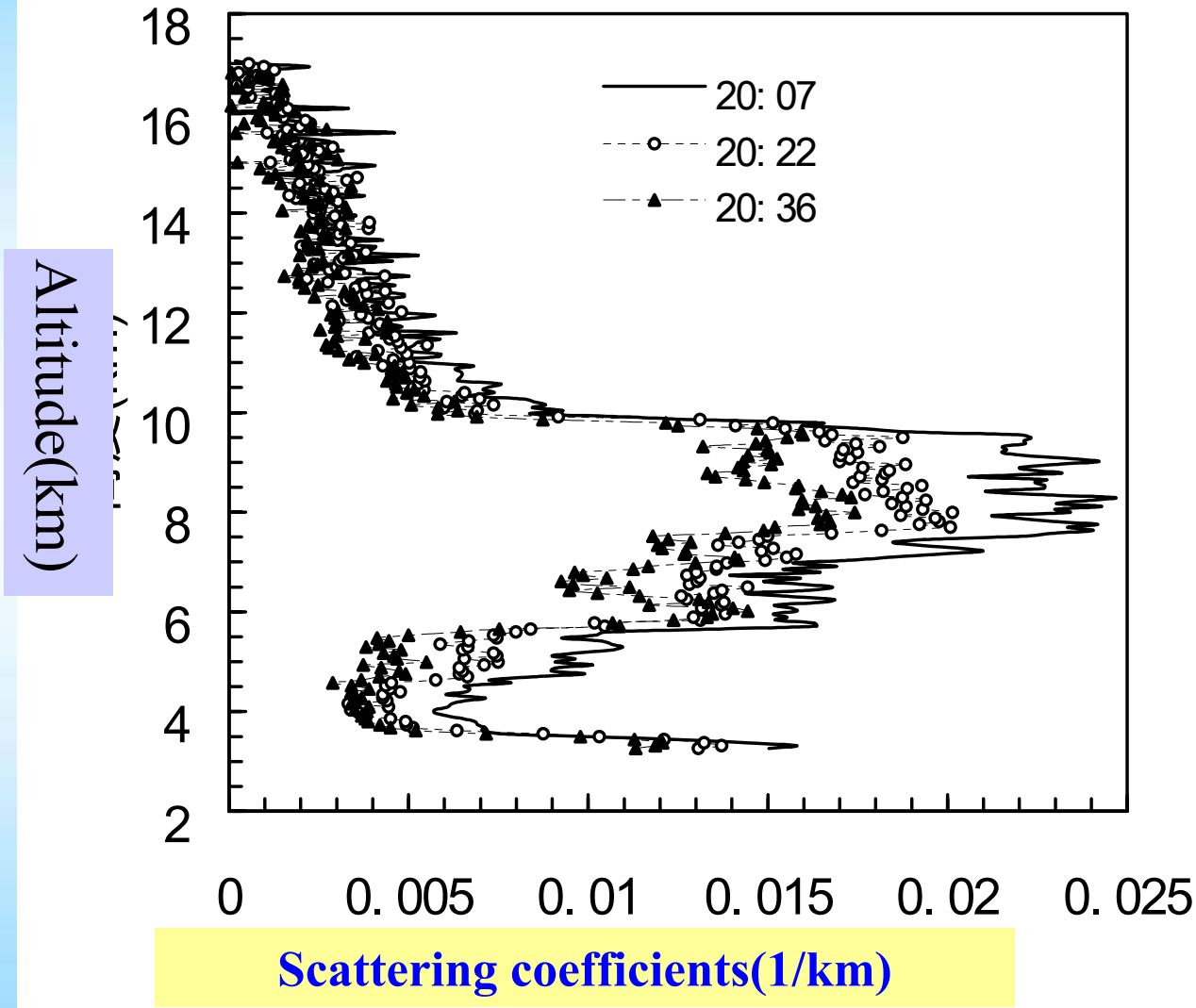
2000Äê4ÔÂ6~7ÈÕ±±¾©É³¾±©Å¨¶È

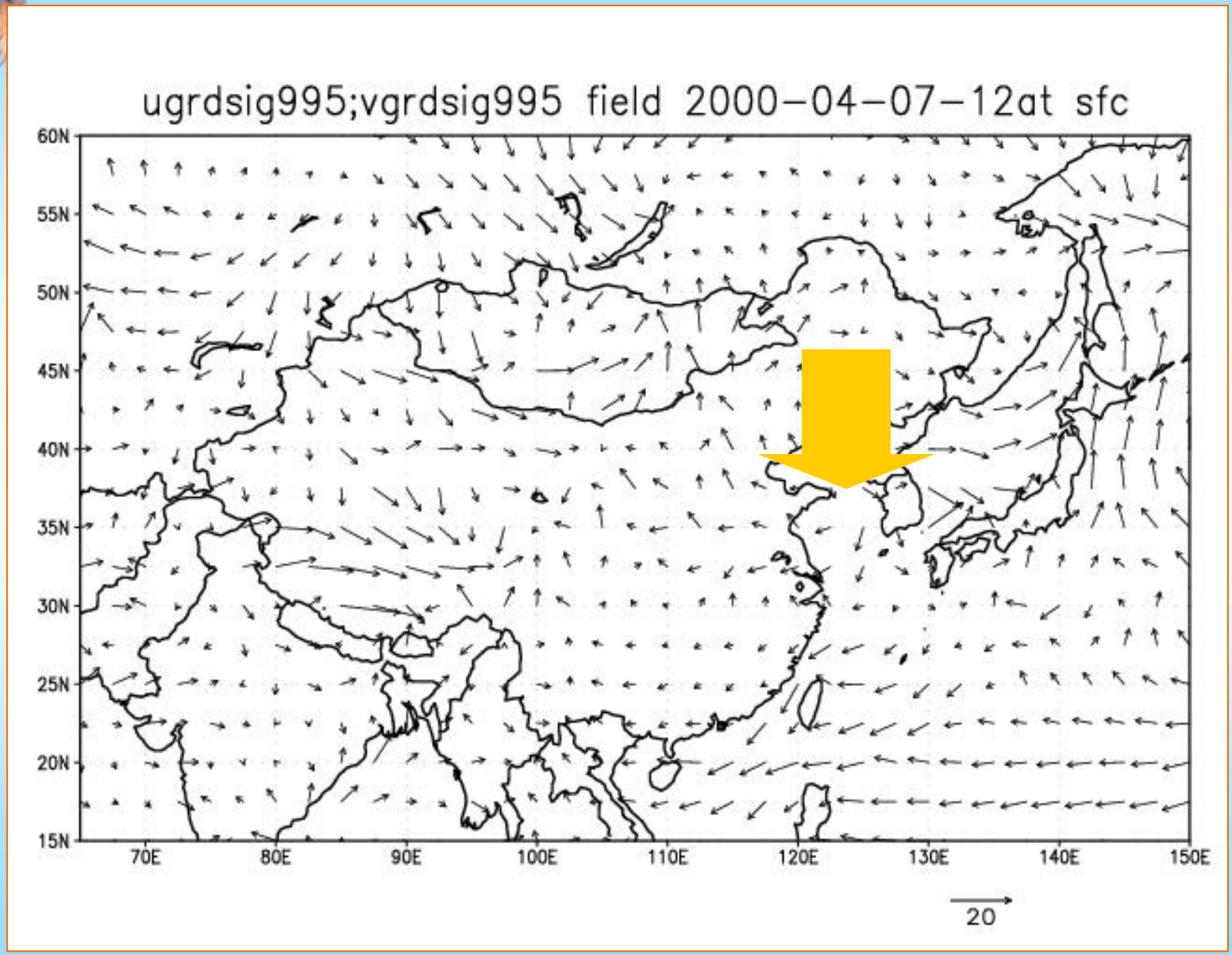



ugrdsig995;vgrdsig995 field 2000-04-06-00at 1000
60N
55N
50N
45N
40N
35N
30N
25N
20N
15N
70E
80E
90E
100E
110E
120E
130E
140E
150E
20

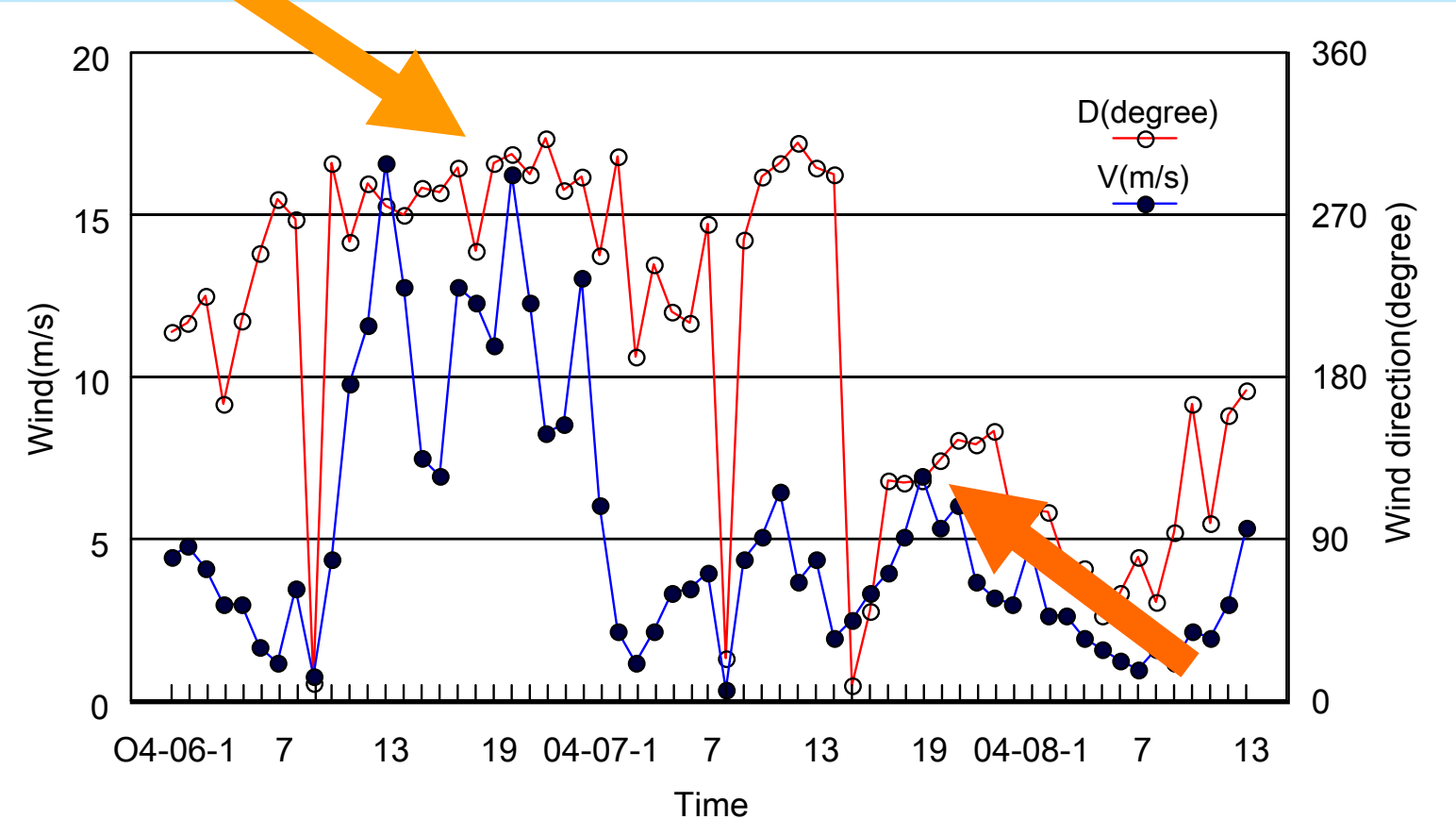

Beijing dust concentration on Apil 25, 2000
Micrograms/m3
600
500
400
300
200
100
0
April 25-1
April 25-2
April 25-3
April 26-1
TSP Soil
Soil<8 microns
Soil<2 microns

April 7,2000,Beijing by Prof.Qiu JH




ugrdsig995;vgrdsig995 field 2000-04-07-12at sfc
60N
55N
50N
45N
40N
35N
30N
25N
20N
15N
70E
80E
90E
100E
110E
120E
130E
140E
150E
20

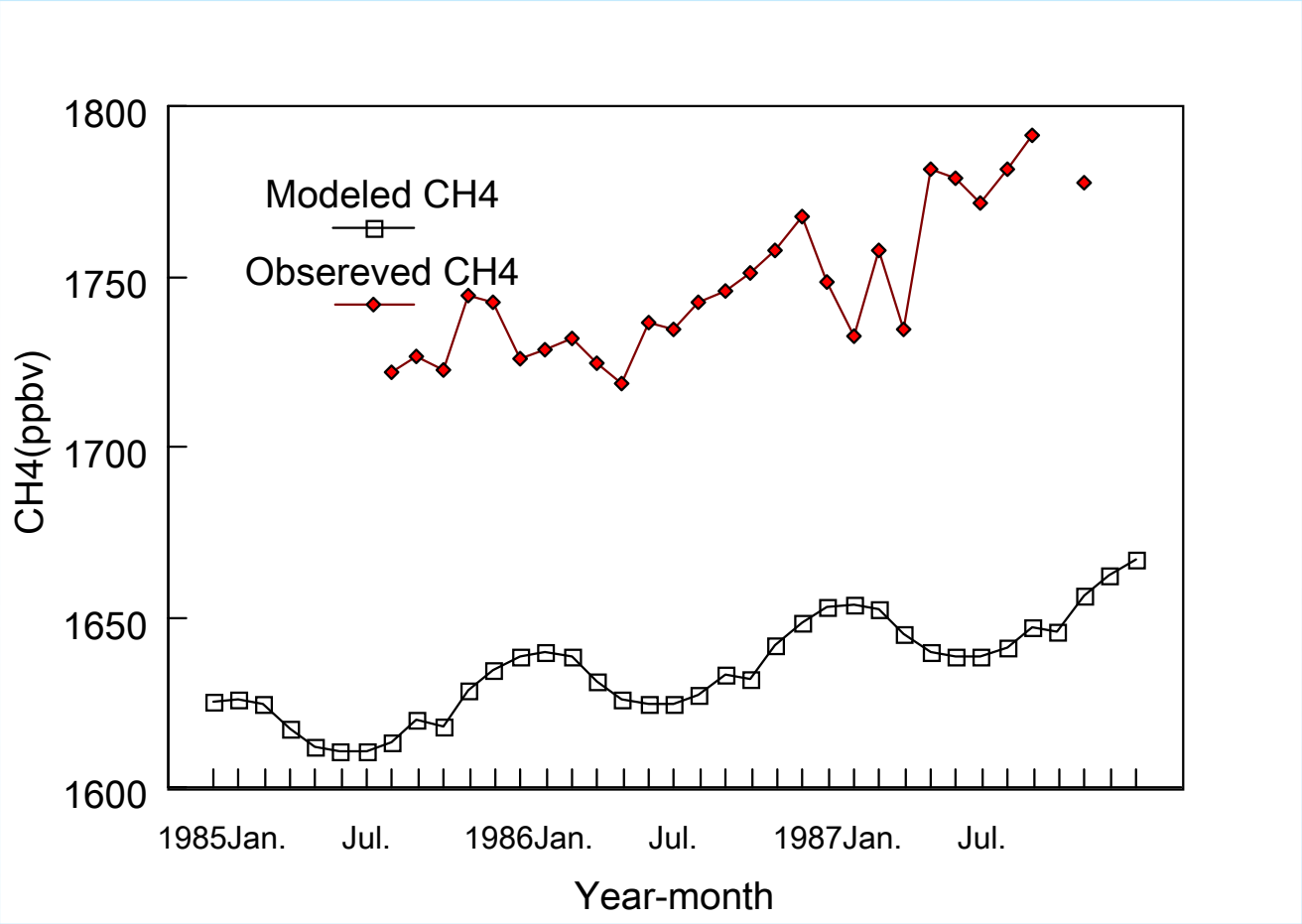
Wind at 102 m high in Beijing



Conclusion

1. Dust storm by surface wind can cause sever pollution(3900 μg/cm3)

2. Downward transportation of dust in upper level can cause sever pollution too(900 μg/cm3)

Thank you

CH_4 Data by Prof.Ren in 1985-1987 is not ideal