

Model evolution of the middle atmospheric palaeoenvironments

GUFRAAN BEIG

Indian Institute of Tropical Meteorology, Pune – 411 008, India

सार - हिम क्रोड वायु विश्लेषण से अतीत के हिमयुग से अब तक के ग्रीन हाउस गैसों CO_2 , CH_4 और N_2O के वायुमंडलीय अंशों में महत्वपूर्ण परिवर्तन का पता चला है। यह तापमान के उर्ध्वाधर वितरण में परिवर्तन लाने में और वायुमंडल की संरचना में सहायक हो सकता है जिसके बारे में बहुत अधिक जानकारी उपलब्ध नहीं है। अतीत के हिम युग से अब तक की तापीय संरचना के वार्षिक उर्ध्वाधर वितरण का पुनः निर्माण करने और मध्य वायुमंडल की गैस सांद्रता का पता लगाने के लिए विकिरण, गतिकीय और रसायन के द्विविमीय अन्वयोन्यक्रिया मॉडल का प्रयोग किया गया है। इस उद्देश्य के लिए, माउंडर अधिकतम, रोमन अधिकतम, पूर्व औद्योगिक युग और अतीत के हिमनद युग सहित विभिन्न समय अवधियों के मॉडलों में उक्त बलीयन प्राचलों के हिम क्रोड वायु आँकड़ों का निवेषी सूचना के रूप में प्रयोग किया गया है। इस निदर्श के परिणामों से पता चला है कि इस समय की तुलना में अतीत के हिमयुग में ग्रीन हाउस गैस अंश में पर्याप्त कमी आने के कारण क्षोभमंडल में शीतलन हुआ और उपरी समतापमंडल में 10 से 15°K तक उष्णन हुआ। तापमान में परिवर्तन का जल वाष्प अंश के साथ निकट संबंध है। अतीत के हिमनद युग में ओजोन सांद्रता में ऊपरी समतापमंडल में ध्रुवों के निकट अधिकतम 50 प्रतिशत तथा उष्णकटिबंध में लगभग 10 प्रतिशत तक का परिवर्तन हुआ है। अतीत के हिम युग में हाइड्रॉक्सिल अंश में महत्वपूर्ण कमी के कारण 30 कि.मी. से ऊपर ओजोन अंश में वृद्धि हुई। तथापि, विभिन्न प्रति-संतुलन प्रभावों के कारण सकल समाकलित ओजोन अंश में अतीत के हिम युग से अब तक नाममात्र के परिवर्तन का पता चला है।

ABSTRACT. Ice core air analysis has indicated a significant variation in the atmospheric contents of the greenhouse gases CO_2 , CH_4 and N_2O from the last ice age to the present period. This may have contributed in altering the vertical distribution of temperature and composition of the atmosphere about which not much information is available. The two dimensional interactive model of radiation, dynamics and chemistry has been used to reconstruct the annual vertical distribution of thermal structure and trace gas concentrations of the middle atmosphere for the periods extending from last ice age to the present. For this purpose, ice core air data of the above mentioned forcing parameters are used as input to the model for different time frames including Mounder Maximum, Roman maximum, pre-industrial period and the last glacial period. Model results show that the considerable reduction in the greenhouse gas content for the last ice age has resulted in cooling of troposphere and a warming by about 10 to 15°K in the upper stratosphere as compared to present. The variation in temperature is closely related with the water vapour content. The percentage change in ozone concentration for the last glacial period is to a maximum of 50% near the poles in the upper stratosphere and about 10% in the tropics. A significant decrease in the hydroxyl content in the last ice age must have contributed in increasing the ozone content above 30 km. However, the total integrated ozone content appears to show marginal variations from last ice age to the present due to several counter-balancing effects.

Key words – Ozone, Last ice age, Mounder maximum, Stratosphere, Hydroxyl content, Greenhouse gases.

1. Introduction

Global climate has been a key factor to influence the regional changes. However, until early eighties, there were uncertainties about both the causes of the global climate change and the regional interconnections among key parameters of the global climate system. Climate models were not developed enough to test the potential impact of these and other factors. COHMAP (Cooperative Holocene Mapping Project) researchers have initiated to systematically assemble data that provide geological records of spatial and temporal changes in climate (COHMAP, 1988) and later used general circulation models to identify and evaluate causes and mechanism of climatic change. Thereafter, the evolution of climate

system components such as temperature, radiative flux and circulation for the palaeoclimate ice age eras have been studied extensively both by observations and theoretical modelling (Crowley and North, 1991 and reference therein). Comparisons of reconstructed palaeoclimates with model simulations provide a vital clue to evaluate mechanisms of climate change. These data also allow us to test the sensitivity of models for simulating the different type of climates of the past.

Ice-core observations have demonstrated large environmental changes for the Last Glacial Maximum as compared to present conditions and a marked CO_2 depletion (Delmas, 1993). Some literature is also available about ozone content in the oxygen poor earth's

palaeoatmosphere (Francoise and Gerald, 1988). However, most of the work in 1980s have several assumptions and were based on the indirect estimates of the gas content variations in the past. In recent years, information about the earth's climatic records has been deduced from ice cores and ocean sediment samples (Raynand *et al.*, 1993; Delmas, 1993) for the ice ages in the past. These data on CO_2 , CH_4 , N_2O (called forcing parameters) may be used as input to the radiative-dynamical-chemical models to reconstruct quantitatively the global distribution of atmospheric trace gas concentrations (Karol *et al.*, 1995; Beig and Mitra, 1997). However, there are several constraints in reconstructing the past climate using these modelling approach, based on the available information as their may be some other factors which may have some possible variations but cannot be estimated from available data. The ability of models to reconstruct a range of climates is important because the models are used to predict future atmospheric changes due to anthropogenic increase of CO_2 and other forcing parameters. Crutzen and Bruehl (1993) have presented a model analysis of the changes in temperature and the concentration of ozone, hydroxyl and some other photo-chemically active gases in the stratosphere during the glacial, the pre-industrial holocene and the present using 1.5-D model. They considered the change in the emissions of CO_2 , N_2O , CH_4 and various chlorocarbon gases as the boundary conditions in their model calculations and reported a relatively small change in total ozone column between the glacial and pre-industrial holocene (Crutzen and Bruehl, 1993). Beig and Mitra (1997) have reported the changes in several atmospheric chemical composition especially the ion composition resulting from increasing CO_2 , N_2O , CH_4 and chlorine loading for last ice age, present time and 2050. Karol *et al.* (1995) used 1-D radiative-photochemical model to reconstruct the annual global mean vertical distribution of trace gas concentrations during the last glacial and interglacial periods with number of assumptions on lapse rates, radiative and photochemical parameters. However, systematic reconstructions of atmospheric trace gas concentration and thermal structure on various time scales including last ice ages, Roman Maximum, Mounder, Maximum, Pre-industrial to present time have not been adequately done to compare the changes from one time frame to another. Each of the above past time periods has some distinct features, which are likely to affect the resulting changes. Recently Etheridge *et al.* (1998) has reported accurate measurements of methane in air from polar ice and firn from the past decade back to 1000 A.D. With these emerging results of past, it has now become possible to reconstruct the changes in some important atmospheric chemical constituents and do the intercomparison, which may guide us to some of the possible future trends.

The aim of this article is to examine the variations in temperature and the concentrations of ozone, hydroxyle and water vapour which might have changed as a result of the past increases in the atmospheric concentrations of CO_2 , CH_4 , N_2O and CFCs. For the purpose, a 2-D interactive dynamical radiative-chemical model is used (Beig and Mitra, 1997) and the time frame covered were from last ice age -LIA (18,000 yr. BP) to present time through Roman maximum (1000 AD), Mounder Maximum (1650 AD), Pre-industrial (1860 AD) and recent past (1970 AD). In the present work, changes in the low latitude tropical region have been discussed in detail because of their importance in controlling the global stratospheric budget.

2. Interactive two dimensional model

To reconstruct the meridional distribution of atmospheric trace gas concentrations and temperature, averaged over the past time periods of ice ages, interactive radiative-dynamical-chemical two dimensional (2-D) model is used (Beig and Mitra, 1997). However, for such calculations, it is important to understand the sensitivity of the model to the expected variations in those parameters, which cannot be estimated from the ice core data, and to minimize the number of assumptions. The 2-D model used in the present work extends from surface to 85 km and from South to North Pole with a vertical resolution of 1 km and a latitudinal resolution of 5° . Several radiative transfer codes are linked to calculate the cooling from surface to 85 km. Temperatures are specified at their climatological values in the troposphere (0- 15 km). The stratospheric water vapour content is calculated, but in the troposphere, the contemporary climate relative humidity is prescribed and conserved for all the calculated variants. The 15-day time step is considered. The heterogeneous reactions are not considered for past time calculations. To account for the cloud influence on the radiative and thermal regimes of the atmosphere during the glacial and interglacial periods, only one effective cloud layer in the model (Karol *et al.*, 1995) is assumed. A globally and annually averaged solar radiation flux at the top of the atmosphere is considered the same as that of current spectral distribution taken from Neckel and Labs (1984) for all the past periods considered. In palaeoatmospheric composition calculations of Crutzen and Bruehl (1993) and Karol *et al.* (1995), the current cloud optical parameters are used in their models. We have also assumed the current values of cloud optical parameters for all the periods considered in this work. We have not considered the effect of stratospheric sulfate aerosols on the radiation and photochemistry of the palaeoatmosphere as such effect may be significant only during a period of few years after the major volcanic eruptions which will become negligible on long-term

COUPLING AMONG RADIATION, DYNAMICS & CHEMISTRY :

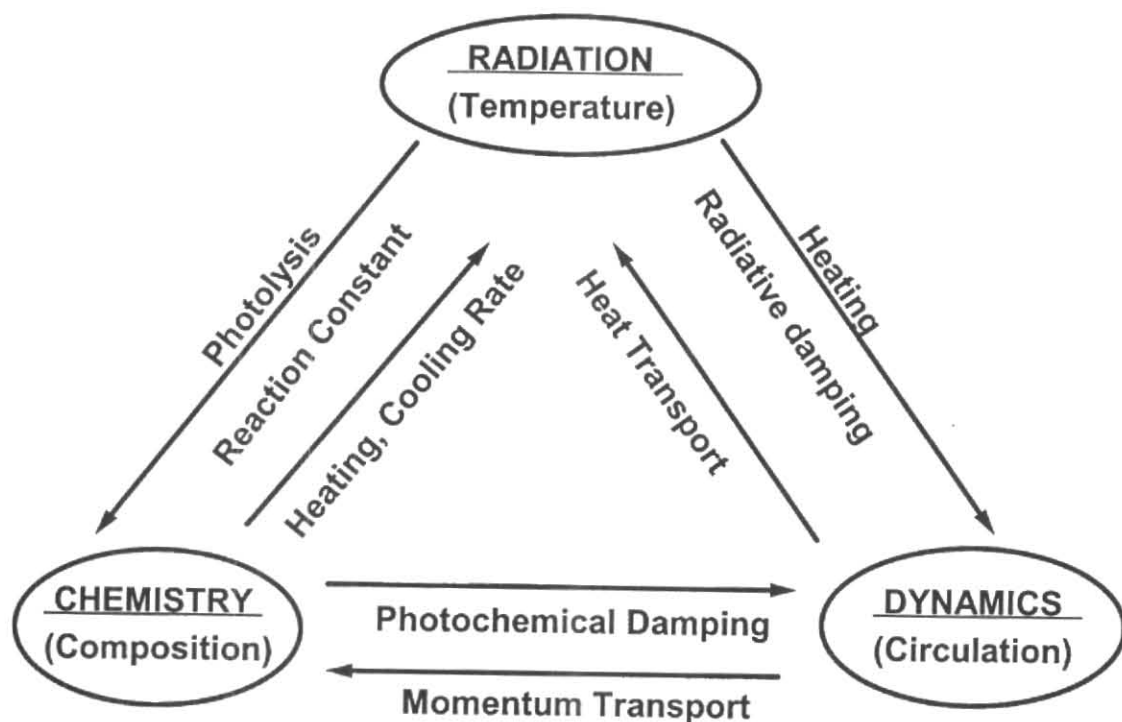


Fig. 1. The interactive processes and the coupling among radiation, dynamics and chemistry as considered in the present dimensional model

averaging. The surface albedo for both hemispheres is taken as 10.5% for all scenarios excepting ice age runs where it is increased to 20% in the northern hemisphere and 14% in the southern hemisphere (COHMAP, 1988).

The 2-D model used in this work treats radiation, dynamics and chemistry interactively (Fig. 1). The physical mechanism for the response to a change in external forcing can be complex because of the interdependency of the chemistry, dynamics and radiation in the model. Changes in the solar heating rate can trigger a response in the temperature and the circulation that can be modified by feedback from mean wind. Radiation can trigger changes in chemical composition by processes of photolysis and reaction rates. However, the chemical species have properties of absorbing and emitting radiation and thereby heating and cooling the atmosphere which in turn may affect the temperature structure. Similarly, dynamics may influence the chemistry by momentum transport. These all processes of interactions and feedback are included in the model.

3. Past scenario

Ice-core measurements have revealed significant changes in the key forcing parameters for the past time

period though last Glacial Maximum as compared to present day. Initially some discrepancies were existing on the results by different groups. However, after several verifications and crosschecks of the data, these differences are now narrowed down (Delmas, 1993). The major forcing parameters are the concentrations of CO_2 , N_2O and CH_4 . The distributions of these parameters at the ground are almost homogeneous as evident from the existing tropospheric concentration and those in the ice cores of Antarctica and Greenland (Chappelaz *et al.*, 1993). Hence, we can use single values for the above gases as input into the 2-D model. The zonally averaged distribution of these gases at the ground may also be considered in a similar fashion as the difference in the concentration of south and north pole is found to be marginal *viz* 2-3% in case of NH_4 (Valentin, 1990). However, for certain other radiatively and photochemically active species, the condition of homogeneity may be invalid and their concentrations are also not properly known for the past time period. These gases include CO , NO_x , CH_3Br , HCFCs *etc.* Some general information about the abundance of these gases for the past are reported in literature (Valentin, 1990) but lack the precision. However, a sensitivity study has been performed in the present work and found that these

TABLE 1

Ice cores and ocean sediment data used for forcing parameters as initial values in the model

Time Periods	CO ₂ (ppm)	CH ₄ (ppb)	N ₂ O (ppb)	CFCs (ppt)
Present Day (1995 AD)	360	1700	308	770
Recent Past (1970 AD)	325	1420	295	180
Pre-Industrial (1860 AD)	280	750	285	0
Mounder Max. (1650 AD)	260	735	280	0
Roman Max. (1000 AD)	250	710	283	0
Last Ice Age (18,000 Yrs BP)	195	350	244	0

species are not playing a major role in the distribution of those species, which are reported in this work. In the present work, several scenarios from the last ice age to the present time are considered. However, we present here the results of last ice age (LIA) in detail. The concentrations of above mentioned forcing parameters considered different scenario in the present work are tabulated in Table 1. The volume-mixing ratio of CO₂ was as low as 195 ppm for the last ice age, which has increased just by 85 ppm upto pre-industrial period of 1860. However, the growth rate is very rapid after 1860 and the present (1995 AD) estimate of CO₂ is around 360 ppm. Similarly for methane, the volume-mixing ratio derived from the ice-core analysis is 350 ppb for last glacial maximum, which has increased to 1700 ppb for present. The N₂O volume mixing ratio was 244 ppb for last ice case which was almost constant from 1000 AD to pre-industrial period (~ 280 ppb) but its volume mixing ratio has touched a value of 300 ppb for present. Chlorofluorocarbons were almost negligible upto pre-industrial period. The loading of CFCs started building up from the industrial revolution and reached to towering 770 ppt until 1995.

4. Results and discussion

In this section, firstly, an attempt has been made to compare model results with the available observations for the present day. Thereafter, model results obtained in this work for the palaeoperiods as described in the last section, are discussed. Several parameters undergo some variations; however only those parameters, which show some significant variation, are discussed in detail. Most of the results reported here for palaeoperiods are for 20° N latitude and the reference level (present) is considered as 1995.

The vertical distributions of major chemical species obtained for present day conditions in this work (dotted lines) as well as the observed data (solid lines) over Indian region for the latitude range from (0°N-30°N) (Beig and Mitra, 1997) are shown in Fig. 2. In this figure, a mean reference profile of ozone over Thumba (8°N) has been constructed using rocket-borne and balloon-borne sensors for the altitude region of 0 to 60 km. The peak ozone concentration over Thumba around 25 km agrees well with the model profile. A range of observed data of ozone is plotted near the tropopause where it exhibits a large variability. The ozone model profile falls toward the higher side of the data range below 20 km above which model values are slightly over estimated. The mean experimental water vapour profile over Thumba, obtained during the last two decades, agrees reasonably well with the model. The CFCs have gained importance only after industrial revolution because of their role in ozone chemistry and global warming. There has been a significant effort to construct a global estimate of CFCs in the last two decades. However, there are only a few measurements over the tropics. The volume mixing ratios of the two major species namely CFC11 (F11) and CFC12 (F12) of this family are almost constant due to their large lifetime. In the stratosphere, CFCs get photodissociated to release chlorine molecule. Model profiles of CFCs are calculated taking the initial values of 1990 on which most of the observed data is averaged. The model profiles agree well with data. For N₂O and CH₄, a broad agreement is clear. Model values of hydroxyl concentration are lower than the observed values (WMO, 1992). Nitric oxide plays a significant role in D-region ion chemistry. In this altitude region, the model underestimates nitric oxide concentration but a broad minimum around 80 km is well reproduced.

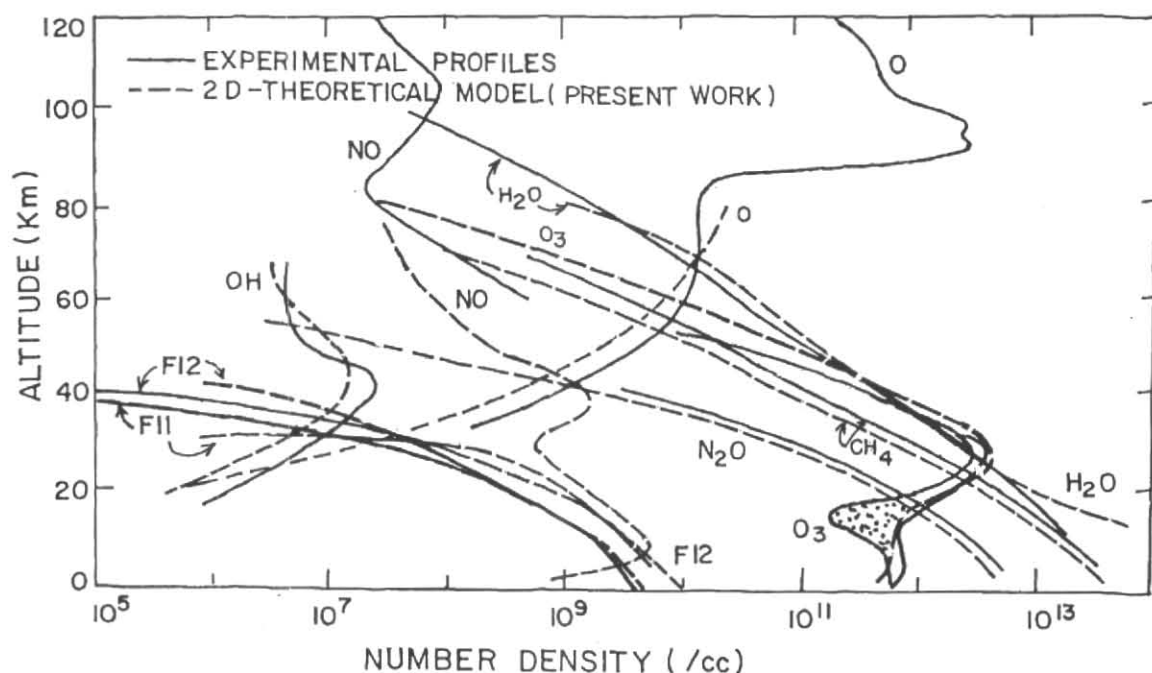


Fig. 2. A comparison of models of vertical distribution of several minor constituents with the experimental data in the middle atmosphere

Fig. 3(a) shows the difference in temperature ($^{\circ}\text{K}$) at 40 km altitude for different time frames starting from last ice age to the recent past (1970) as compared to present time. Results of five distinct time periods, are shown. A common heating trend is seen for all the periods excepting the Mounder Maximum when intensity of sun was very low. The largest variations of temperature from the present time occur in the last ice age case. The temperature at 40 km height is higher than that of present day by 12°K . The upper stratospheric warming is determined by the low CO_2 mixing ratio during the last ice age and Roman maximum period. The temperature difference at pre-industrial period is around 5°K , which is about 7°K cooler as compared to last ice age. In both the cases (LIA and pre-industrial), the concentration of CFCs were negligible but the difference in CO_2 volume mixing ratio has played a major role in this direction. The variation in temperature from 1970 to the present is around 2°K at 40 km which is roughly in agreement with the trend in experimental data available from 1970 to 1992 using rocket borne technique (Beig and Mitra, 1997). To study the variation in temperature with latitude, model results for the last ice case are shown in Fig. 3b. Fig. 3b shows the meridional distribution of the vertical structure of the absolute difference in temperature from LIA to the present. It is clear from this figure that the maximum heating is near the poles and higher latitudes in the upper stratosphere. Model result shows a

cooling of the order of -1°K to -2°K in the troposphere. The tropospheric temperature variation is found to be directly correlated with the water vapour content present in that region. The upper stratospheric temperature during the last glacial period is found to be higher by 15°K (~ 45 km) for the middle and higher latitudes. The northern hemisphere appears to be more sensitive to CO_2 change and found to show more warming as compared to southern hemisphere.

Fig. 4(a) shows the percentage change in ozone number density for different time frames as compared to present day at 40 km altitude. The increase in ozone by about 13% for the last ice age as compared to present is the result of combined effect of several counteracting processes in the stratosphere. The less amount of ozone catalytic substances (NO_x and HO_x) during the LIA due to less amount of CH_4 and N_2O would lead to less catalytic loss of ozone and thus will lead to higher stratospheric ozone concentration. However, it should also be noted that the less amount of HO_x reduces loss of NO_x to HNO_3 and hence NO_x rich atmosphere would be available which will enhance the ozone loss by NO_x catalytic cycle. In the stratosphere, chemistry of ozone is highly dependent on temperature sensitive reaction rates. The production reaction of ozone has a temperature dependence of $(300/T)^{2.8}$ (T = temperature). Hence if the temperature in the stratosphere increases, the production of ozone

Change in Temperature Through Ages as Compared to 1995

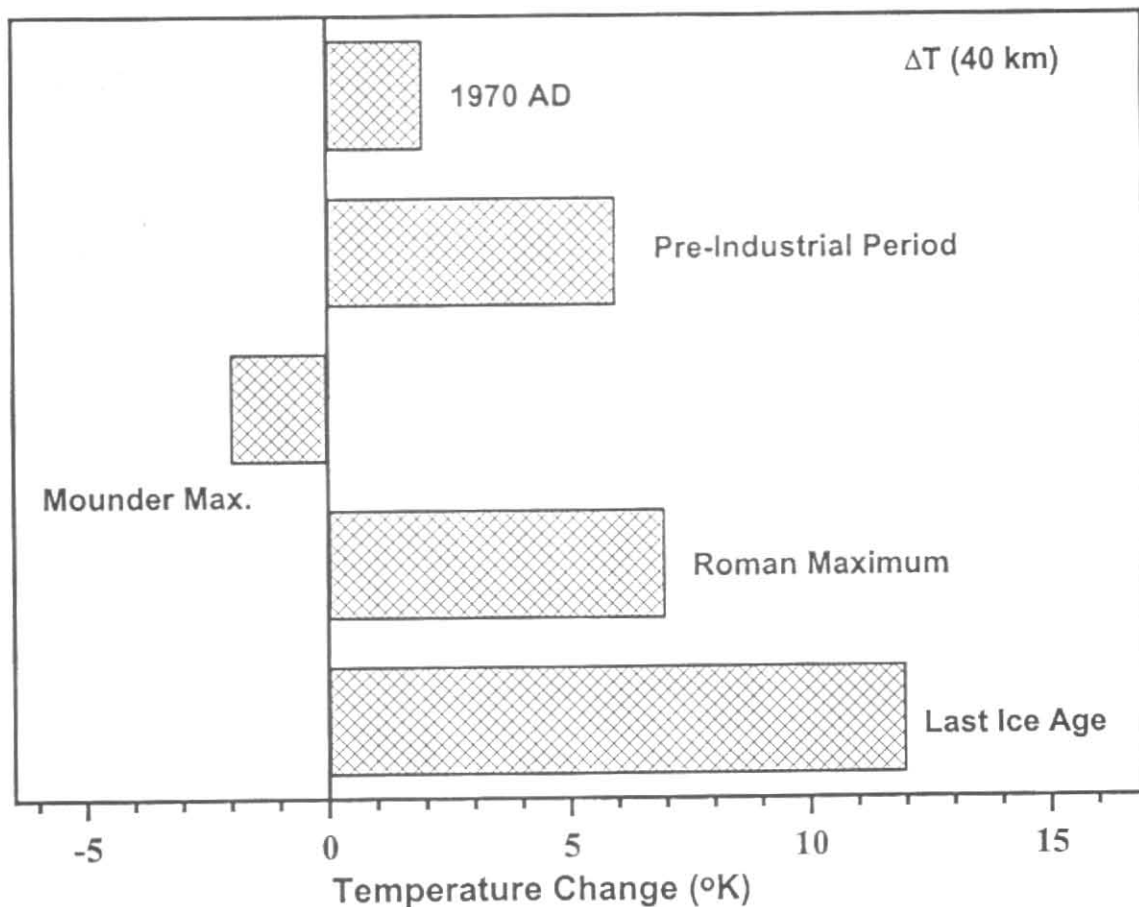


Fig. 3(a). The absolute difference in temperature for different palaeoperiods as compared to present, calculated in this work for 40 km altitude

Absolute Difference in Temperature for Last Ice Age (LIA - 1995)

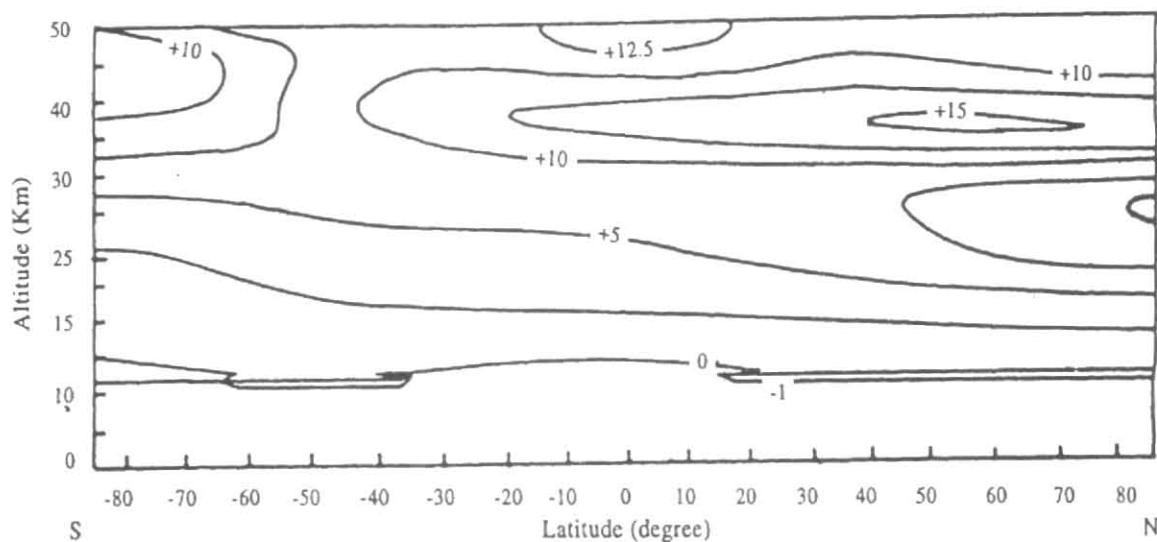


Fig. 3(b). The meridional distribution of the absolute difference in temperature for the last ice age as compared to present

Change in Ozone Number Density Through Ages as Compared to 1995

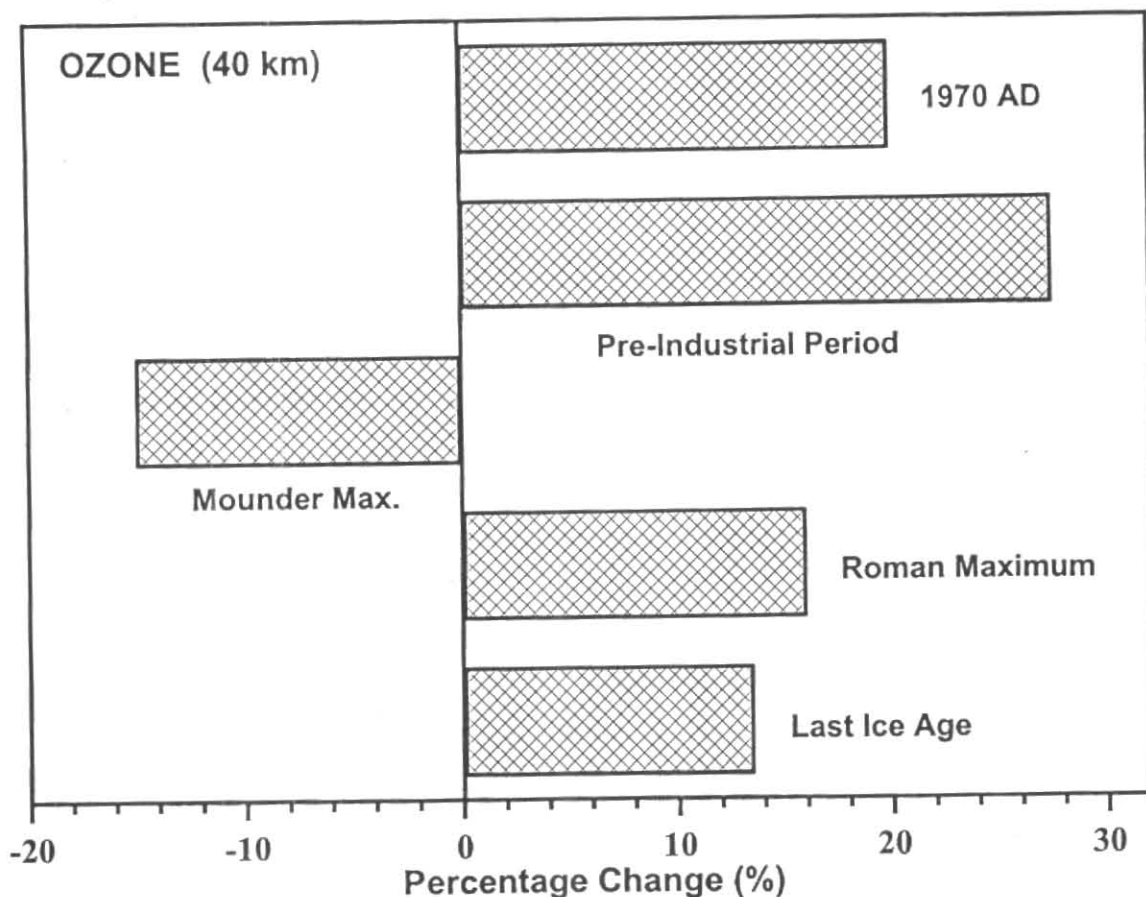


Fig. 4(a). The model simulated percentage change in ozone number density for different palaeoperiods as compared to present, calculated for 40 km altitude

becomes slow. Similarly most of the loss rate are temperature dependent and proportional to a factor $\sim \exp(-1/T)$. Hence, an increase in temperature will make the loss of ozone faster. In both the cases, an increase in temperature, which is the case for all the palaeoperiods, will lead to reduce ozone concentration. However, as compared to present period, the past glacial period was free from any CFCs and hence no chlorine loading and subsequent destruction mechanism for ozone was present. This mechanism would give rise to an enhancement of ozone in the past time period as compared to present. The later mechanism supersede the earlier and the combined effect of all the above mentioned counter-balance mechanisms will give rise to an increase in ozone concentration for last ice age as well as for Roman maximum (Fig. 4a). In case of Mounder Maximum, where due to the very low solar flux, several different mechanisms were activated; the production of ozone must have been reduced due to the low photo-dissociation rate.

This must have led to reduced ozone by -15% at 40 km for this time period as calculated by the model. The ozone is calculated to be maximum (25% at 40 km) for pre-industrial period followed by 1970 as compared to present. For the pre-industrial period, CO_2 concentration was sufficiently high as compared to ice ages. This give rise to a cooling in the stratosphere which led to enhance production of ozone. However, this production channel for pre-industrial period was slower as compared to present due to higher volume ratio of CO_2 now. But the loss due to CFCs was not present for pre-industrial period. The combined effect of both the mechanisms is reflected in Fig. 4(a). In case of 1970, the percentage increase in ozone is mainly due to the less amount of chlorine loading due to CFCs, which play a major role in recent ozone depletion.

Fig. 4(b) shows the meridional distribution of the percentage change in ozone for the last ice age case as

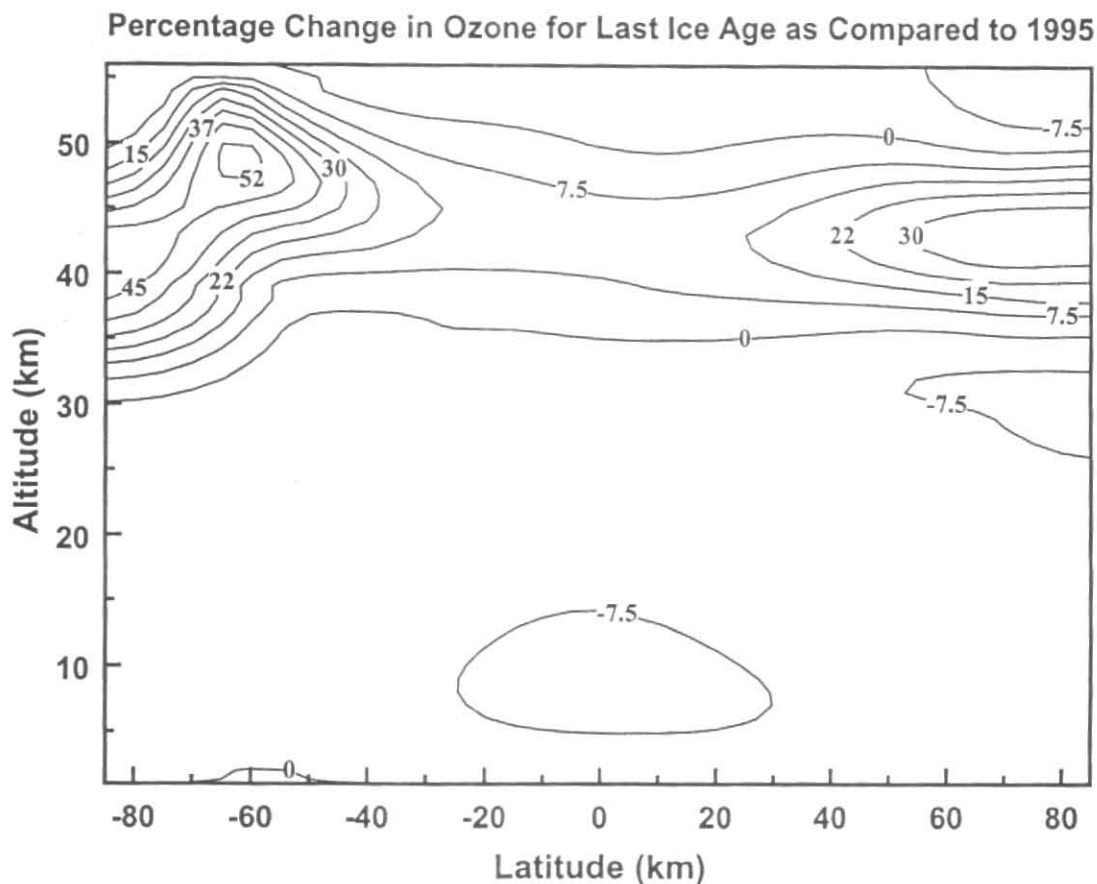


Fig. 4(b). The meridional distribution of the percentage change in ozone number density for the last ice age as compared to present

compared to present. It is evident from Fig. 4(b) that the change in ozone amount is almost negligible for the lower stratosphere and the decrease in tropospheric ozone and an increase in upper stratospheric ozone is also clear. The maximum percentage increase is confined near the poles. The increase in ozone is maximum in southern hemisphere with a value of about 50% at about 45 km near pole. Since most of the ozone is concentrated in the lower stratosphere, it is important to mention here that total ozone content undergoes negligible change for the ice-ages as compared to pre-industrial era. Total ozone stability during glacial and interglacial periods was also reported earlier by Karol *et al.* (1995) and Crutzen and Bruehl (1993). In addition to the above, the tropospheric ozone deficit in palaeoperiods is compensated partly by the ozone increase in the upper stratosphere.

Fig. 5 shows the bar diagram for the percentage change in hydroxyl number density for different palaeoperiods as compared to present. It is interesting to note that the concentration of -OH was less for all the

palaeoperiods as compared to the present. A decrease by -20% for the last ice age and a maximum decrease by -30% for the Mounder Maximum periods are calculated by the model (Fig. 5) at 40 km altitude. This is mainly due to the less amount of CH_4 in the ice age era.

Hydroxyl is formed by the action of ultraviolet radiation on ozone and H_2O as follows –



In the stratospheric altitude, the oxidation of methane is a known source of water vapour and hence for OH as shown above. The OH not only participates in catalytic ozone destruction reactions, but also converts ozone - destroying NO_x radicals into far less reactive HNO_3 by the reaction-



Change in Hydroxyl Concentration Through Ages as Compared to 1995

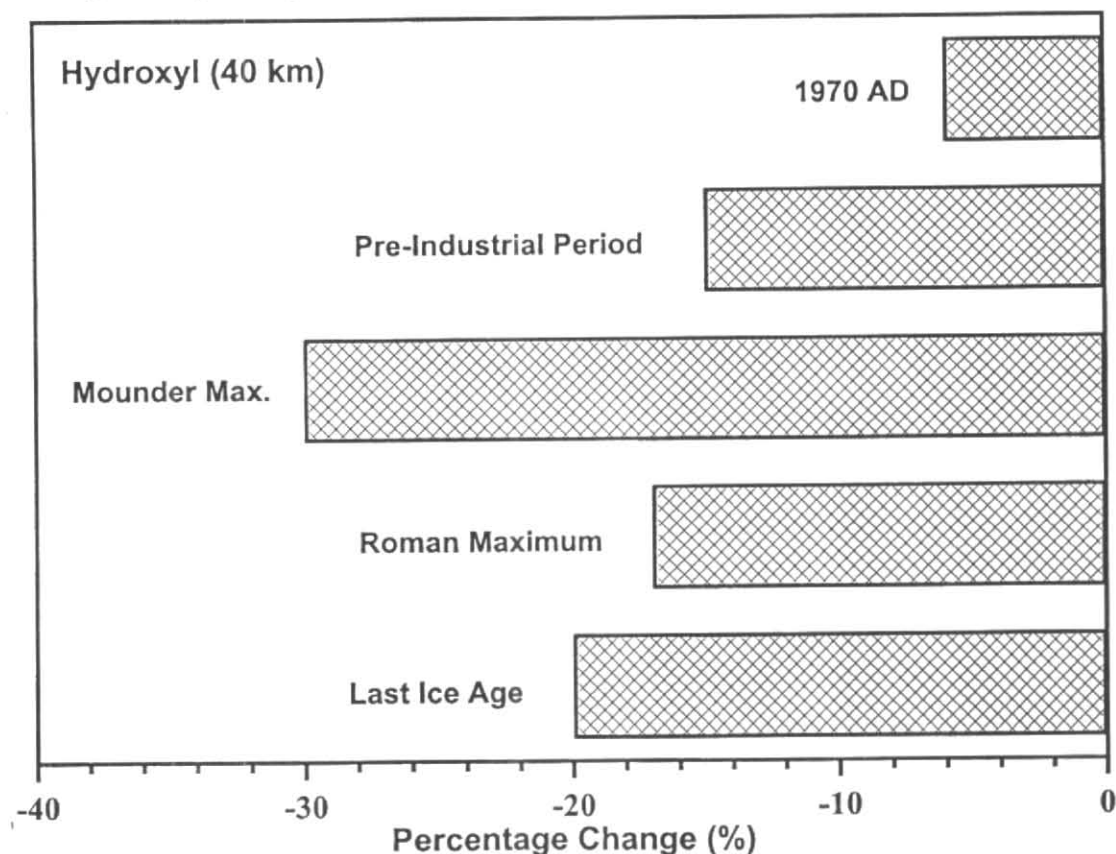


Fig.5. The model simulated percentage change in hydroxyl number density for different palaeoperiods as compared to present calculated for 40 km altitude

Hence the deficit in the CH_4 would lead to decrease in OH. This deficit in OH, which acts as atmospheric detergent and the main oxidizing gas, would have played an important role in changing the palaeoenvironment.

Fig. 6 shows the meridional distribution of the percentage change in water vapour content in the altitude range of surface to stratopause as compared to present. This figure shows a significant reduction in water vapour for the stratosphere but the tropospheric profile is almost close to zero. The dry stratosphere is very well associated with the warmer temperature for the last ice age case. The warmer temperature must have vaporized sufficient water vapour until the partial pressure limit is reached. The deficit in H_2O is another reason for reduction in hydroxyl number density as per the above-mentioned reaction.

5. Conclusion

In a relatively new approach, simulations were made to reconstruct the atmospheric composition and thermal

structure of the palaeoperiods. Reported results are the reflection of large increases in the surface abundance of CO_2 , N_2O , CH_4 and CFCs from past to the present. It is interesting to note that the deficit in tropospheric ozone and an increase in upper stratospheric ozone have nearly counterbalanced the total ozone content for glacial periods. However, the tropospheric cooling is not sufficient to compensate the large increase in temperature calculated in the stratosphere for the last ice age. The role of altered hydroxyl radical and water vapor concentrations is quite evidence in understanding the variations in several key chemical species.

Present study on model reconstruction of atmospheric composition has certainly increased our understanding on radiative and chemical structure of the palaeoenvironment. It is likely to be more realistic than the earlier work reported in literature since it involves interactive processes and minimum number of assumptions in 2-D domain. Earlier studies were based on

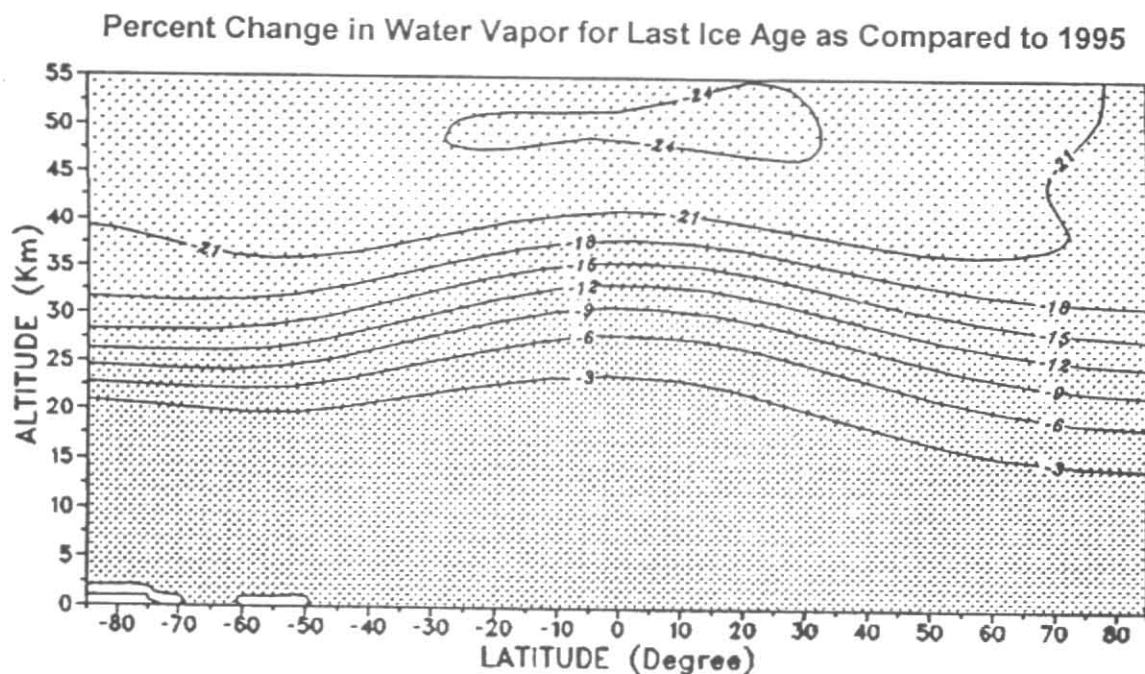


Fig. 6. The meridional distribution of the percentage change in water vapor number density for the last ice age as compared to present

1-D and 1.5-D models without interactive processes. However detailed study by considering the realistic input data of palaeoperiods for several other forcing parameters, about which no information is available till date, are suggested.

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