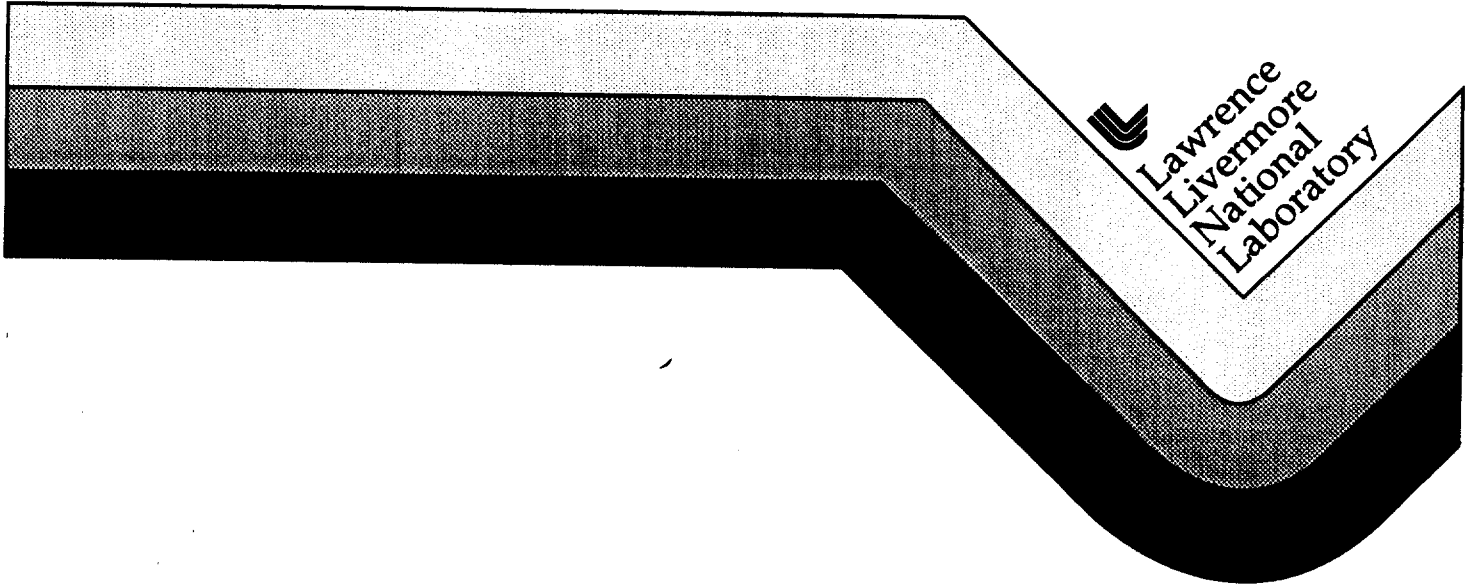
CONF-970284

GRI Methane Chemistry Program Review Meeting

J. Dignon, K. Grant, A. Grossman, D. Wuebbles, G. Brasseur,
S. Madronich, T. Huang, J. Chang, B. Lott

February 1997



GRI METHANE CHEMISTRY PROGRAM REVIEW MEETING

Monday - Tuesday February 3 - 4, 1997

LIST OF PARTICIPANTS

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AGENDA
for
GRI METHANE CHEMISTRY PROGRAM REVIEW MEETING

Monday - Tuesday February 3 - 4, 1997

Monday February 3, 1997

0900	Welcome	A. Grossman
0915	GRI Perspectives	B. Lott
0945	Atmospheric Chemistry, Climate Change, and Climate Policy Considerations Related to Methane	D. Wuebbles
	Integrated Science Assessment Modeling	D. Wuebbles A.K. Jain K. Hayhoe
	Methane Modeling and Abatement Studies	D. Wuebbles K. Hayhoe A.K. Jain
1015	Break	
1045	The Images Model at NCAR	G. Brasseur
1115	Analysis of Chemical Processes, Computational Efficiency and Grid Resolutions of 3-D Regional-scale Models	J. Chang
1145	Lunch	
1330	Methane Perturbation Lifetimes for Global Warming Potential Calculations	A. Grossman J. Dignon
1400	Estimates of the methane response time with the NCAR 2D model	T. Huang
1430		S. Madronich
1500	Break	
1530	General Discussion of Global Warming Potential Scenarios	All
1700	Adjourn	

Tuesday January 4, 1997

0900	General Discussion of Future Directions and Modeling Efforts By All Groups In The GRI Methane Chemistry Research Program	All
1200	Adjourn	

HIGHLIGHTS

- A joint report to be issued by this group in the June 1997 timeframewill have the following outline:

  1. Global Warming Potentials,
     a. Definitions
     b. Pulse Size
     c. Time Horizon

  2. Concerns For Natural Gas Industry

  3. Direct Global Warming Potentials
     a. Radiative Forcing
     b. Response time or lifetime

  4. Indirect Global Warming Potentials
     a. Ozone
     b. Water Vapor

  5. Effects of Non Methane Hydrocarbons

  6. Data

  7. Conclusions.

- Good agreement between NCAR and LLNL 2-D model methane lifetime values (8 - 9) years.

- Initial 3-D GRANTOUR chemistry-transport model pulse response time reported by LLNL of ~12 years agrees with NCAR 2-D model response time.

- NCAR 3-D Mozart chemistry model can be used to look at methane and ozone distributions.

- Integrated Assessment Models are needed to look at methane and carbon dioxide emission scenarios.

ABSTRACTS

Atmospheric Chemistry, Climate Change, and Climate Policy Considerations Related to Methane

Donald J. Wuebbles

University of Illinois
Department of Atmospheric Sciences

Methane is an important greenhouse gas which affects the atmosphere directly by the absorption and re-emission of infrared radiation as well as indirectly, through chemical interactions. Emissions of several important greenhouse gases (GHGs) including methane are increasing, mainly due to human activity. Higher concentrations of these gases in the atmosphere are projected to cause a decrease in the amount of infrared radiation escaping to space, and a subsequent warming of global climate. It is therefore vital to understand not only the causes of increased production of methane and other GHGs, but the effect of higher GHG concentrations on climate, and the possibilities for reductions of these emissions.

In GRI-UIUC methane project, the role of methane in climate change and greenhouse gas abatement strategies is being studied using several distinct approaches. First, a detailed treatment of the mechanisms controlling each important methane source and sink, and hence the atmospheric concentration of methane, is being developed for use with the UIUC Integrated Science Assessment Model. The focus of this study is to resolve the factors which determine methane emissions and removal, including human population, land use, energy demand, global temperature, and regional concentrations of the hydroxyl radical, carbon monoxide, nitrous oxides, non-methane hydrocarbons, water vapour, tropospheric and stratospheric ozone.

Methane Modeling and Abatement Studies

D. J. Wuebbles, K. A. S. Hayhoe, and A. Jain

University of Illinois
Department of Atmospheric Sciences

A study is being conducted which considers the economic and climatic benefits of simultaneous carbon dioxide (CO2) and methane (CH4) abatement, as opposed to carbon dioxide abatement alone. Estimates of the costs associated with methane abatement have been compiled and an empirical abatement cost for methane emissions derived, in a similar manner to accepted carbon dioxide abatement cost functions. The methane abatement function has now been applied using the Economic Greenhouse Gas Abatement Model (EGGAM), a numerical model developed as a component of this project. A least-cost approach is taken to compare the costs of CO2 to simultaneous CO2 and CH4 emission reductions under the restrictions imposed by various scenarios for the stabilization or reduction of greenhouse gases and radiative forcing. Recent results demonstrate that near-term reductions in methane could be obtained at relatively low cost when compared to the equivalent amount of carbon dioxide abatement. However, in order to meet long-term commitments to reductions in radiative forcing or CO2-equivalent greenhouse gas emissions, significant reduction of carbon dioxide emissions is also necessary.

Lastly, it was also proposed to evaluate the climatic impact of fuel-switching, one of the short-term mitigation strategies discussed by the IPCC (1996). Changes in emissions of carbon dioxide, methane, and sulfate aerosols associated the replacement of coal use by natural gas in the utility sector have now been assessed. The impact of these changes on climate have been modelled, showing that the climatic benefits of fuel-switching will not become apparent for at least a decade due to the initial reduction in aerosol emissions. In addition, the overall benefits are very sensitive to the sulfur content of the coal used, the fraction of natural gas lost during extraction and transportation, and particularly the value of radiative forcing for sulfate aerosols within the range given by the IPCC (1996).

Methane Perturbation Lifetimes for Global Warming Potential Calculations

Jane Dignon, Allen S. Grossman, and Keith E. Grant

Atmospheric Science Division
Lawrence Livermore National Laboratory
Livermore, Ca. 94550

An ambient atmospheric model obtained using the LLNL GRANTOUR 3-D chemistry-transport modal was analyzed to obtain average methane lifetimes that were used to calculate Global Warming Potentials (GWP's). The methane chemical lifetimes in each of the twenty five thousand GRANTOUR parcels was calculated using a perturbation model applied to a simplified, three reaction chemistry set consisting of the species CH_4, CO, and OH. Appropriate global ensemble average CH_4 lifetimes were calculated for the ambient atmosphere and for an atmosphere in which a small methane pulse was applied. Effects of non methane hydrocarbon species were simulated by including isoprene in the ambient atmosphere. The differences between 2-D and 3-D models were investigated by comparing the lifetime analyses in a zonally averaged 3-D model to those of the 3-D model. The effect of different CH_4 lifetimes on the GWP will be discussed. The results of the calculations give unperturbed CH_4 lifetimes of ~8 years which is in good agreement with the latest published results (8.0 - 8.9 years). CH_4 pulse lifetimes of ~12 years were obtained with the perturbation model. When isoprene is not included in the ambient atmosphere the lifetimes decrease by about ten percent. Approximate direct GWP's for CH_4 obtained with the perturbation model were 44, 17, and 5 for forcing times of 20, 100, and 500 years respectively. Future calculations will involve GRANTOUR calculations of ambient atmospheres using the full seventy six prognostic species and perturbation lifetime analyses. LLNL 2-D model runs will be used to evaluate indirect ozone and water vapor GWP's.

Estimates of the Methane Response Time With the NCAR 2-D Model

T. Huang

NCAR

It is well known that CH4 perturbation decays more slowly then by its implied lifetime because of the OH feedback effect, which may have a significant impact on the calculation of the GWP from the conventional formulation. The methane reponse time is estimated with the up dated NCAR two-dimensional model that includes relatively detailed tropospheric chemistry of hydrocarbon species, in addition to the NOy and HOx species. The methane concentration was increased by 20% and 50% from the CH4 level of the base control run to a steady state condition. The OH tropospheric concentration was decreased by 6% and 12%, for the CH4 increase of 20% and 50% respectively. With the feedback factor (F) defined as the relative percentage change in the OH amount for a 1% increase in CH4 concentration, the ratio of CH4 adjustment time and the CH4 lifetime can be derived as 1/(1+F). With this formulation, the model calculation implies that the CH4 response time depends on the size of the perturbation, with an increase from its lifetime by 42% for a 20% perturbation on CH4, and an increase from its lifetime by 31% for a 50% perturbation on CH4.

Exploratory Studies of Methane Chemistry

S. Madronich

NCAR

We have carried out several modeling studies of the non-linear photochemistry of methane in the troposphere. These included (a) a re-examination of the OH production from the photolysis of tropospheric ozone, with a re-evaluation of quantum yields based on model-measurement comparisons; (b) observation of increased CO and CH4 levels in the tropics, for several months after the Mt. Pinatubo eruptions, that can be explained by lower OH formation (again from ozone photolysis) due to enhanced stratospheric SO2 and sulfate aerosols and associated reduction of UV transmission through the stratosphere to the troposphere; (c) detailed characterization of tropospheric chemical oscillations, including an analytic formulation for the period of oscillation; and (d) sensitivity studies on the role of aerosols in the removal of oxigenated organics from the boundary layer, with the implication that if such processes are indeed common, the effect of non-methane hydrocarbons on oxidant levels (e.g., ozone, OH) is considerably smaller than currently allowed in the models.

Jane Dignon
Allen S. Grossman
K.E. Grant

Lawrence Livermore National Laboratory

METHANE PERTURBATION LIFETIMES FOR GLOBAL WARMING POTENTIAL CALCULATIONS

Jane Dignon, Allen S. Grossman, and K. E. Grant

Atmospheric Science Division
Lawrence Livermore National Laboratory
Livermore California, 94551

For presentation at the
GRI Methane Chemistry Program Revue Meeting
February 3 - 4, 1997

INTRODUCTION

OUTLINE OF THE CALCULATION

- An ambient atmospheric model obtained using the LLNL GRANTOUR 3-D chemistry-transport model will be analyzed to obtain average methane lifetimes that can be used for Global Warming Potential (GWP) calculations.

- The methane chemical lifetimes will be calculated in each of the 25000 GRANTOUR parcels using a simplified perturbation model suggested by M. Prather (1994).

- An appropiate global average lifetime will be obtained for use in GWP calculations.

- Effects of non methane hydrocarbons will be simulated by including isoprene in the chemical model. Ambient model runs both with and without isoprene will be analyzed for lifetime differences.

- The differences between 2-D models and 3-D models will be discussed by comparing lifetime analyses from the zonally averaged 3-D model to those of the 3-D model.

OUTLINE OF PRESENTATION

1 • Introduction

2 • GRANTOUR Model

3 • Methane Lifetime Perturbation Model

4 • 3-D Results

5 • 2-D Results

6 • Methane Lifetime and GWP Estimates

We've developed a global, three-dimensional, photochemical-transport-deposition model (GRANTOUR)

METHOD:

Lagrangian parcel

6 hr time step

CHEMISTRY:

76 prognostic species:

O_3, OH, NO_x, PAN, HNO_3, CO, CH_4, C_2H_6, C_3H_8,
C_{4-5} & C_{6-8} alkanes, isoprene, alkenes, aromatics, etc.

(Lurmann et al., 1986; Sillman, 1991)

METEOROLOGY:

CCM1 (present); ECHAM (future)

4.5 x 7.5 degree resolution

Seasonal (Jan - Dec)

Updated every 12 hrs

GRANTOUR Model Description

Method: Lagrangian parcel (25K constant mass parcels)

Chemistry: Prather (1994) simple chemistry
OH, CH_4, CO and X

Meteorology: General Circulation Model (interactive or off-line)
ECHAM
NCAR's CCM
Jan-Dec; 12 hr updates

Emissions:

Natural		Anthropogenic
Isoprene*	(NMHCs)	Fossil Fuel
Oceans		Biomass burning

2 model scenarios

Without NMHCs:

model chemistry with CO, CH_4 and OH only.

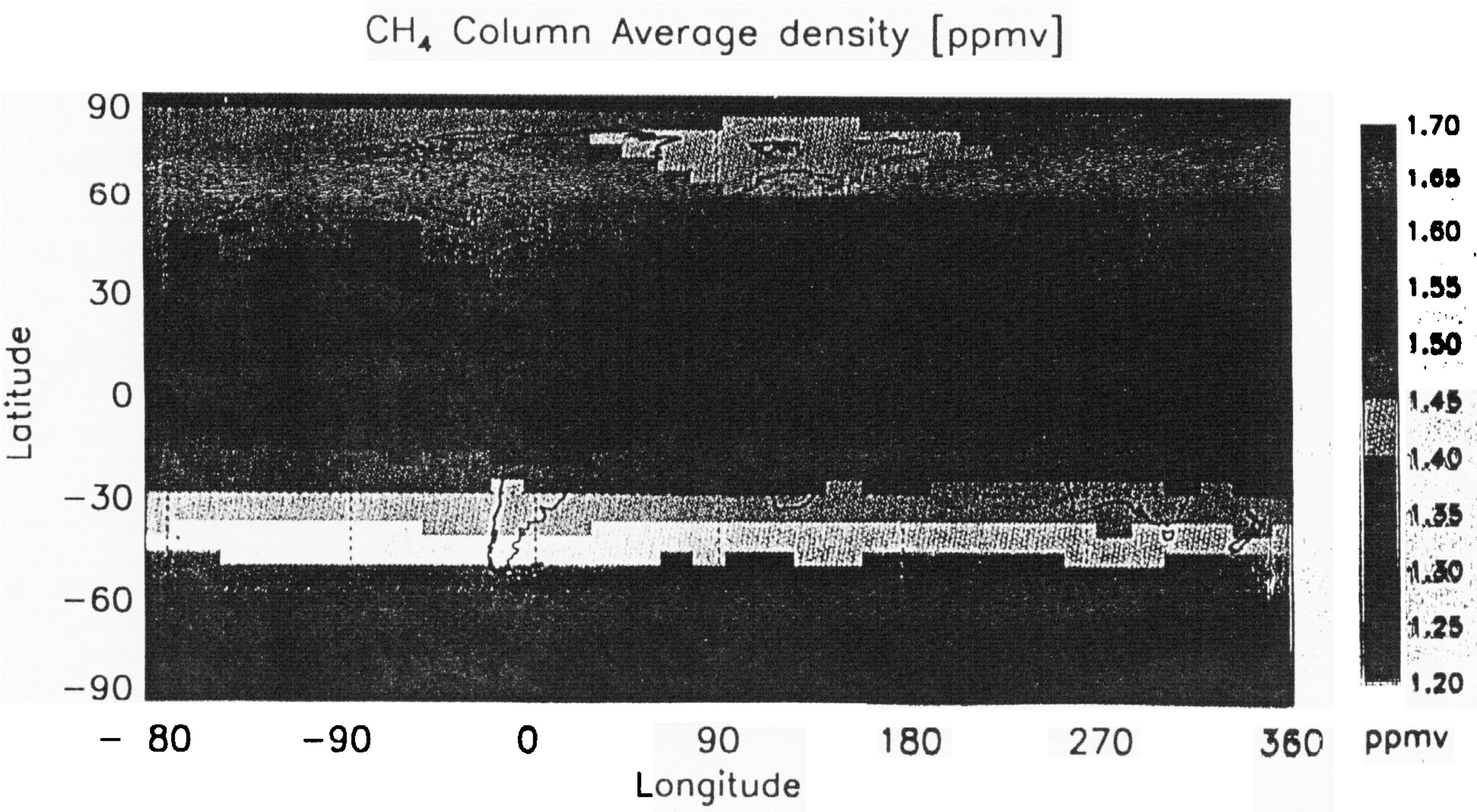
With NMHCs

Isoprene was used as a surrogate for NMHCs

Yield of CO from isoprene was obtained from the work of Altschuller (1991), Hatakeyama et al. (1991), and Hatakeyama et al. (1994)

Donald J. Wuebbles

University of Illinois



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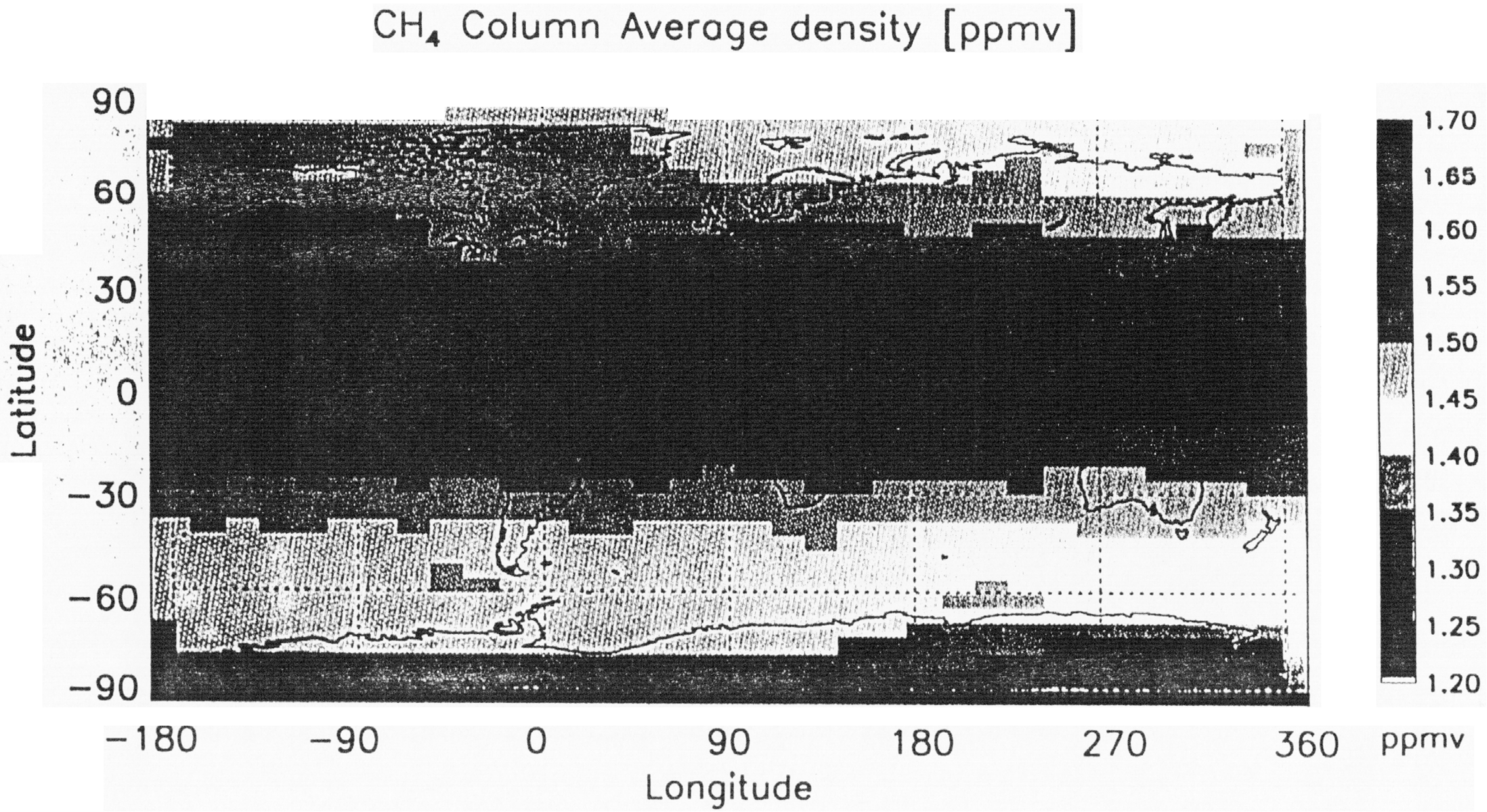

CH_4 Column Average density [ppmv]

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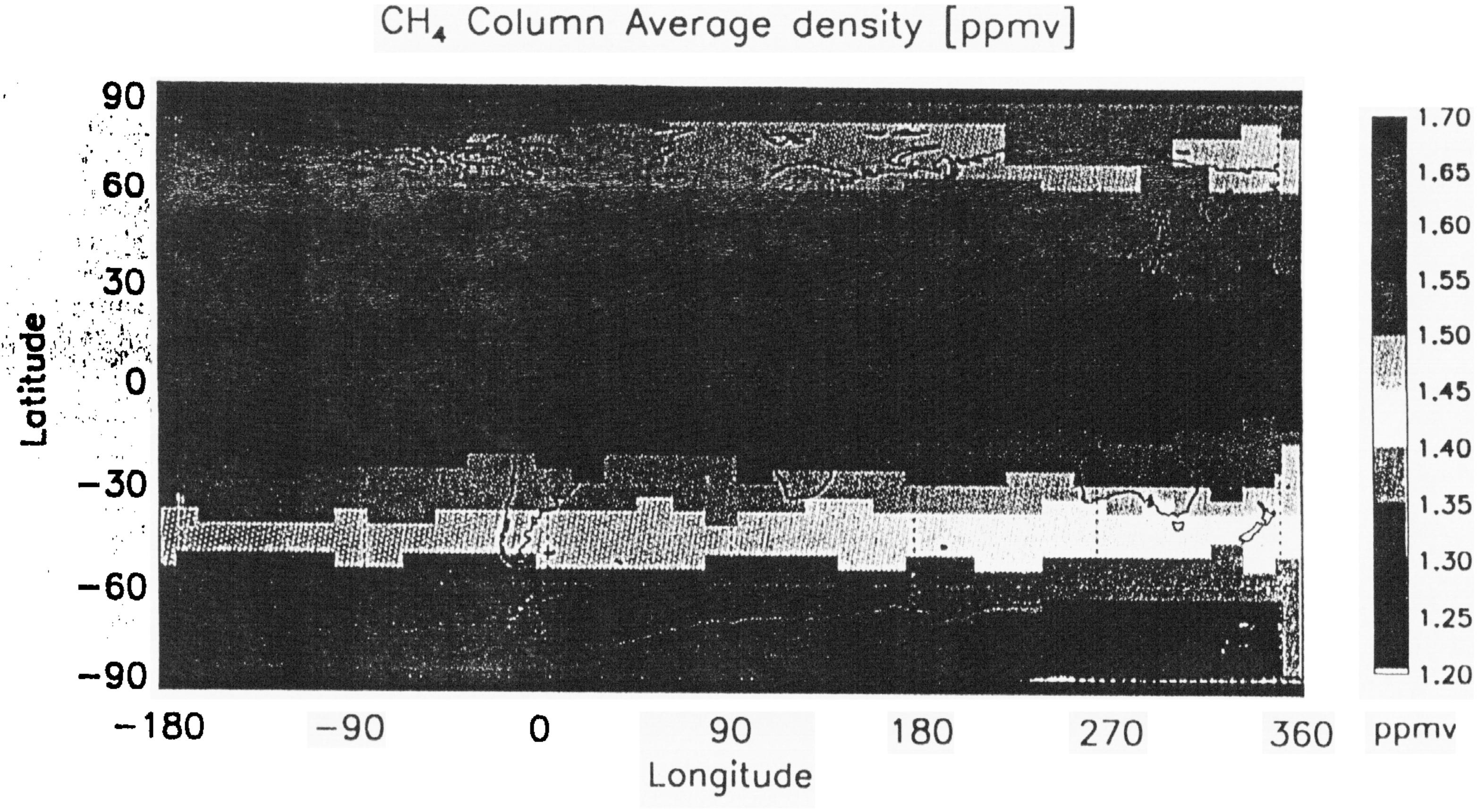

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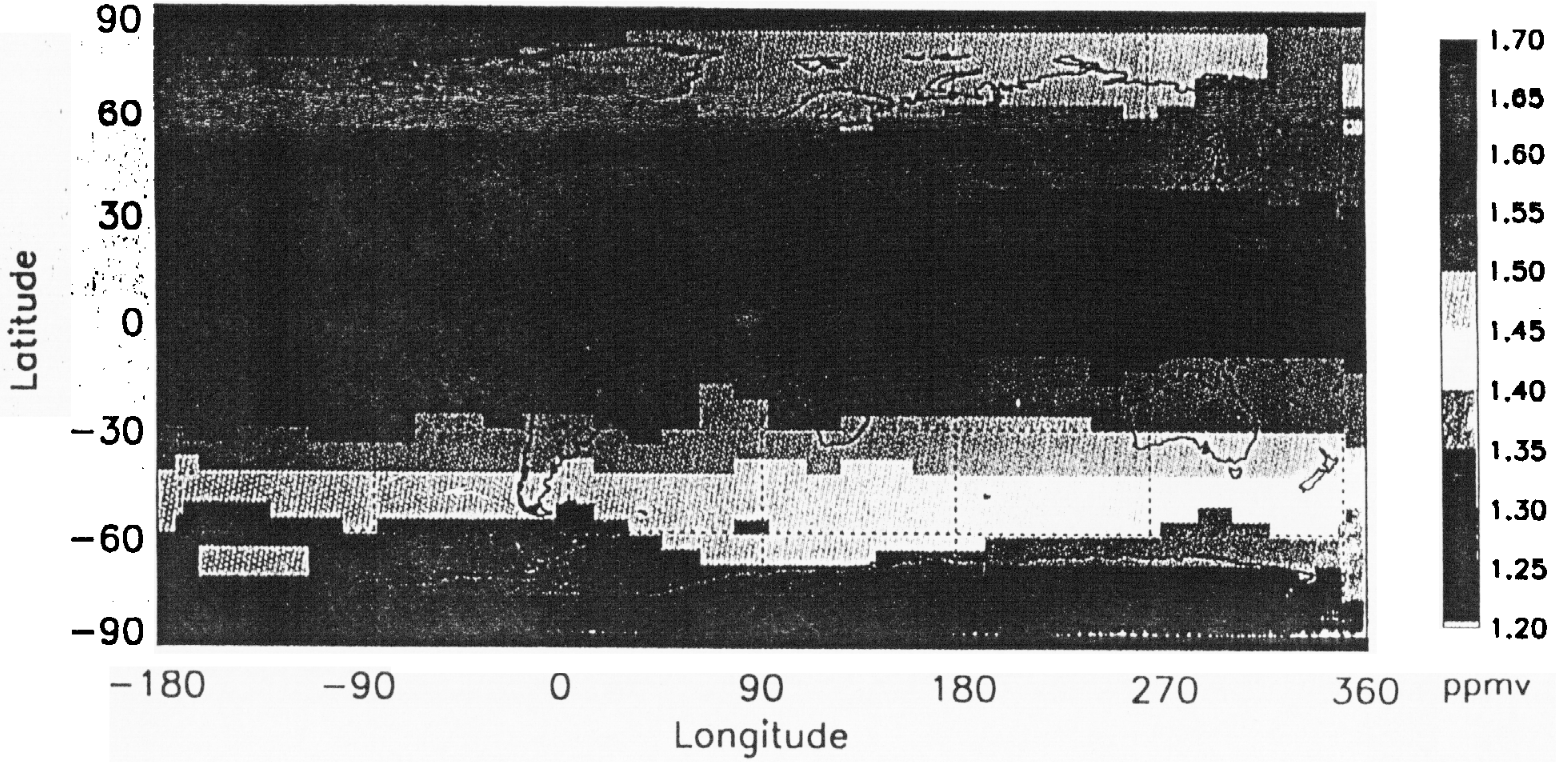

CH$_4$ Column Average density [ppmv]

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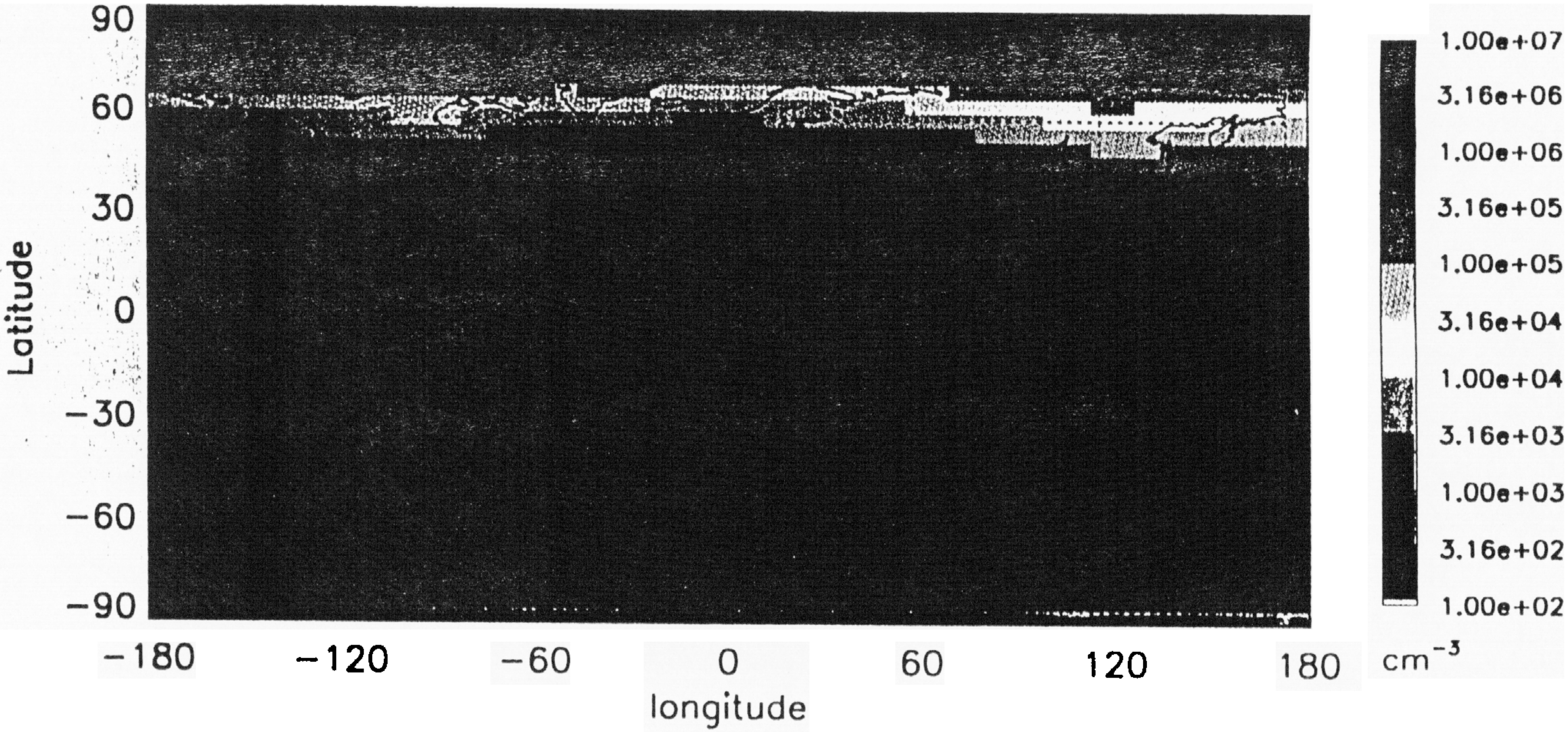
OH Column Averaged density [cm^{-3}]



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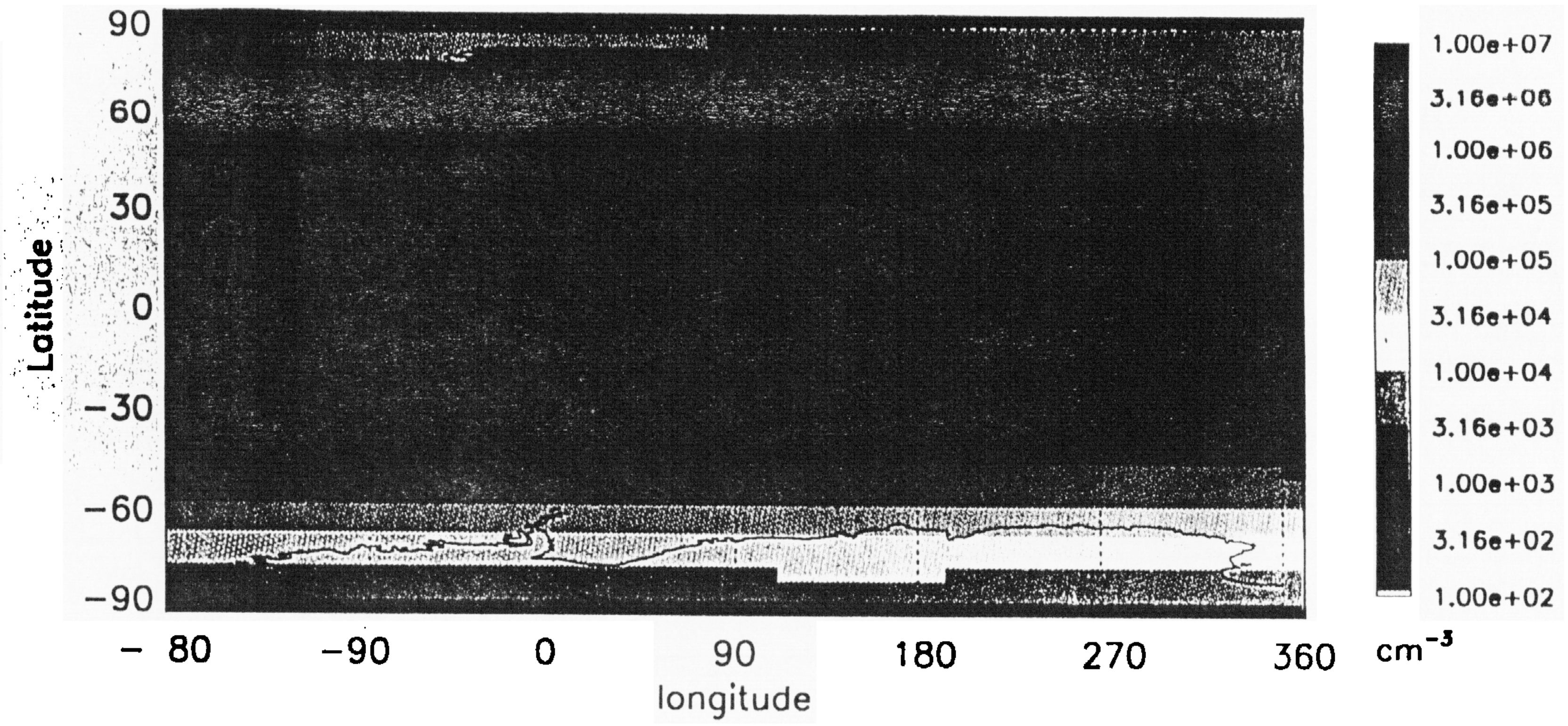
OH Column Averaged density [cm^{-3}]



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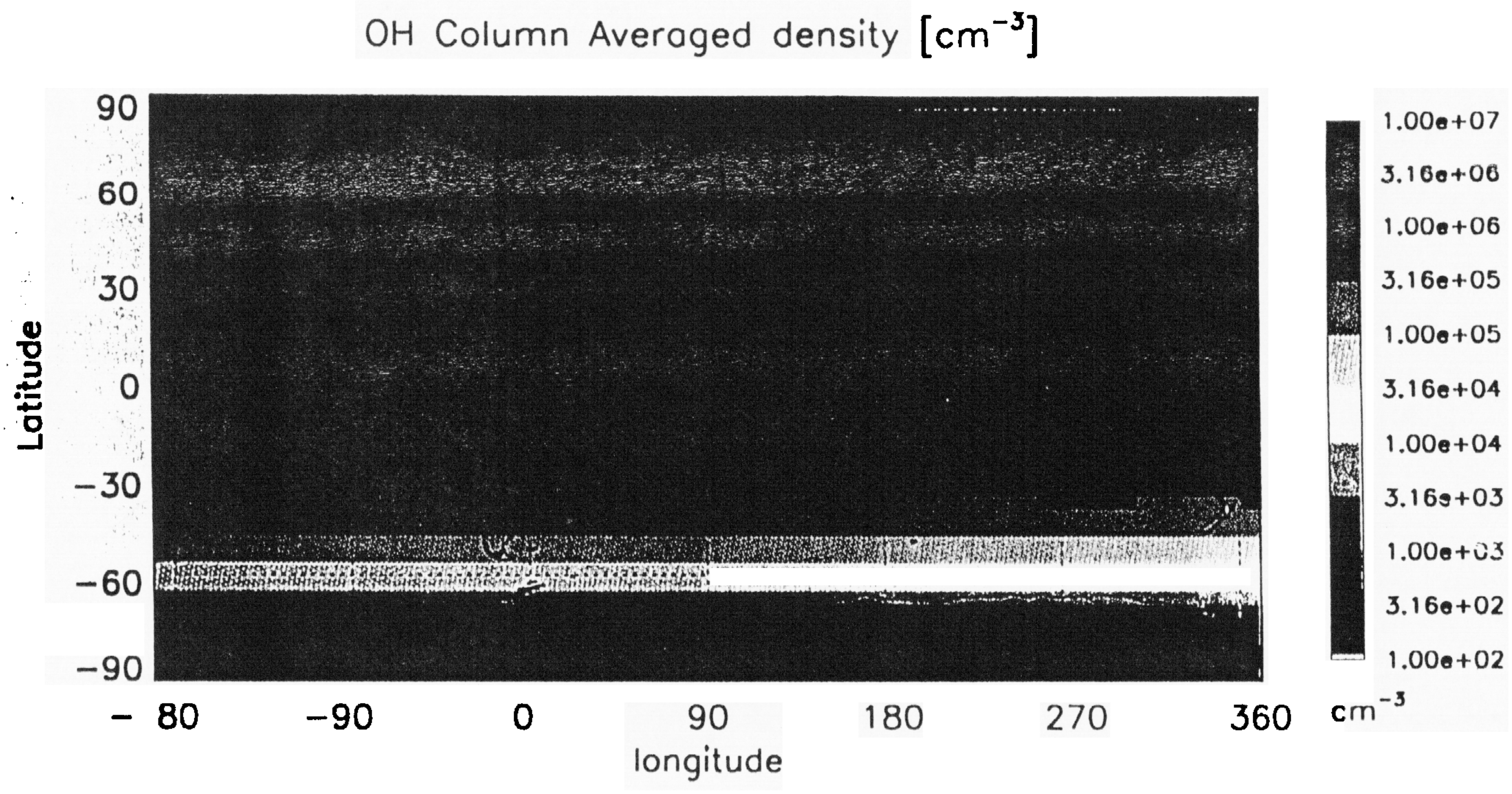

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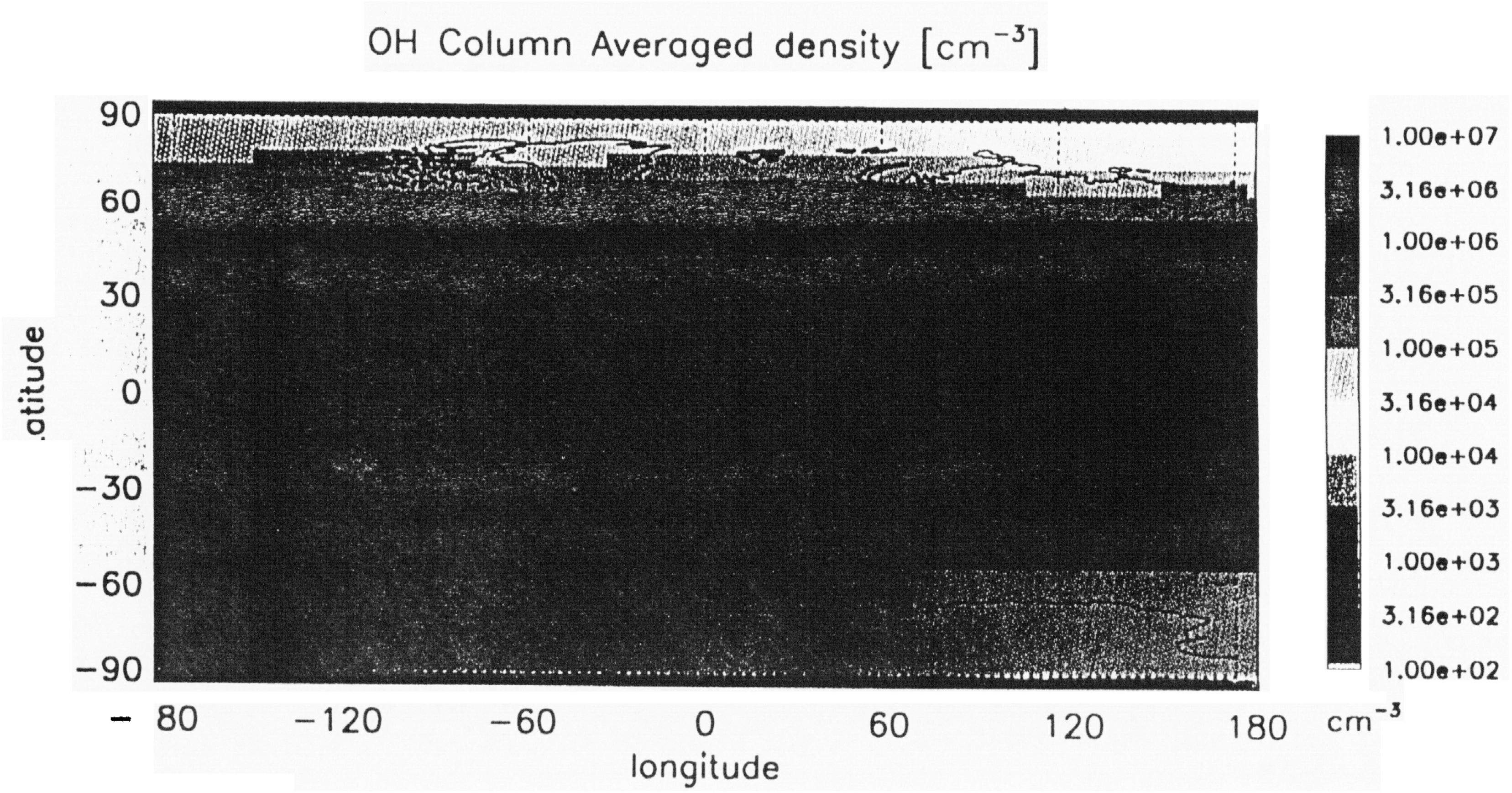

OH Column Averaged density [cm^{-3}]

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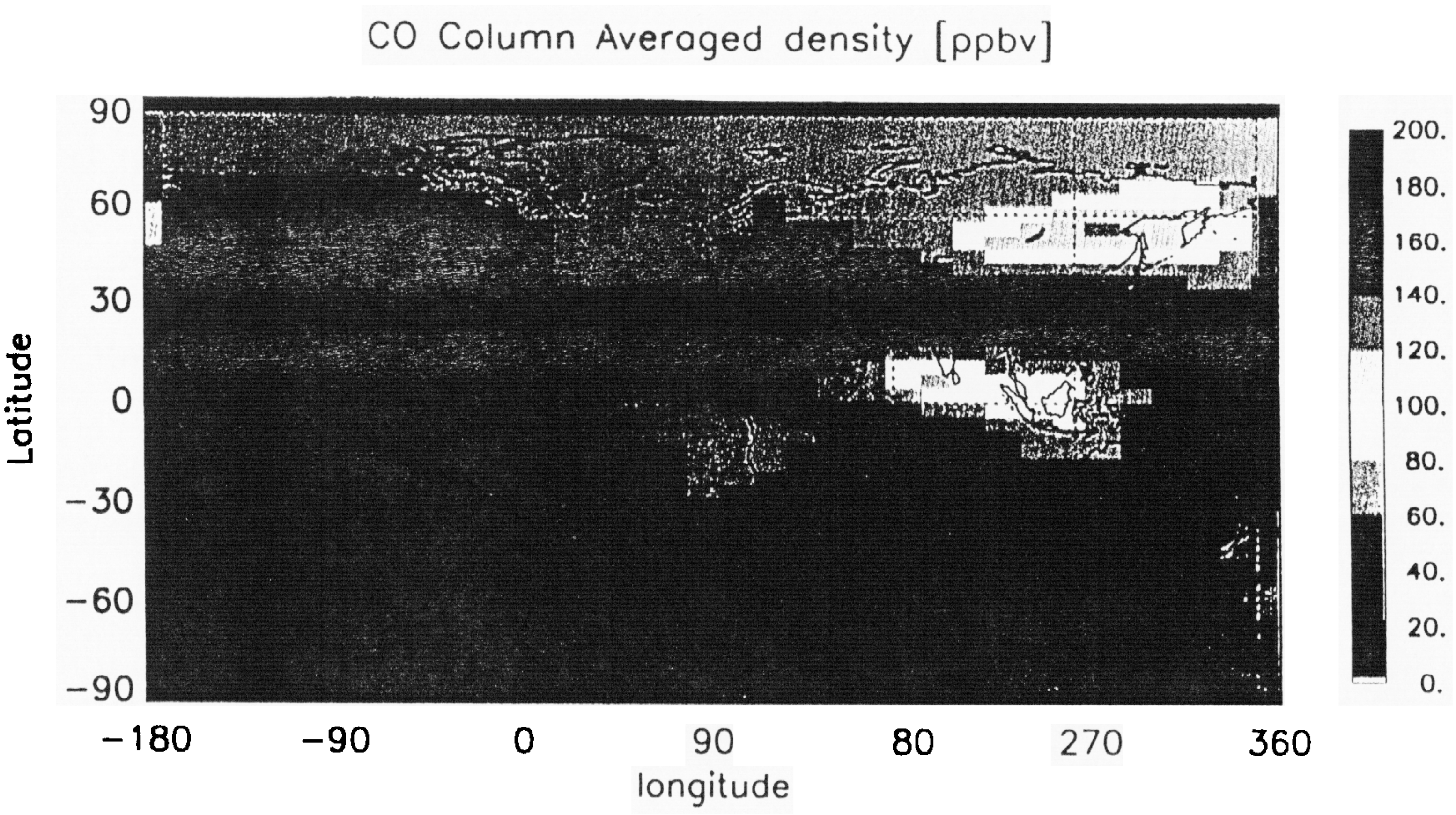

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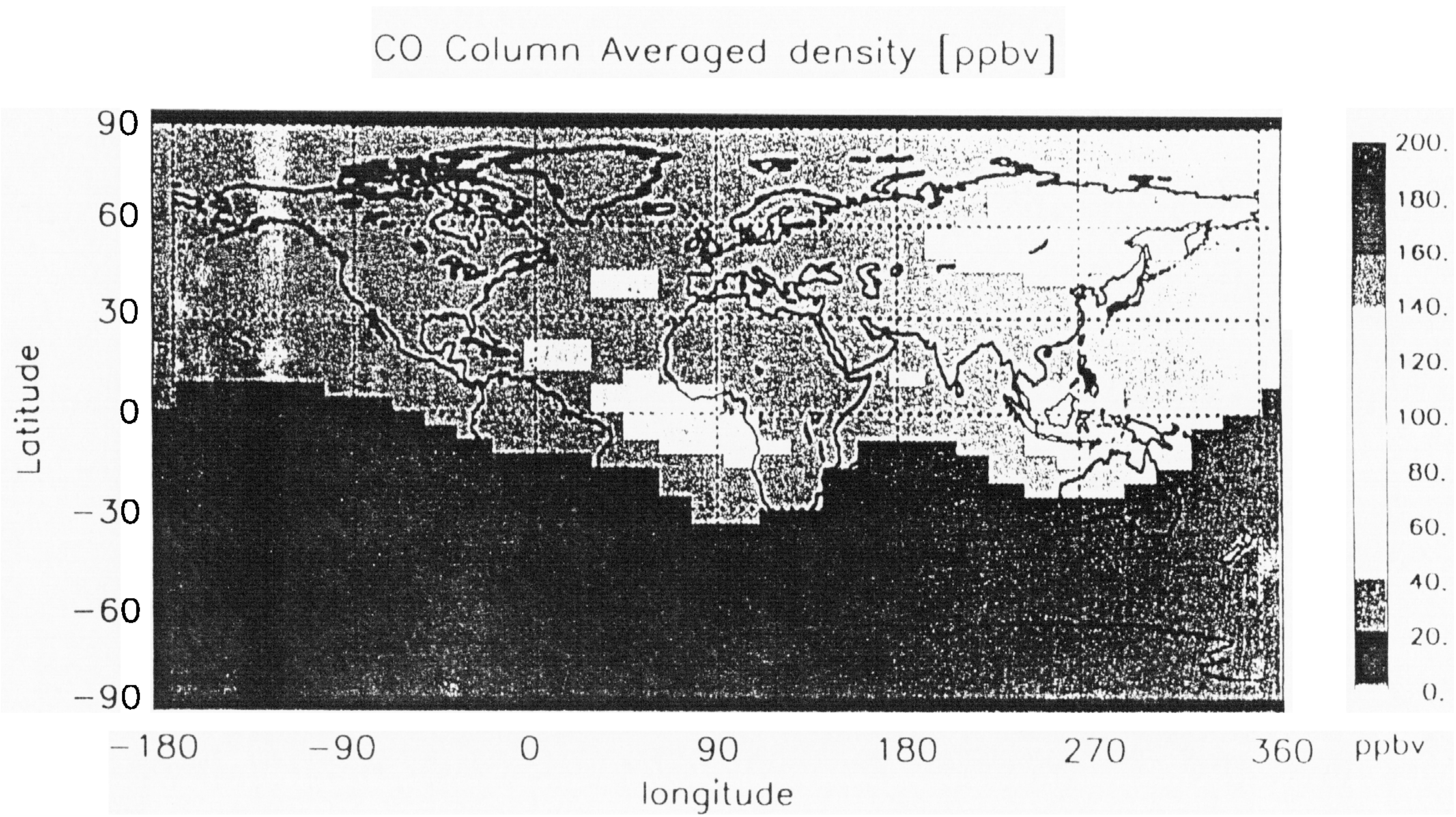
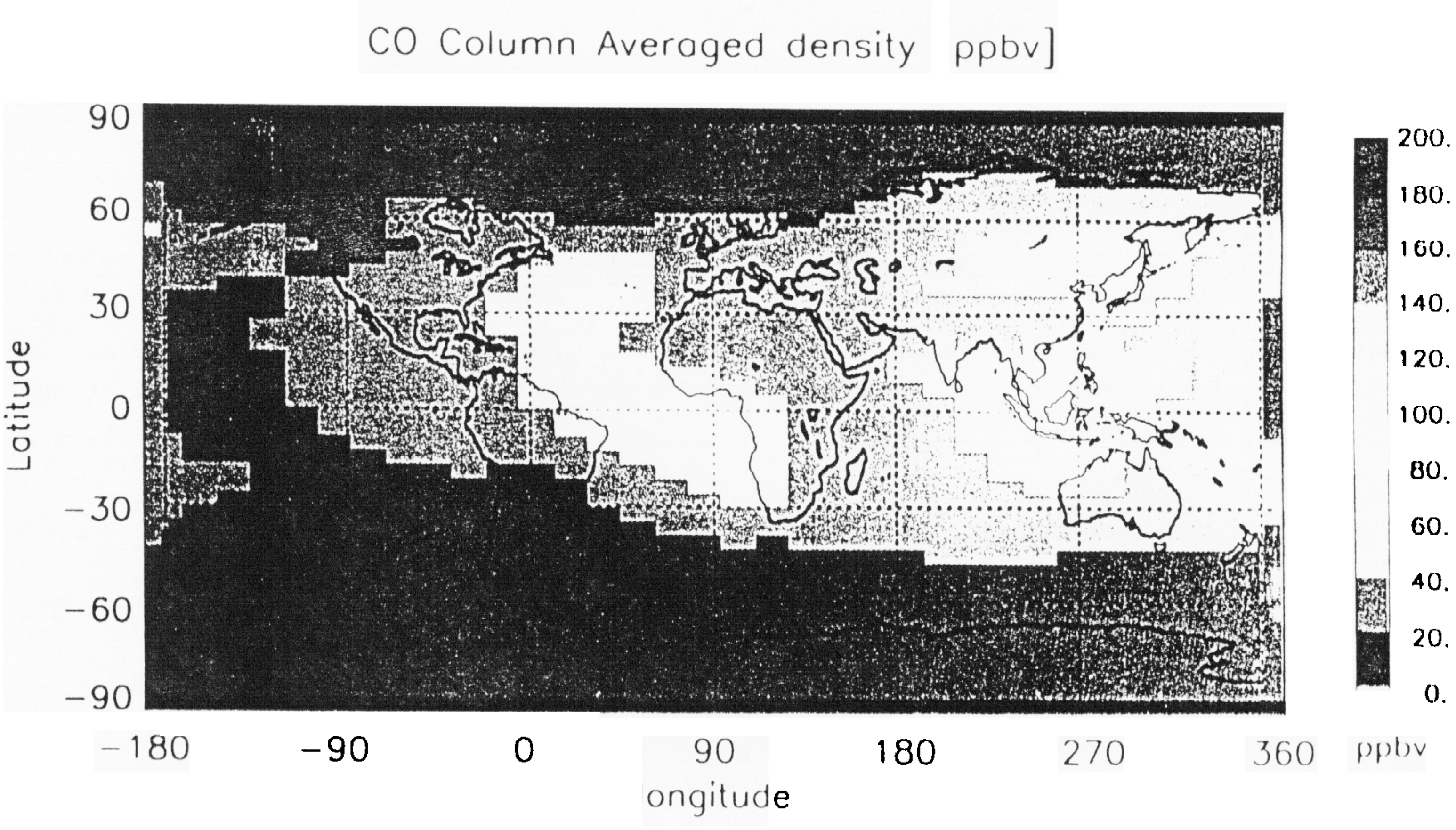


CO Column Averaged density [ppbv]

colco 04 - From 960917



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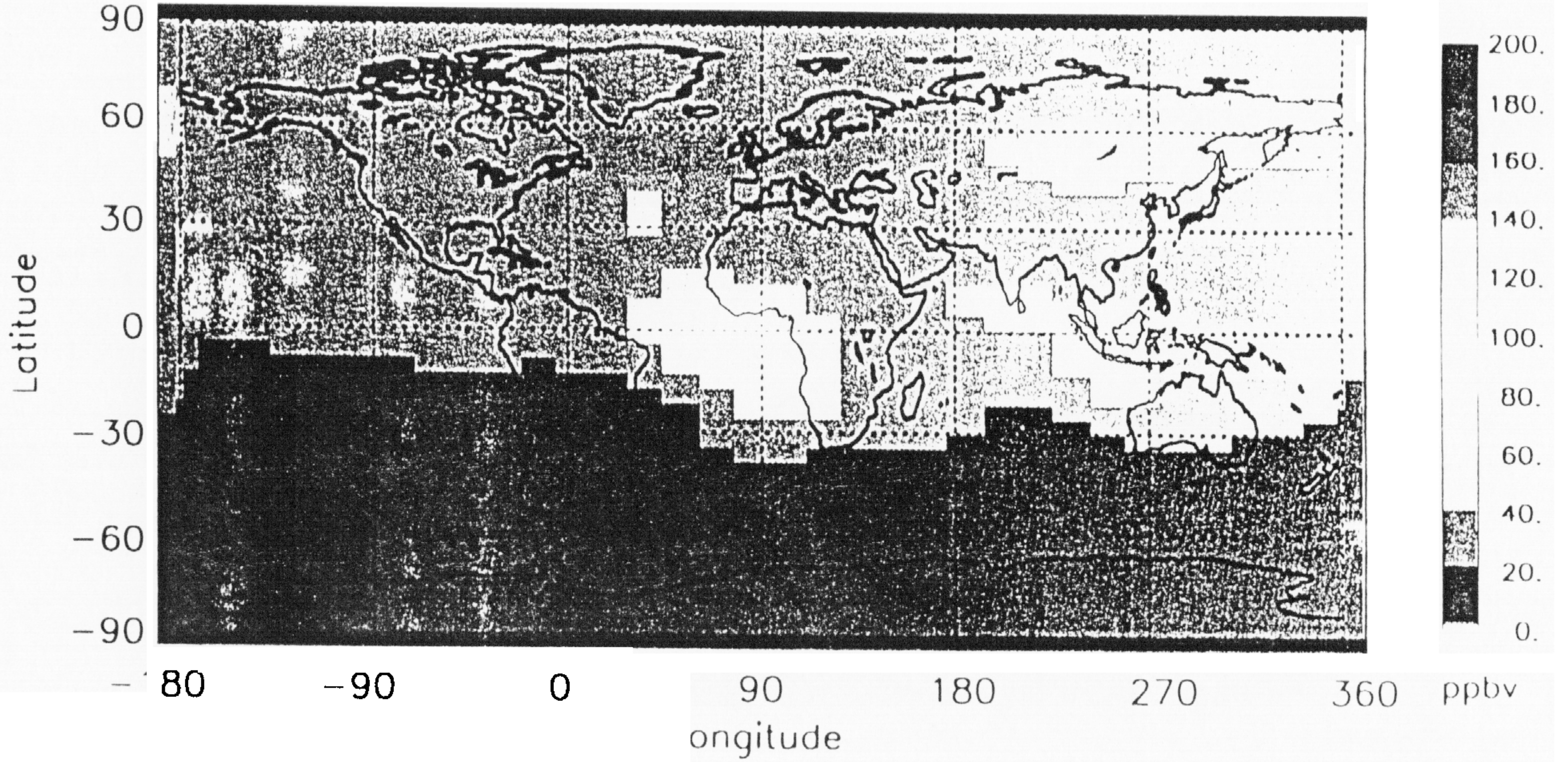
CO Column Averaged density [ppbv



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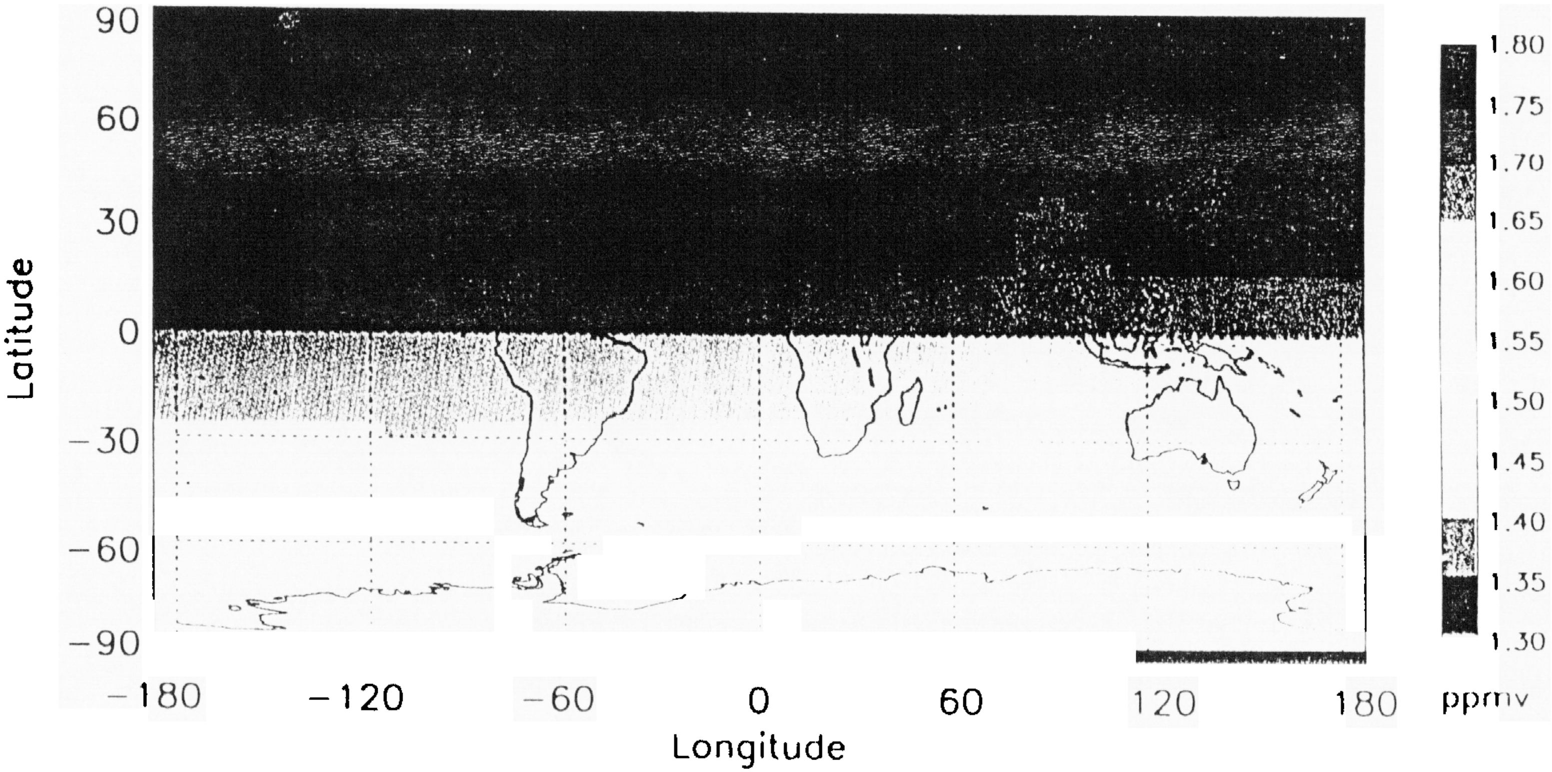
CH_4 Concentration at the Surface



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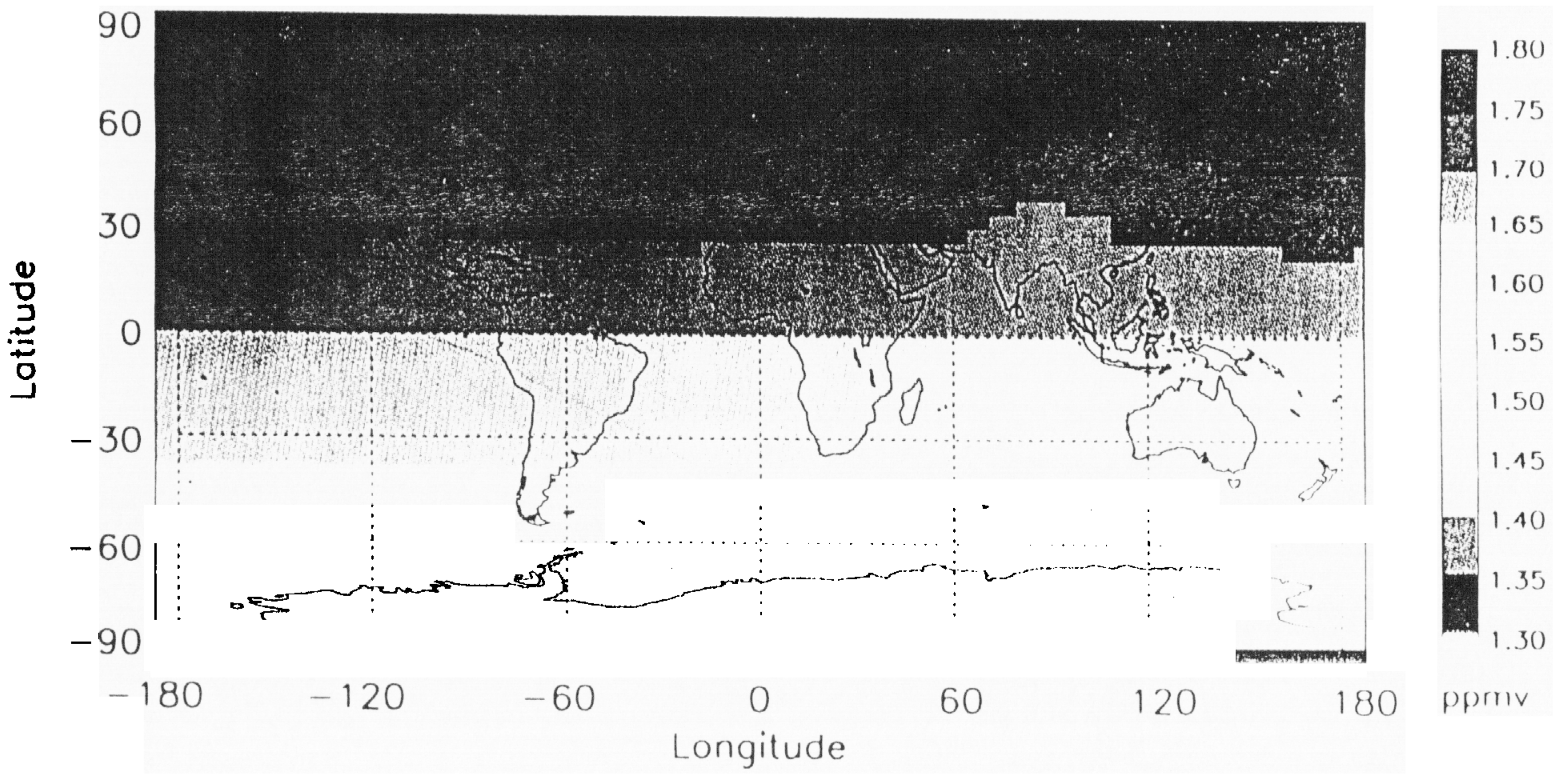
CH$_4$ Concentration at the Surface



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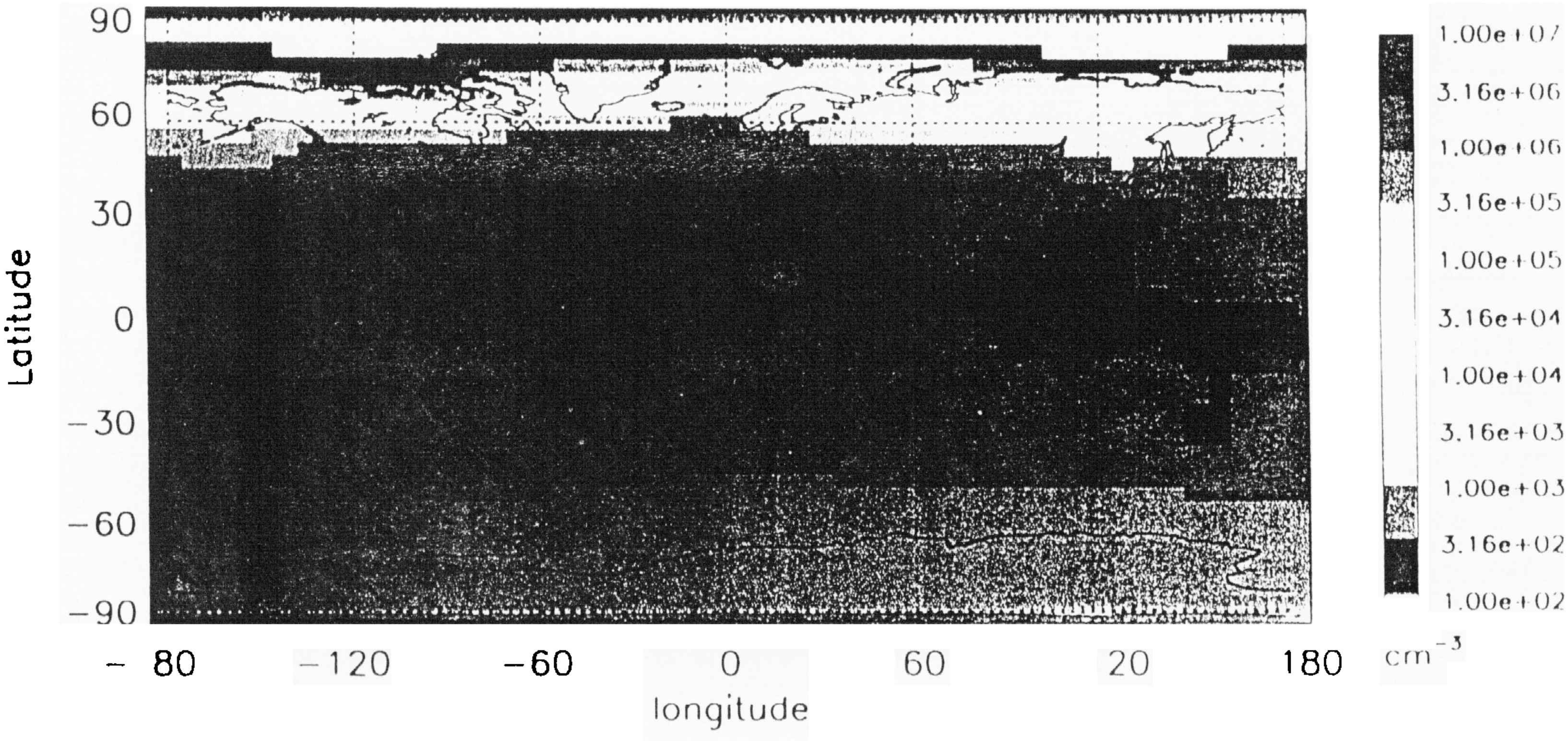
OH Surface Concentration [cm^{-3}]



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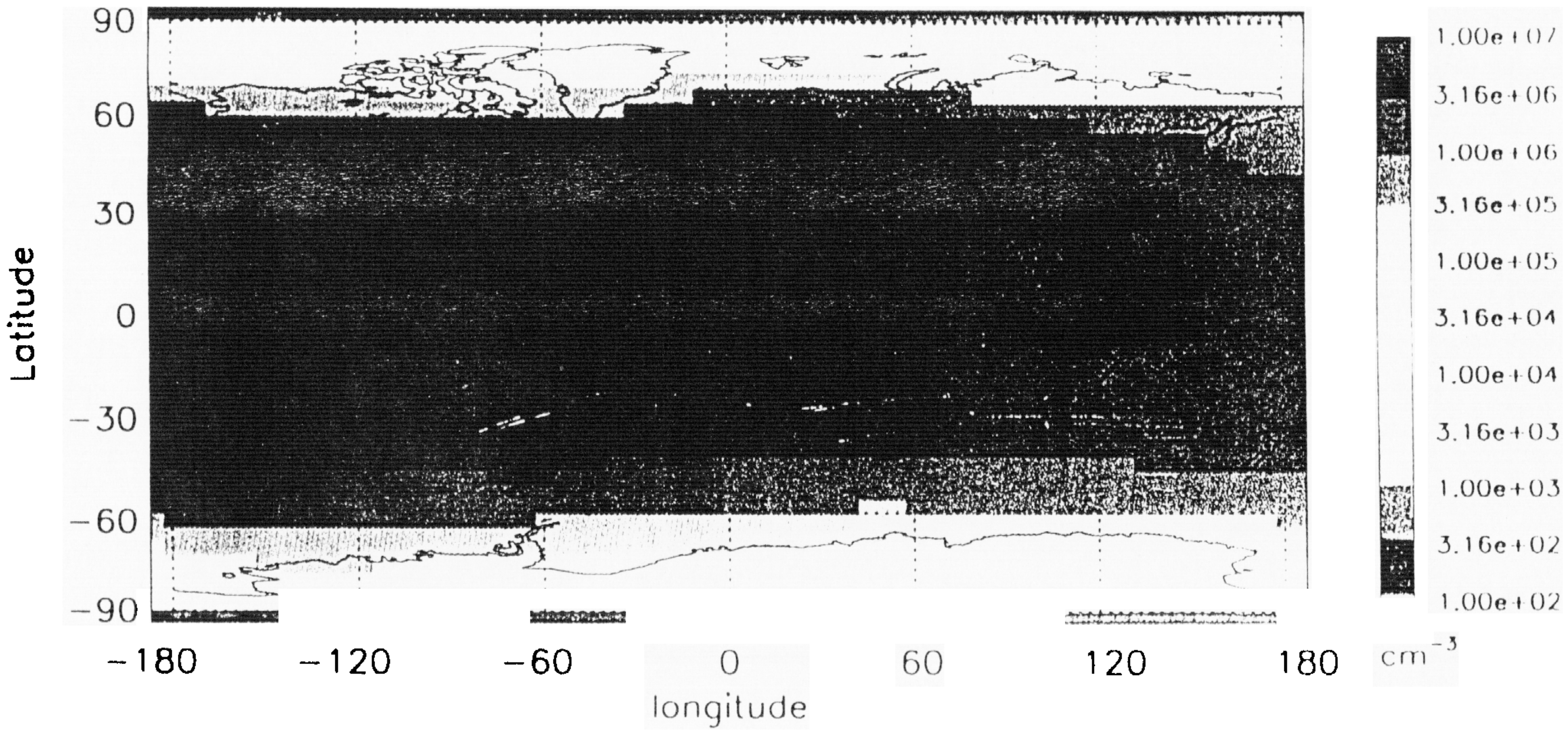

OH Surface Concentration [cm^{-3}]

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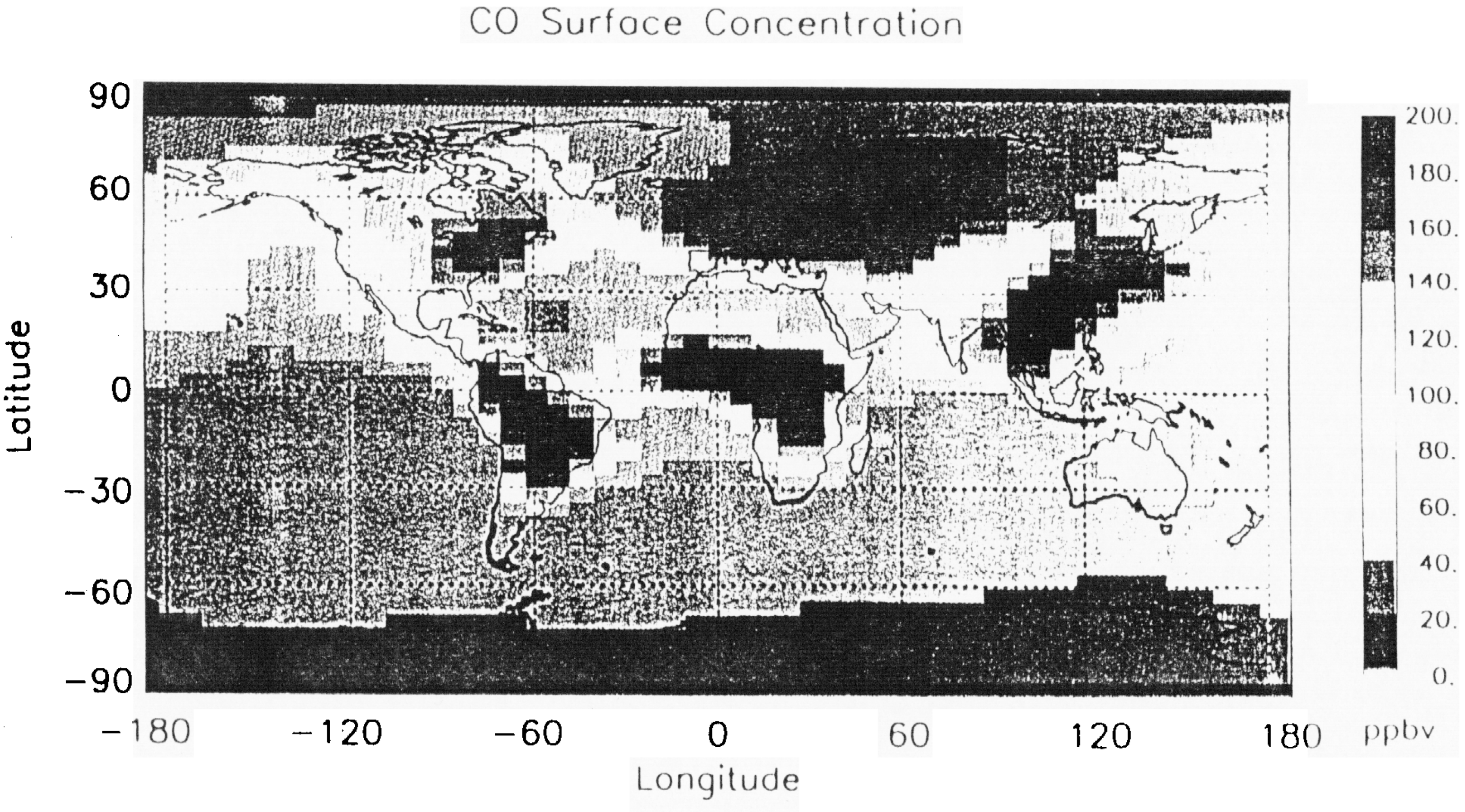

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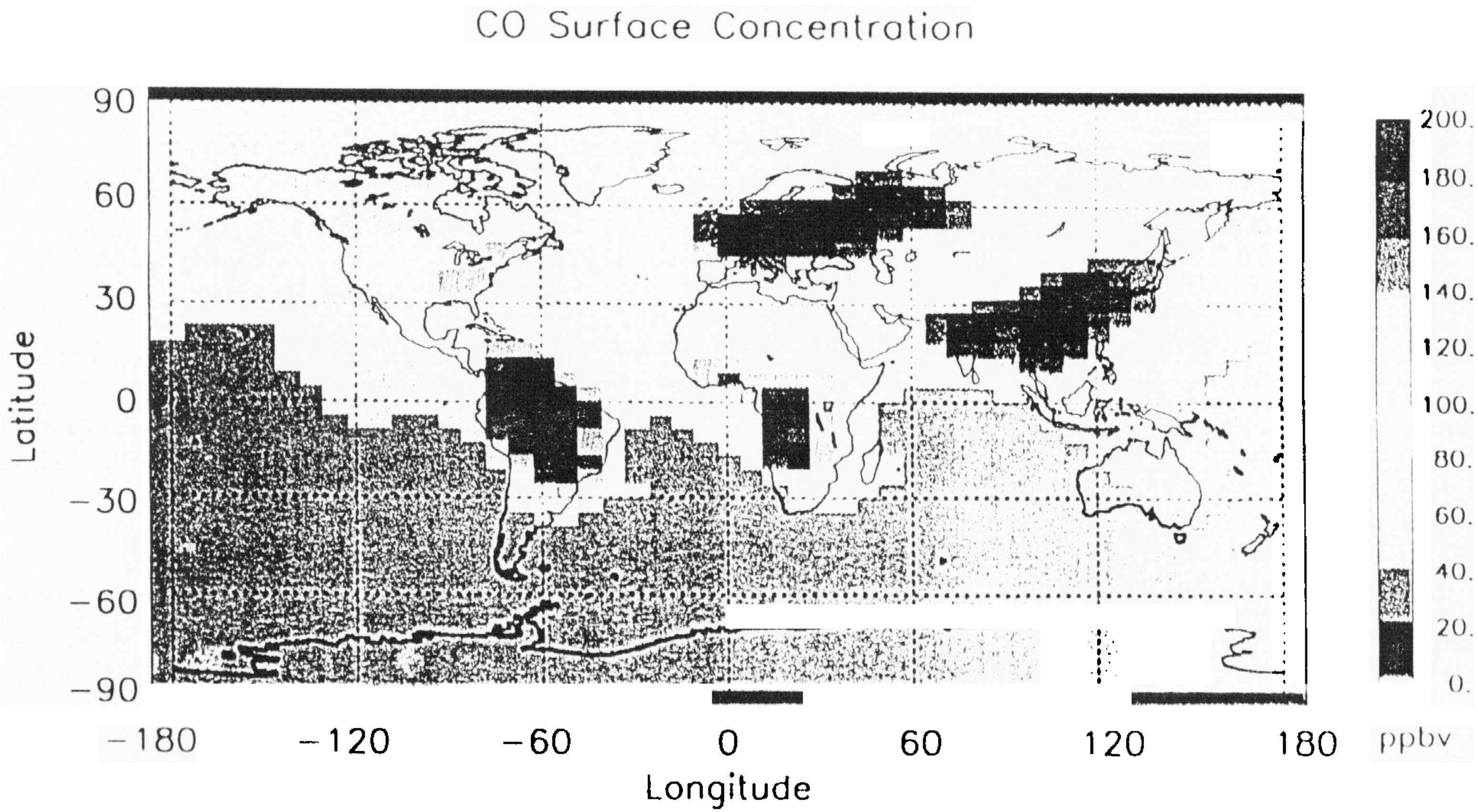

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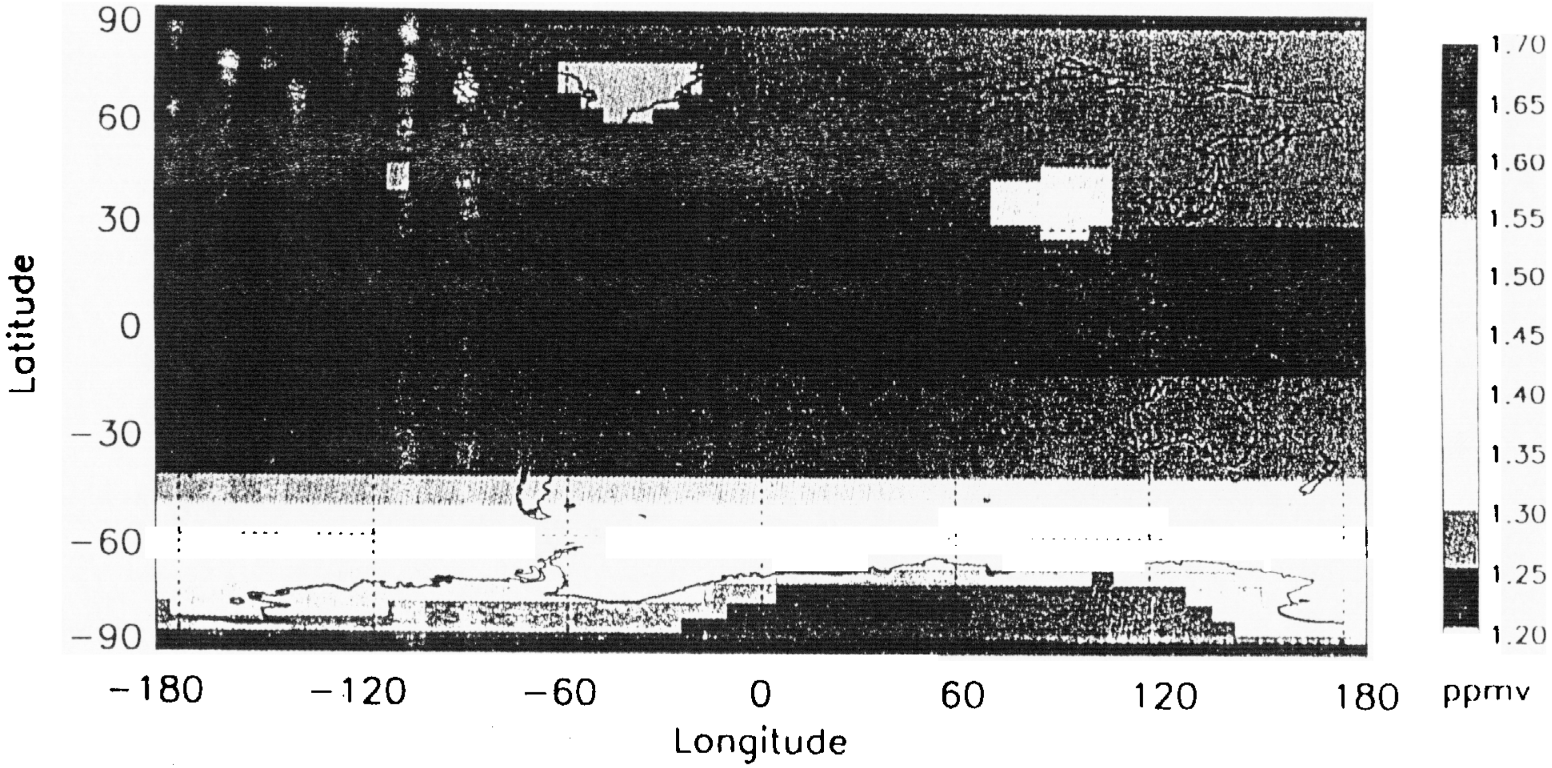
CH_4 Concentration at 500mb



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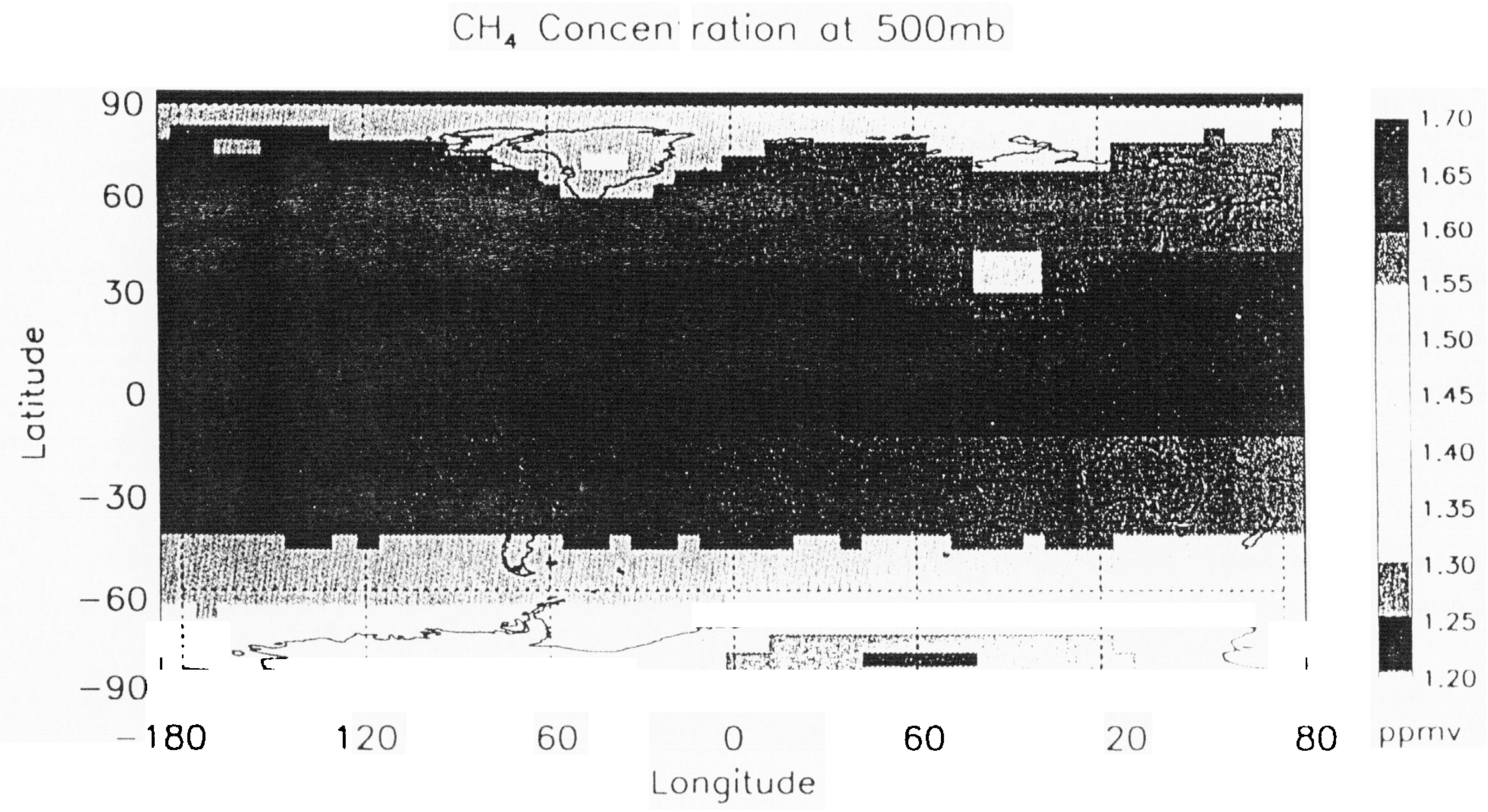

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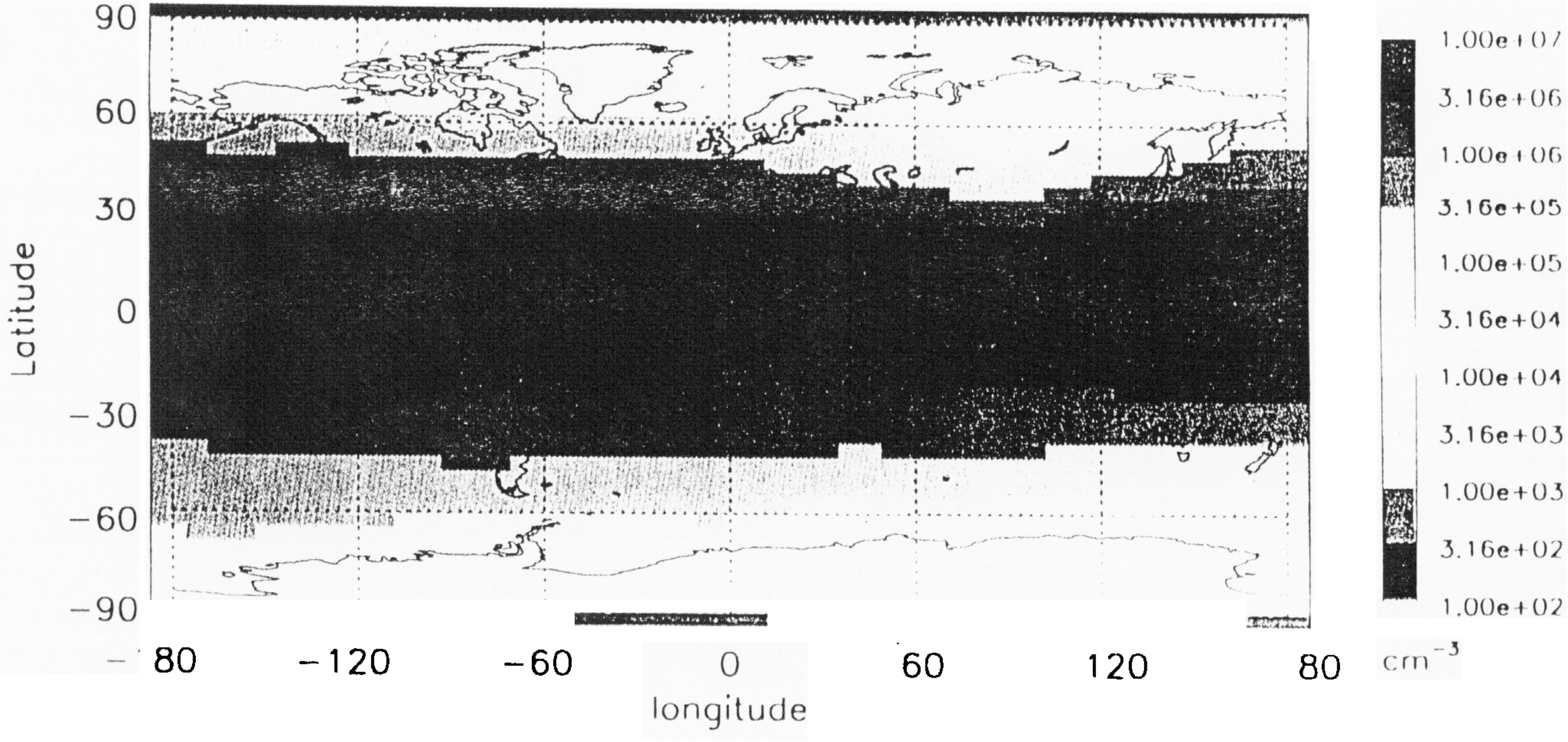
OH concentration at 500 mb $[cm^{-3}]$



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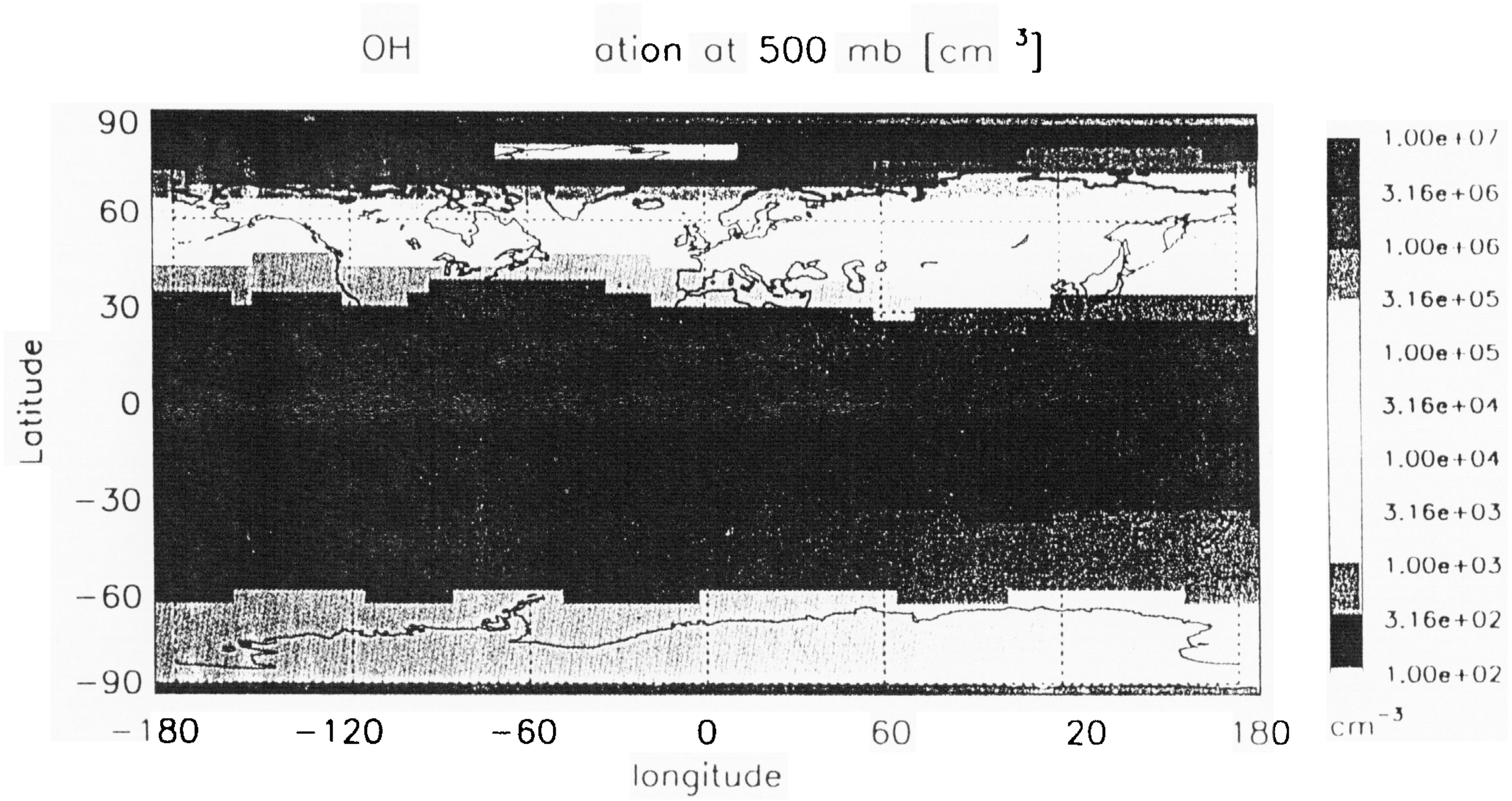

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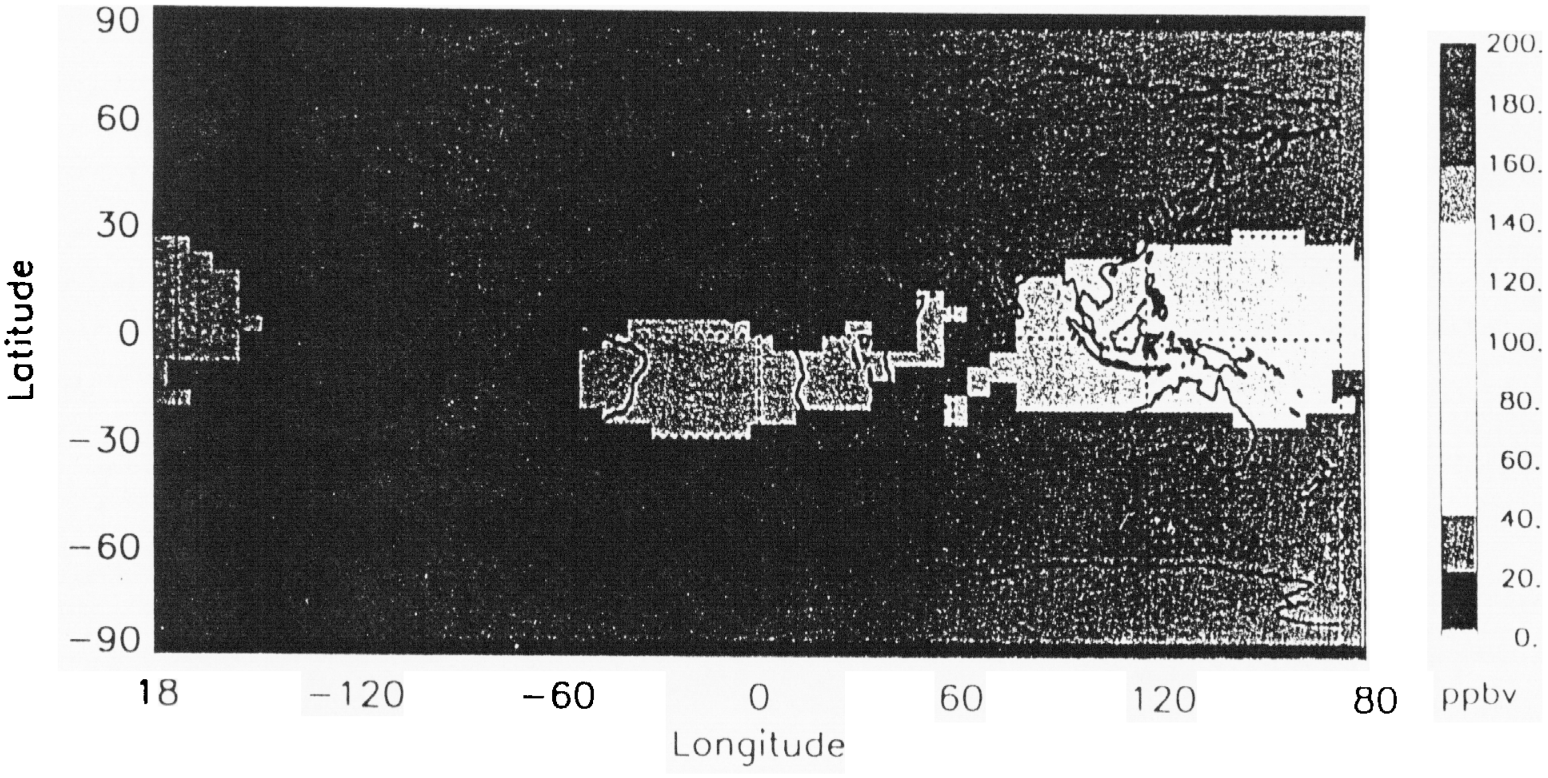

CO Concentration at 500 mb

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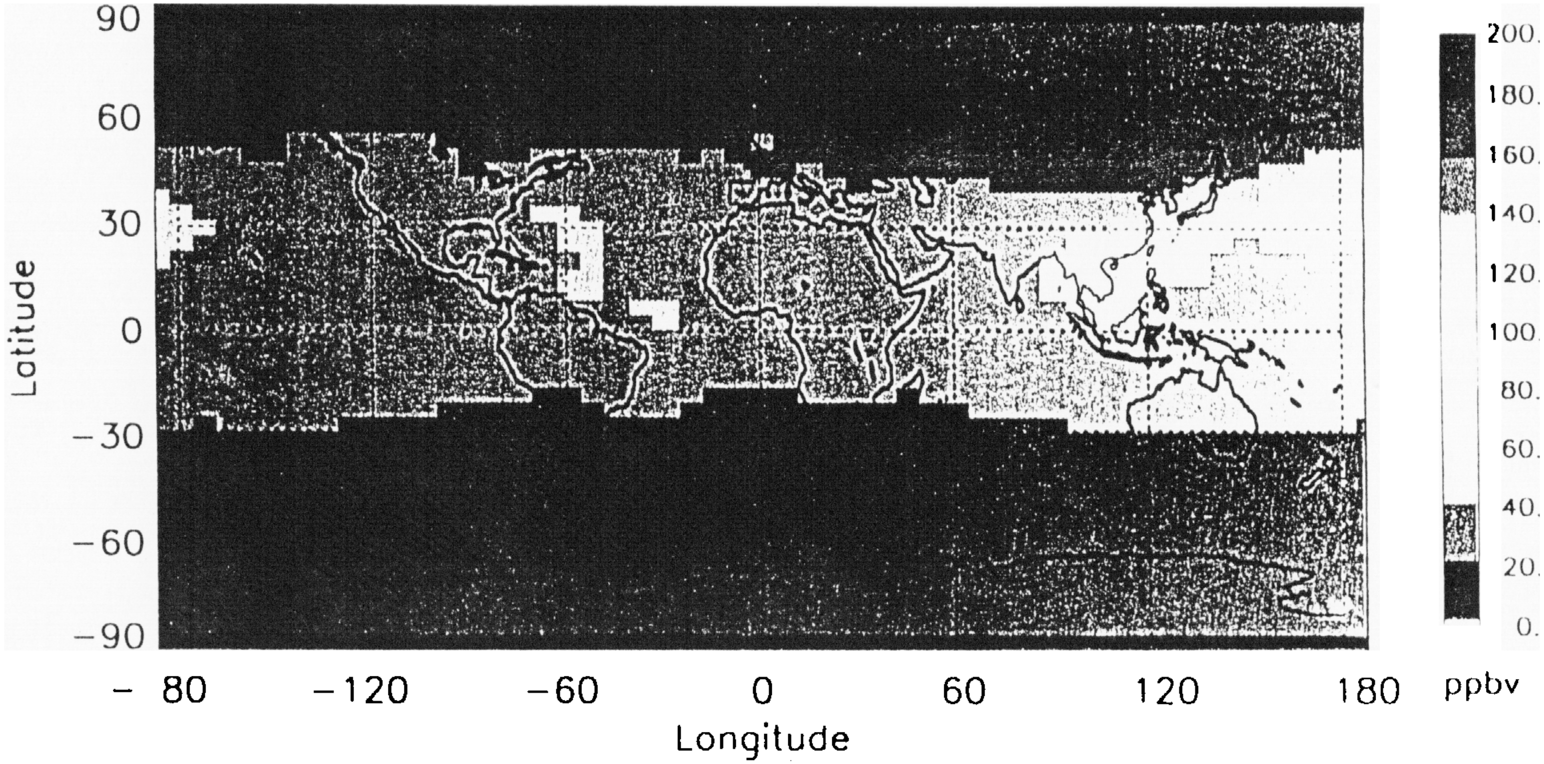
CO Concentration at 500 mb



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APPROXIMATE METHANE PERTURBATION MODEL

- Using average values of [CH4], [CO], [OH], k1, k2, k3[X], SCH4, SCO, and SOH taken from the ambient model, the above set of equations are solved for [CH4] as a function of time for a small methane perturbation.

- This result is used to obtain a perturbation lifetime. For the baseline atmosphere an unperturbed (constant [OH], [CO]) methane lifetime of ~8 years is obtained compared to a perturbed lifetime (variable [OH] and [CO]) of ~12.0 years obtained from the model run.

- These results are in agreement with those of Prinn et al. (1995) which give unperturbed methane lifetimes of between 8.0 and 8.9 years based on new determinations of CH3CCl3 lifetimes and OH concentrations.

- Calculations are performed for the months of January, March, July, and September.

- Global average lifetimes are obtained by taking a methane mass weighted average of the inverse lifetimes (perturbation and basic) for each GRANTOUR parcel .

APPROXIMATE METHANE PERTURBATION MODEL

- **Following Prather (1994), the response of the atmosphere to a methane perturbation can be approximated by the solution of the following equation set.**

$OH + CH_4 \Longrightarrow$ (multiple steps) $\Longrightarrow CO +$ products (1)
$OH + CO \Longrightarrow CO_2 + H$ (2)
$OH + X \Longrightarrow$ products (3)

with rates

$R_1 = k_1 [OH] [CH_4]$ (4)
$R_2 = k_2 [OH] [CO]$ (5)
$R_3 = k_3 [OH] [X]$. (6)

The only product we are concerned with is the production of CO in R_1. The inclusion of surrogate X allows for OH sinks that are independent of the CH_4-CO system. The time-dependent equations describing the concentrations $[CH_4]$, [CO], and [OH] are then,

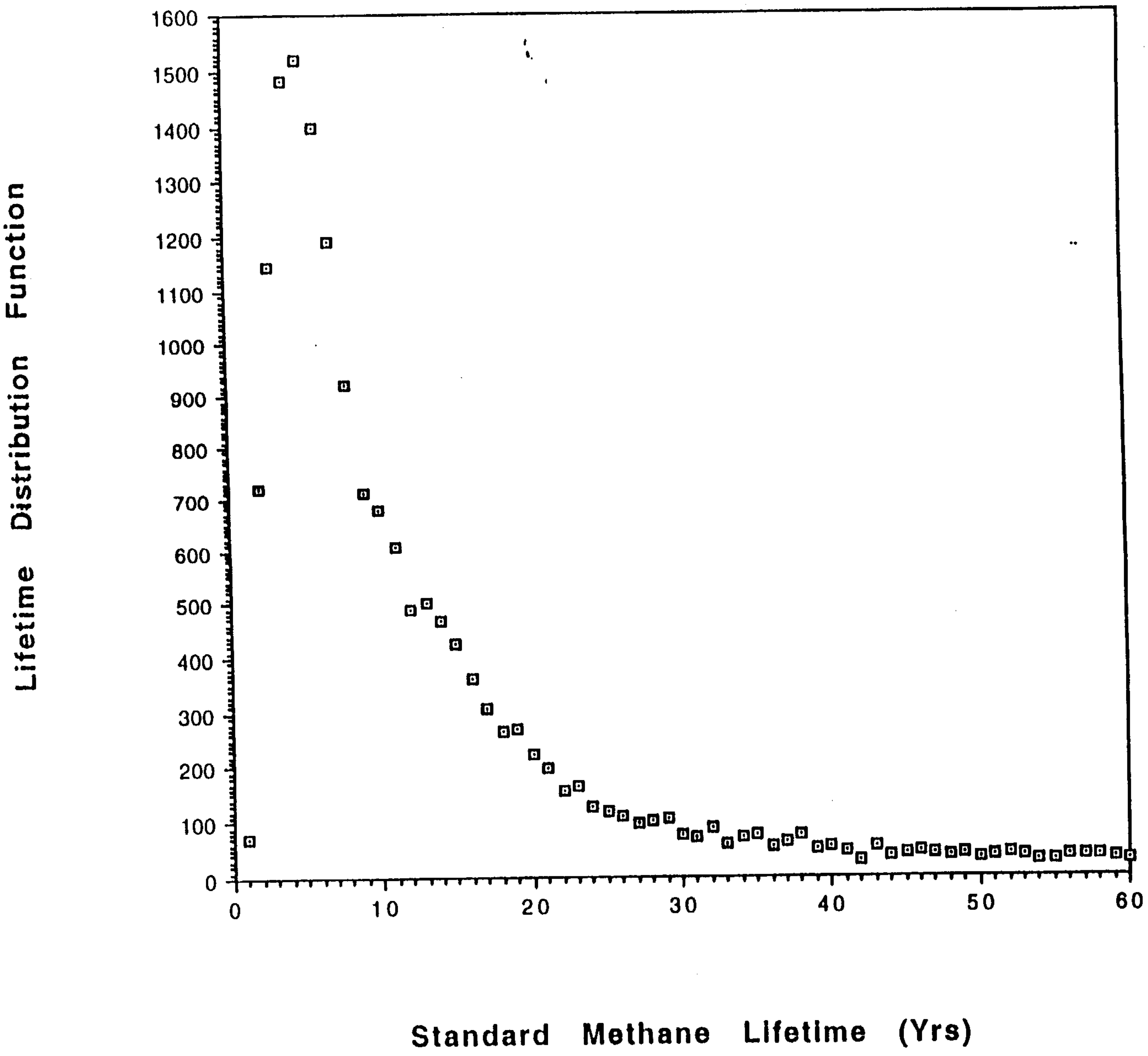
$d[CH_4]/dt = S_{CH4} - R_1$ (7)
$d[CO]/dt = S_{CO} + R_1 - R_2$ (8)
$d[OH]/dt = S_{OH} - R_1 - R_2 - R_3$ (9)

where constant source terms (S) for each species are included. At steady state (i.e., d[]/dt = 0), one can show that $R_1 = S_{CH4}$ and then $R_2 = S_{CO} + S_{CH4}$. Thus positive solutions for [OH] occur only if $S_{OH} > 2 \times S_{CH4} + S_{CO}$, i.e., the source of

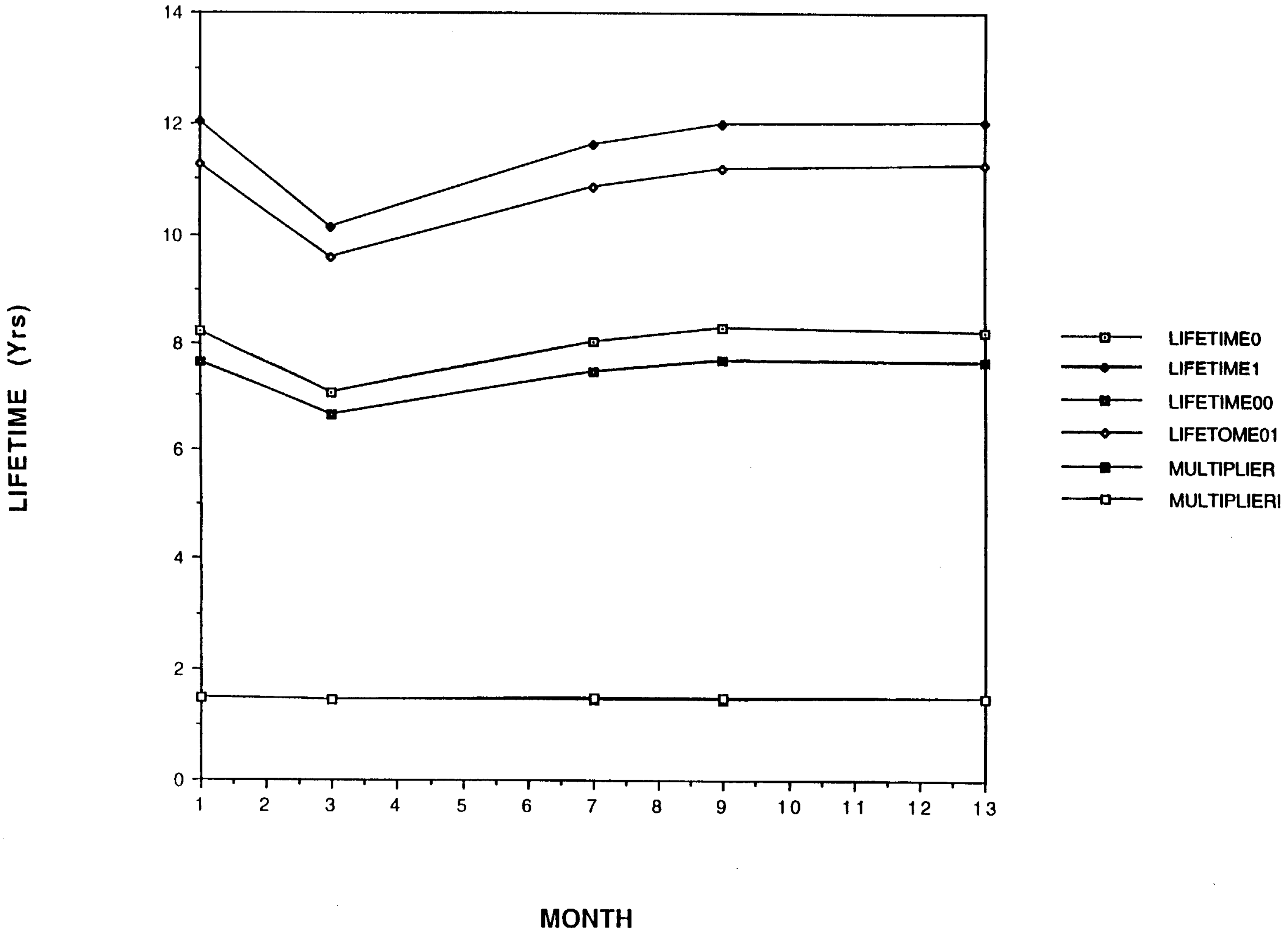
3-D MODEL RESULTS

- GRANTOUR Results for CH4, CO, and OH concentrations.
- Sample distribution of methane lifetimes for a GRANTOUR run.
- Perturbation model results for the perturbed methane lifetime, unperturbed methane lifetime, and perturbed lifetime to unperturbed lifetime ratio.

STANDARD METHANE LIFETIME DISTRIBUTION FOR 25000 GRANTOUR CELLS FOR JANUARY



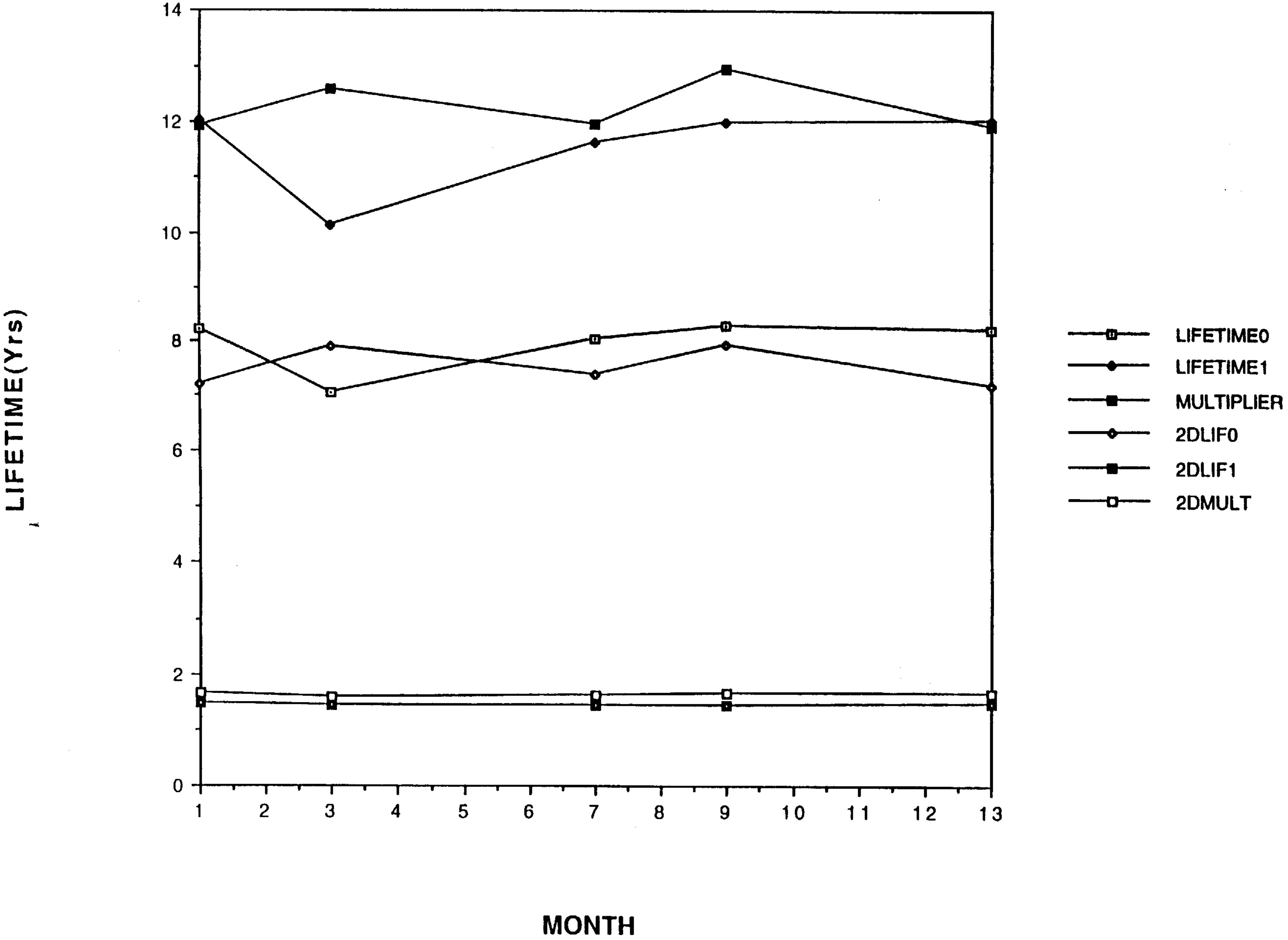
ANNUAL VARIATION OF METHANE CHEMICAL LIFETIMES (WITH AND WITHOUT ISOPRENE)



APPROXIMATE 2-D/3-D MODEL COMPARISON

- The 3-D GRANTOUR results were mapped onto a longitudinally averaged 2-D grid containing 16 latitudes and 23 altitudes.
- The perturbation model was run at each latitude and altitude point to calculate the methane lifetimes.
- Appropiate latitudinal and mass averages of tthe inverse lifetimes were taken to obtain the global average lifetime.
- The results are compared to those obtained with the full 3-D model data set.

ANNUAL VARIATION OF METHANE CHEMICAL LIFETIMES (WITH ISOPRENE) 2-D/3-D COMPARISON



Global Warming Potentials (GWPs) — IPCC (1990, 1992)

$$GWP(x,t) = \frac{\int_0^t \Delta Q(x)\,dt}{\int_0^t \Delta Q(CO_2)\,dt}$$

$\Delta Q(x)$ = radiative forcing (at tropopause) following a per unit mass increase in the emission into the atmosphere of species X.

Global Warming Potentials are a relative measure of the possible globally-averaged warming effect from the per unit mass instantaneous release of a greenhouse gas as compared to that from the per unit mass instantaneous emission of CO_2.

GWPs provide a means of comparing the effects of emission control strategies for different greenhouse gases.

SENSITIVITY OF GWP TO METHANE LIFETIMES

- Given two methane lifetimes ($\tau 1$ and $\tau 2$) the change in GWP can be expressed as

$$\Delta GWP = \tau 1 / \tau 2 * [1- \exp(- t / \tau 1)] / [1 - \exp(- t / \tau 2)]$$

- For t values of 100 and 500 years the ΔGWP is the lifetime ratio.

- For a t value of 20 years the ΔGWP will be

0.81, $\tau 1$ = 12yrs, $\tau 2$ = 18 years, $\tau 1 / \tau 2 = 0.67$

1.33, $\tau 1$ = 12yrs, $\tau 2$ = 8 years, $\tau 1 / \tau 2 = 1.5$

1.05, $\tau 1$ = 8 yrs, $\tau 2$ = 7.5 years, $\tau 1 / \tau 2 = 1.07$

ESTIMATE OF GLOBAL WARMING POTENTIALS

- Estimates of the new direct GWP of methane are made using:

1. Lifetime from the simlified box model,
2. Instantaneous radiative forcing formula from IPCC (1990),
3. Approximate GWP model.
4. CFC11 lifetime and GWP (IPCC, 1994)

	Lifetime		GWP(20y)	GWP(100y)	GWP(500y)
IPCC(94)	12 - 18	(Direct + Indirect)	48 - 90	20 - 43	8 - 15
LLNL(94)	17.44	(Direct + Indirect)	79	35	11
LLNL(94)	17.44	(Direct)	53	23	7
LLNL(97)	11.95	(Direct)	44	17	5

FUTURE WORK

- Analyse different GRANTOUR baseline atmospheres (full chemistry) with different methane compositions (pre industrial, present day, assumed future).
- New 2-D model runs using new, fast running, IR and Short Wave radiation models.
- Obtain 3-D atmosphere runs from IMPACT the new LLNL 3-D chemistry - transport model. This modal will have a more highly resolved stratosphere than GRANTOUR.
- New 3 - D calculations of the indirect methane effect (Ozone, Water Vapor).

FUTURE WORK

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Atmospheric Chemistry, Climate Change, and Climate Policy Considerations Related to Methane

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Formulating greenhouse gas indices

- **No single approach or indexing tool is likely to meet all of the needs for evaluating greenhouse gas effects on climate -- A variety of tools are useful**
  - » e.g., radiative forcing with time
    - – however, dependent on knowing just how emissions will change
  - » but also is useful to consider relative merits per unit emission of different gases

Global Warming Potentials (GWPs)

- CO_2 is reference molecule

$$GWP = \frac{\int_0^t A_x \cdot [x(t)]\,dt}{\int_0^t A_{CO_2} \cdot [CO_2(t)]\,dt}$$

- Assumes instantaneous release of a "unit mass
- Relative to constant background atmosphere
- Ax = radiative forcing of gas x; [x(t)]=concentration of gas x with time, t.

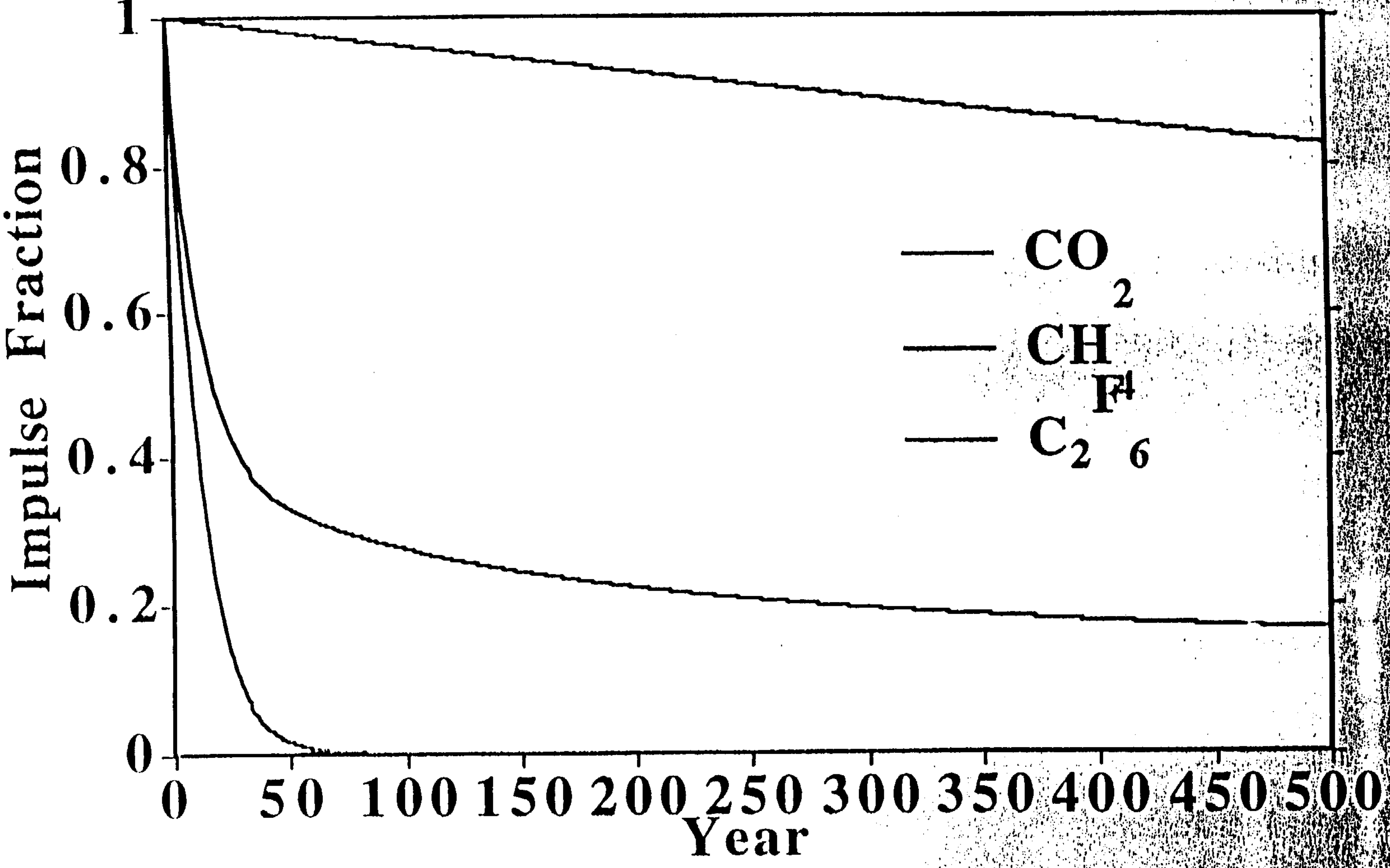
How choose time horizon?

- Somewhat arbitrary
- Dependent on “user” needs
- Steady-state?
  - CO_2 decay too complex (doesn’t go to zero)
- IPCC choose 20, 100, 500 yr. integrations
  - Practical range for many policy-applications
  - But there is no “ideal” given value

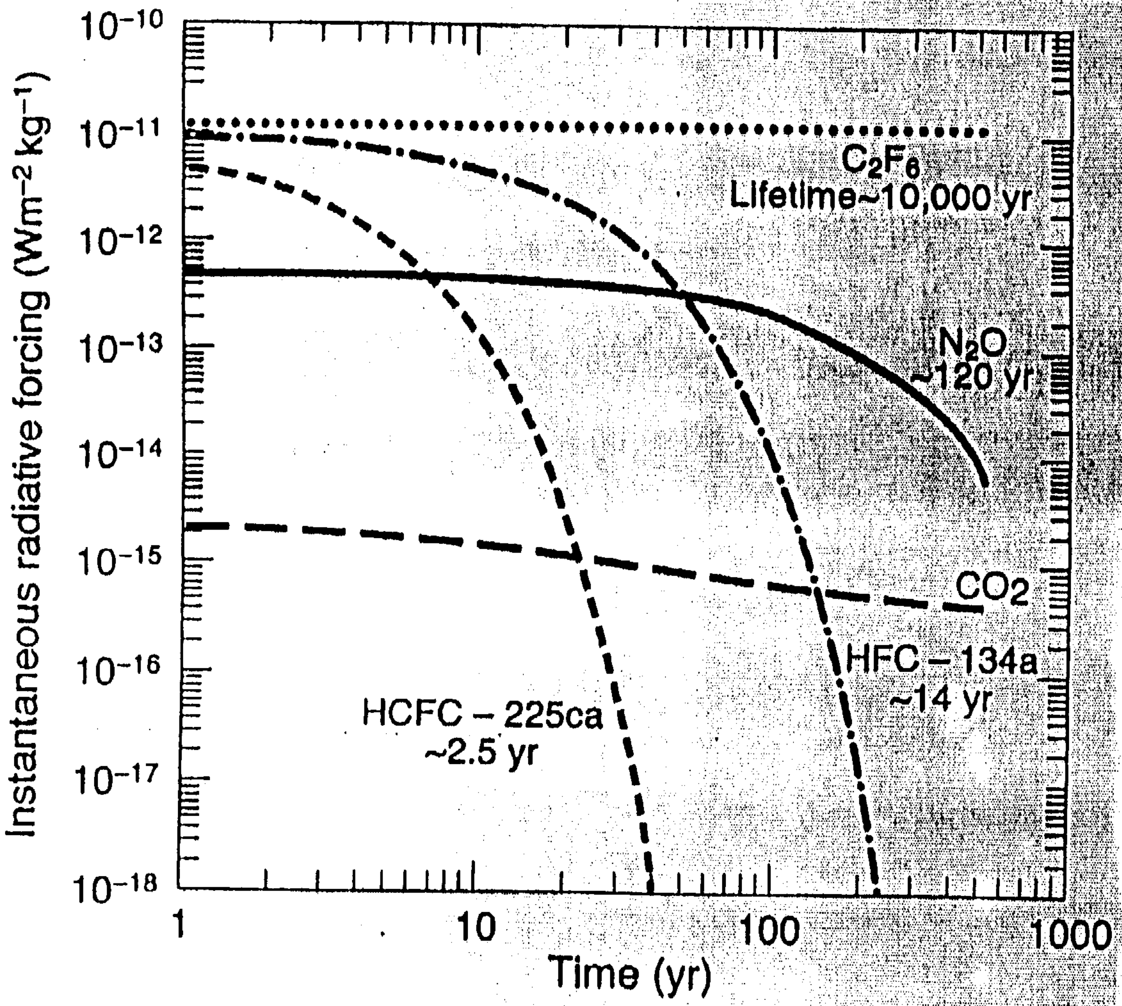
IPCC GWPs

20	Concerns about rate of change of climate or effects on climate
100	Approximate scale of climate response (oceans); a balance between short and long term concerns
500	Concerns about long-term, quasi-irreversible climate changes; cumulative effects

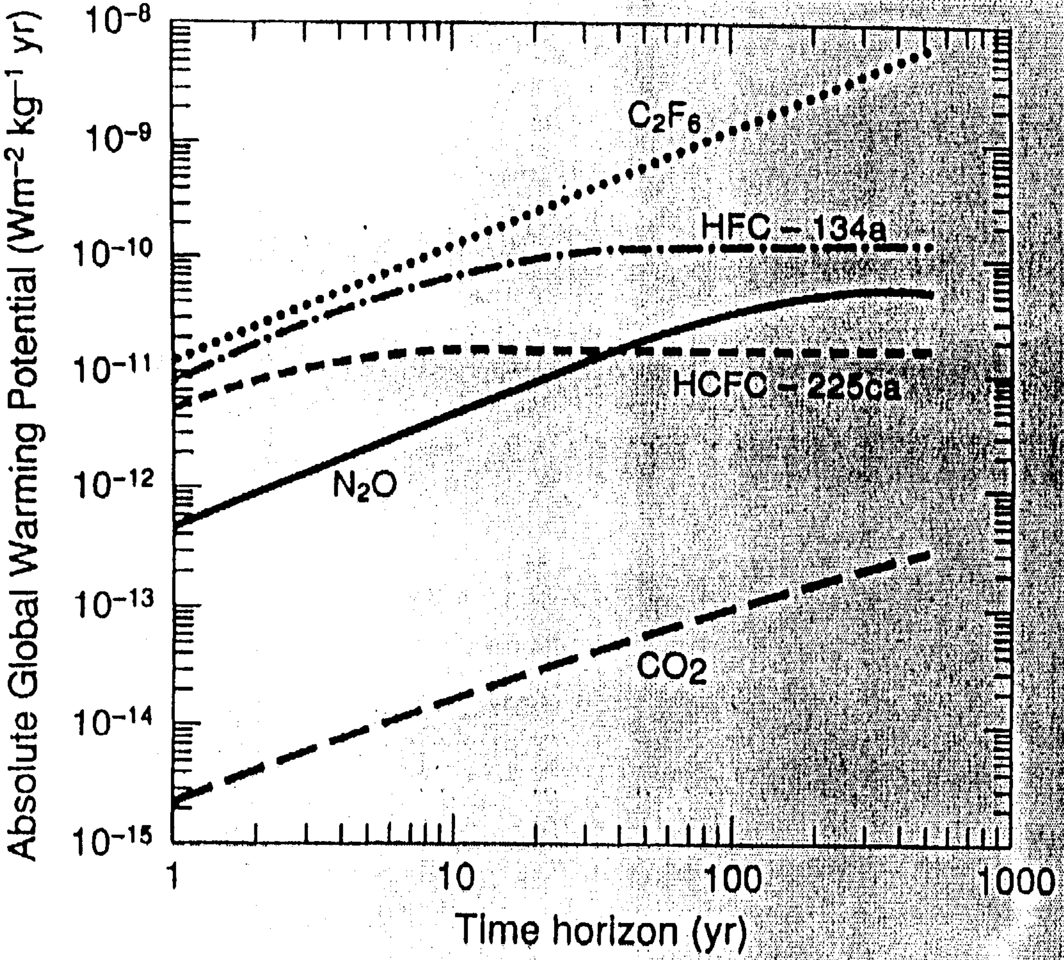
Impulse Response Curves



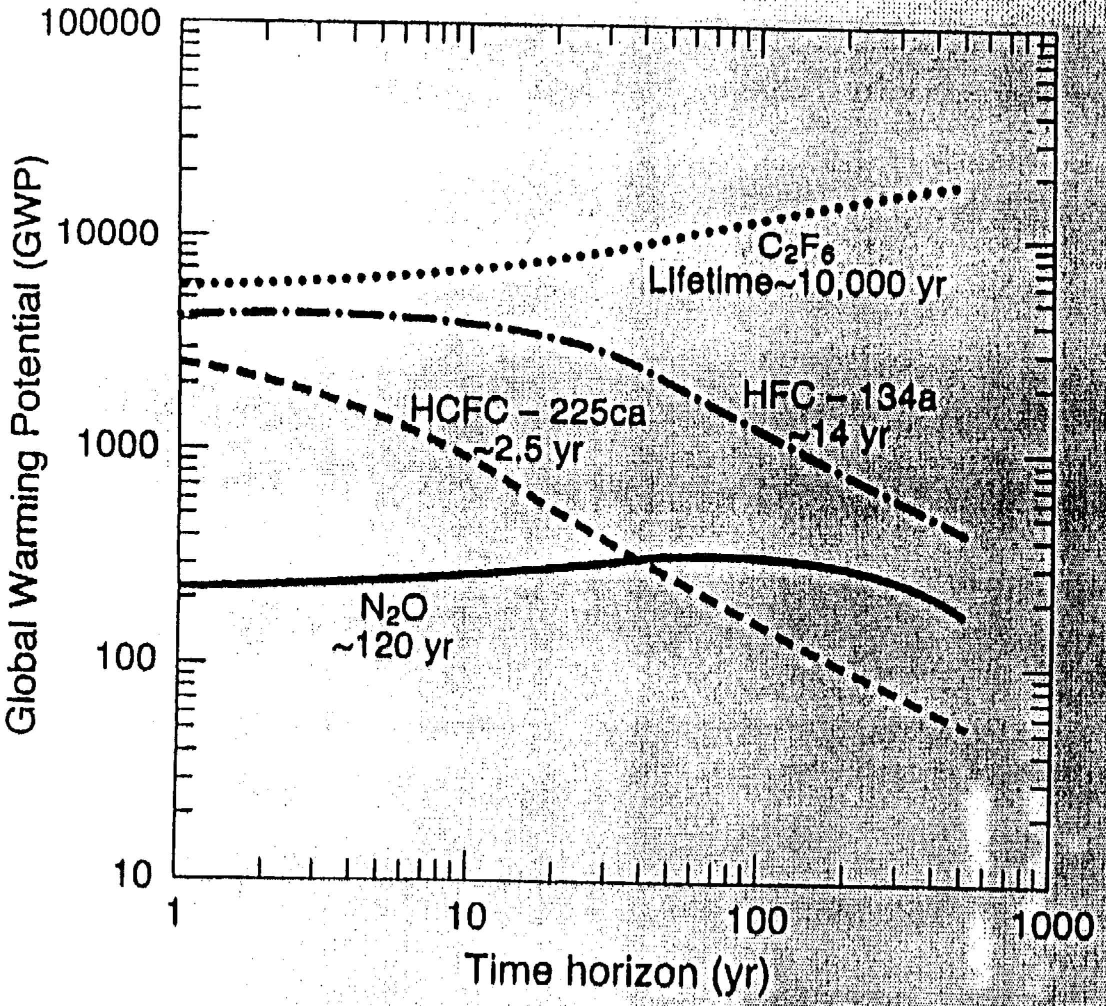
Instantaneous Radiative Forcing



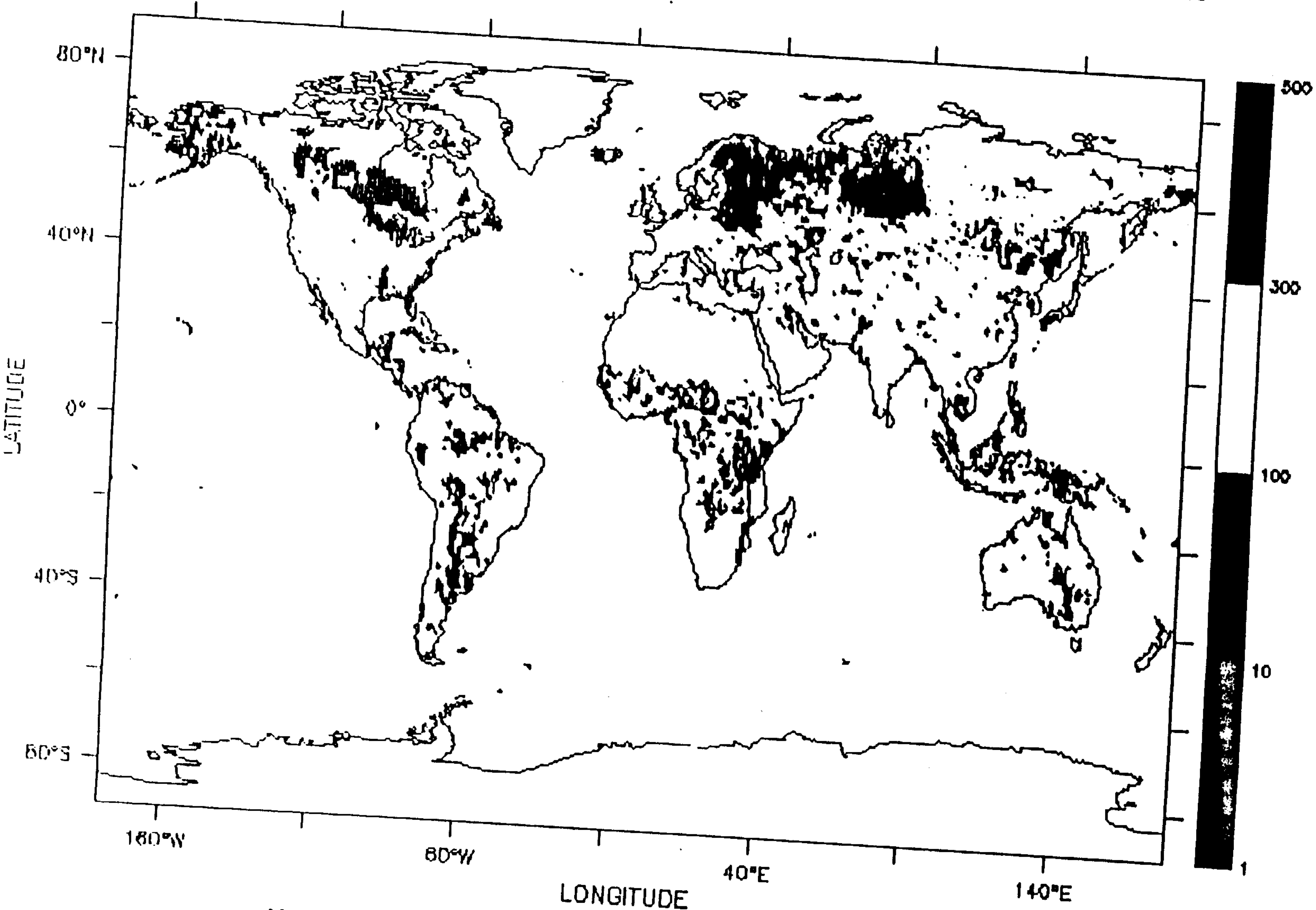
Integrated Radiative Forcing



Global Warming Potential



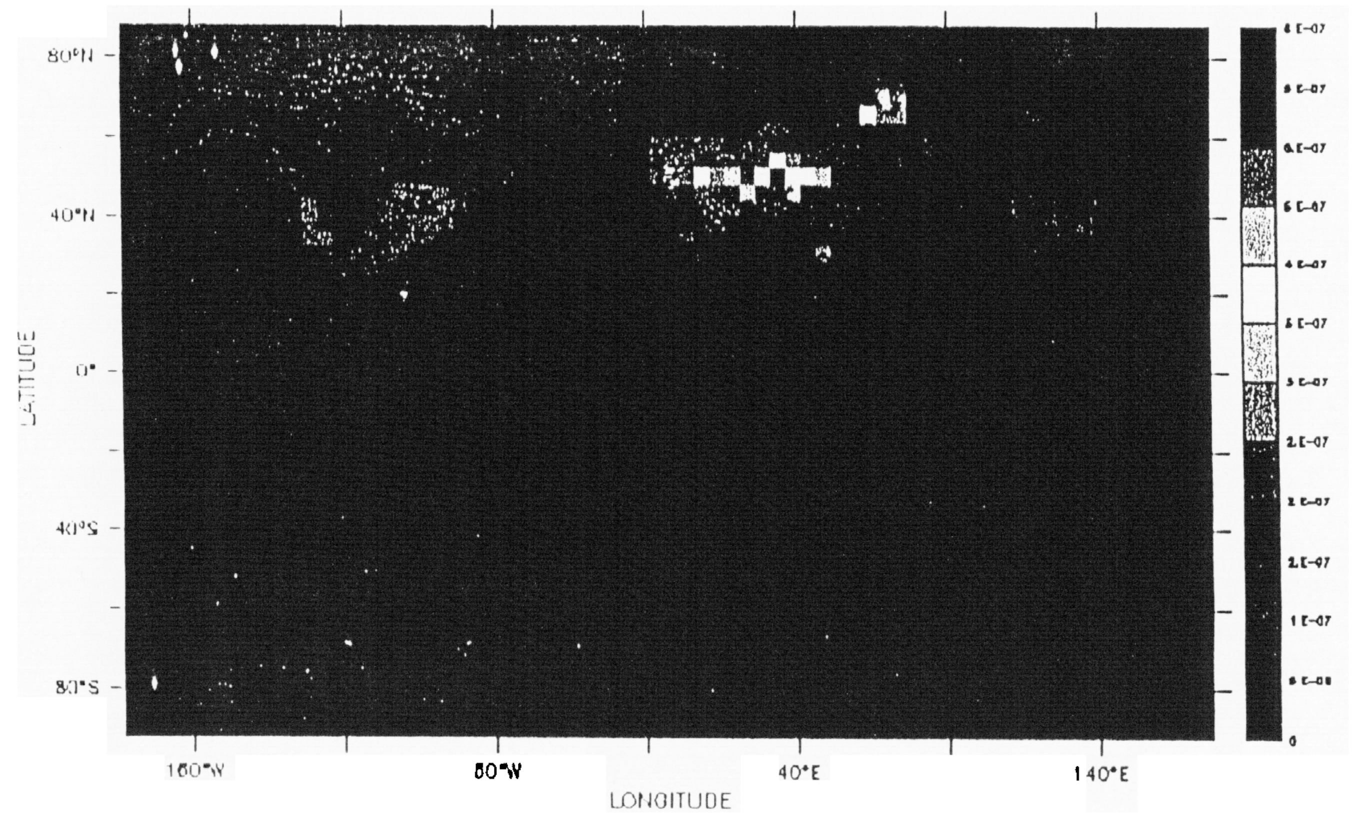
DATA SET: wtl_1x1.mine



methane emission from wetlands,(g*10(-9)/cell/year)

All data from Muller (1991) interpolation from 5x5 on 4x5. Annual flux g/m2/sec

ch4 antropogenic (coal, gas, oil, industry)



Atmospheric Chemistry Activities

- CH_4 BUDGET
- 2-D Model
  - » Improvements to troposphere
    - new NMHC chemistry
    - adding parameterization for convection
    - new latent heat representation
  - » New treatment for Polar Stratospheric Clouds

Atmospheric Chemistry Activities

- 3-D Model
  - » Waiting further model development at LLNL
  - » In meantime, will interact with NCAR in testing and evaluating their MOZART model

Chemistry Research Studies

- Indirect effects of CH_4 on GWPs
  - » with LLNL (A. Grossman)
- Effects of CH_4 controls on stratospheric ozone
  - » update waiting on new PSC treatment
- Evaluation of 2-D tropospheric chemistry
  - » awaiting completion of new model (1-2 months)

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Integrated Science Assessment Modeling

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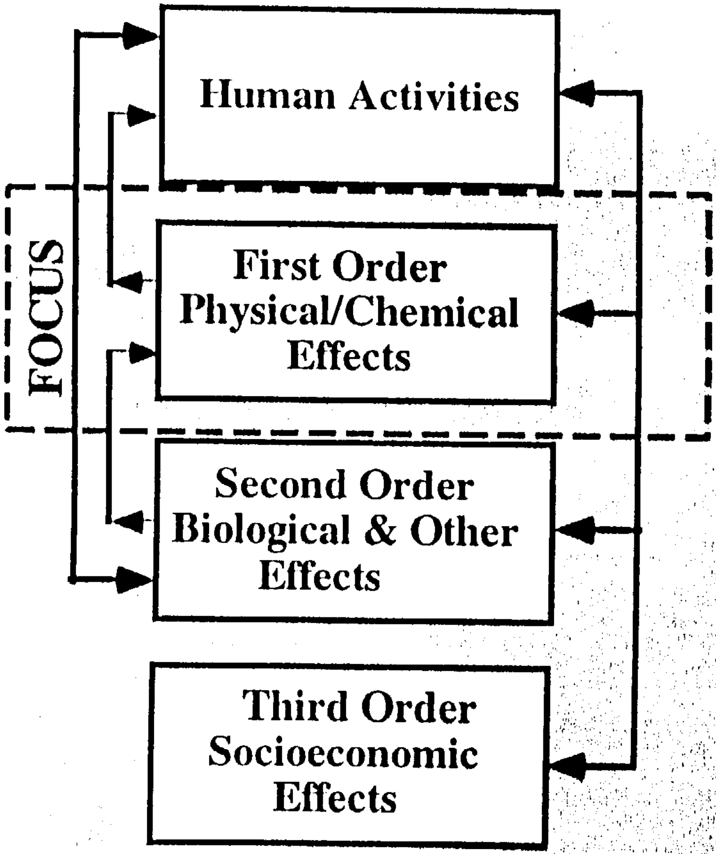
Integrated Assessment

Conceptual Flowchart



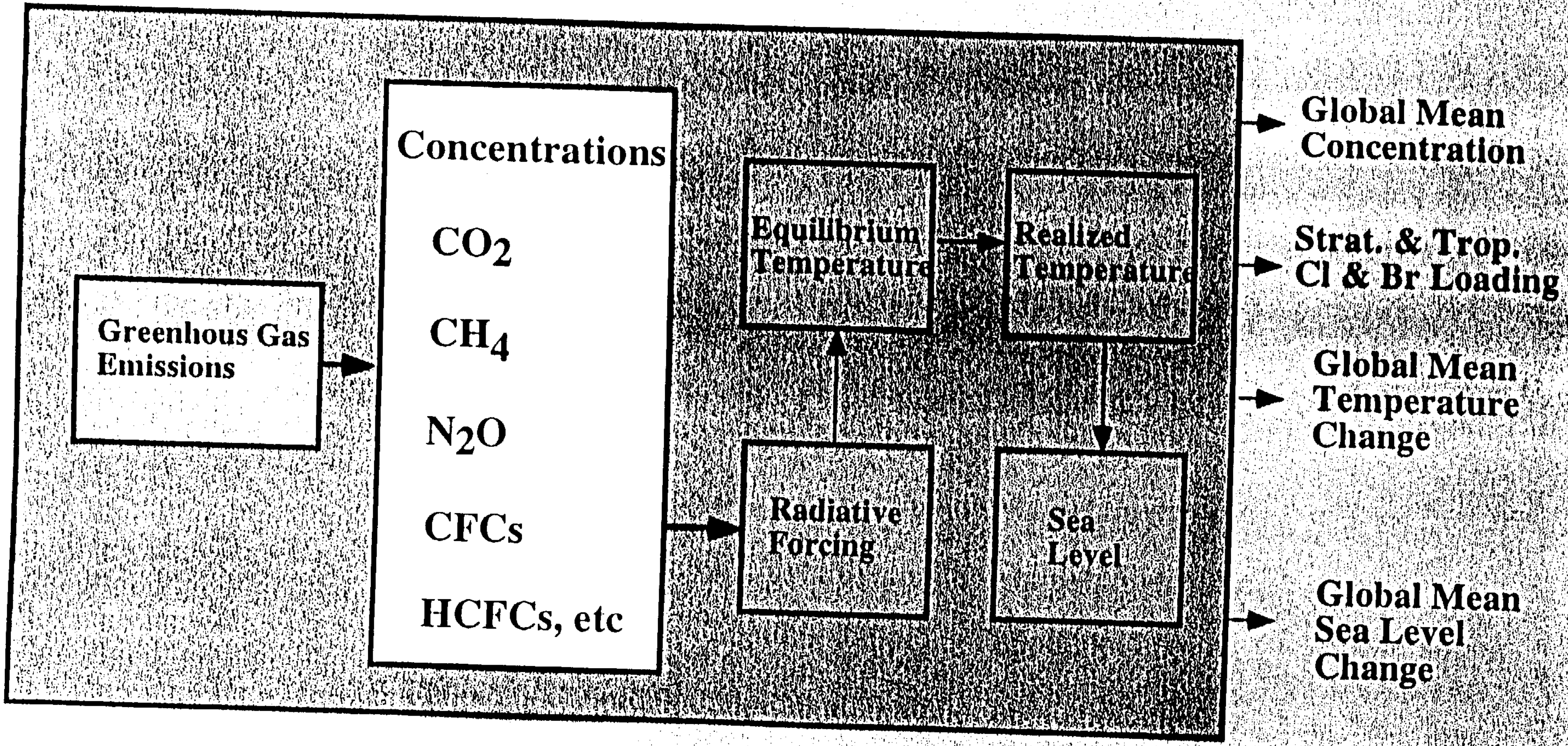
Examples

Energy Use	Land Use (Deforestation)	Transportation	International Trade
Atmospheric Composition	Land Surface Characteristics	Climate, Including Ocean	Hydrological Cycle
Agriculture	Natural Ecosystem	Water Resources	
Biodiversity	Health	Economic Activity	

Integrated Assessment of Global Change
The UIUC Approach

- Form Collaborative interactions towards team of experts
- Integrated Framework, using best components
- Include all key components and interactions
- Consider all human and natural greenhouse forcings
- Treat Uncertainty as an essential feature
- Design to upgrade as knowledge improves
- Be global in scope, but resolve regional distribution

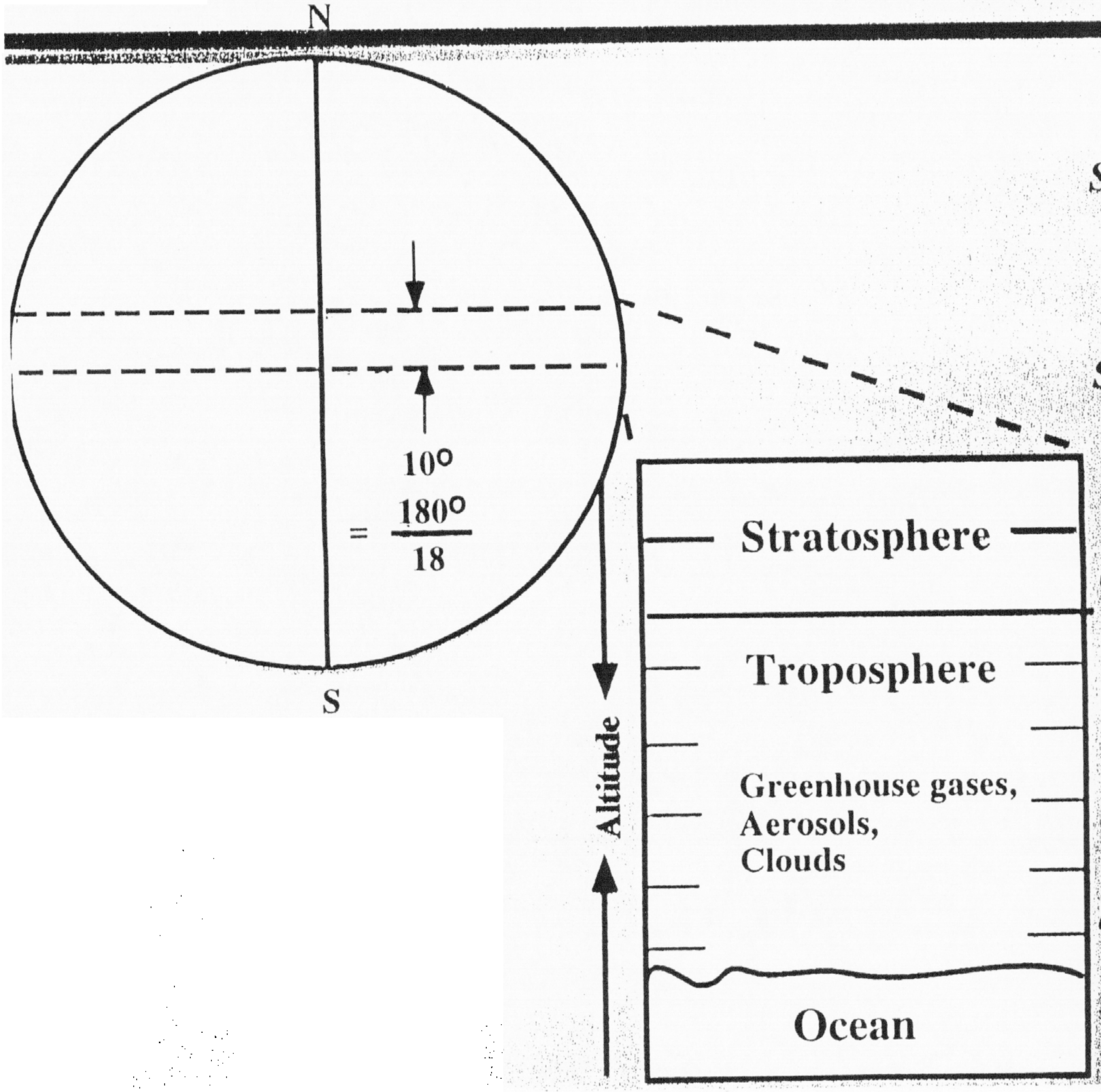
Integrated Science Assessment Model
Initial Phase (Completed)



Physical Science Components

- **Gas Cycle Models**
  - CO_2
  - CH_4
  - N_2O
  - Halocarbons
- **Radiative Forcing**
  - Greenhouse gases
  - Aerosols
- **Climate Models**
  - Global Mean Changes
  - Regional Changes

Integrated Science Assessment Model
Next Phase



Carbon Cycle Module (CCM)

Stage 1: Process-Based Regional Terrestrial Model, Incorporate Nitrogen Cycle & Other Biotic Feedbacks

Stage 2: Ocean CCM with the Marine Biological System

Atmosphere Module

Stage 1: Vertically Integrated Atmosphere Module

Stage 2: Radiative-Convective Module

Ocean Module

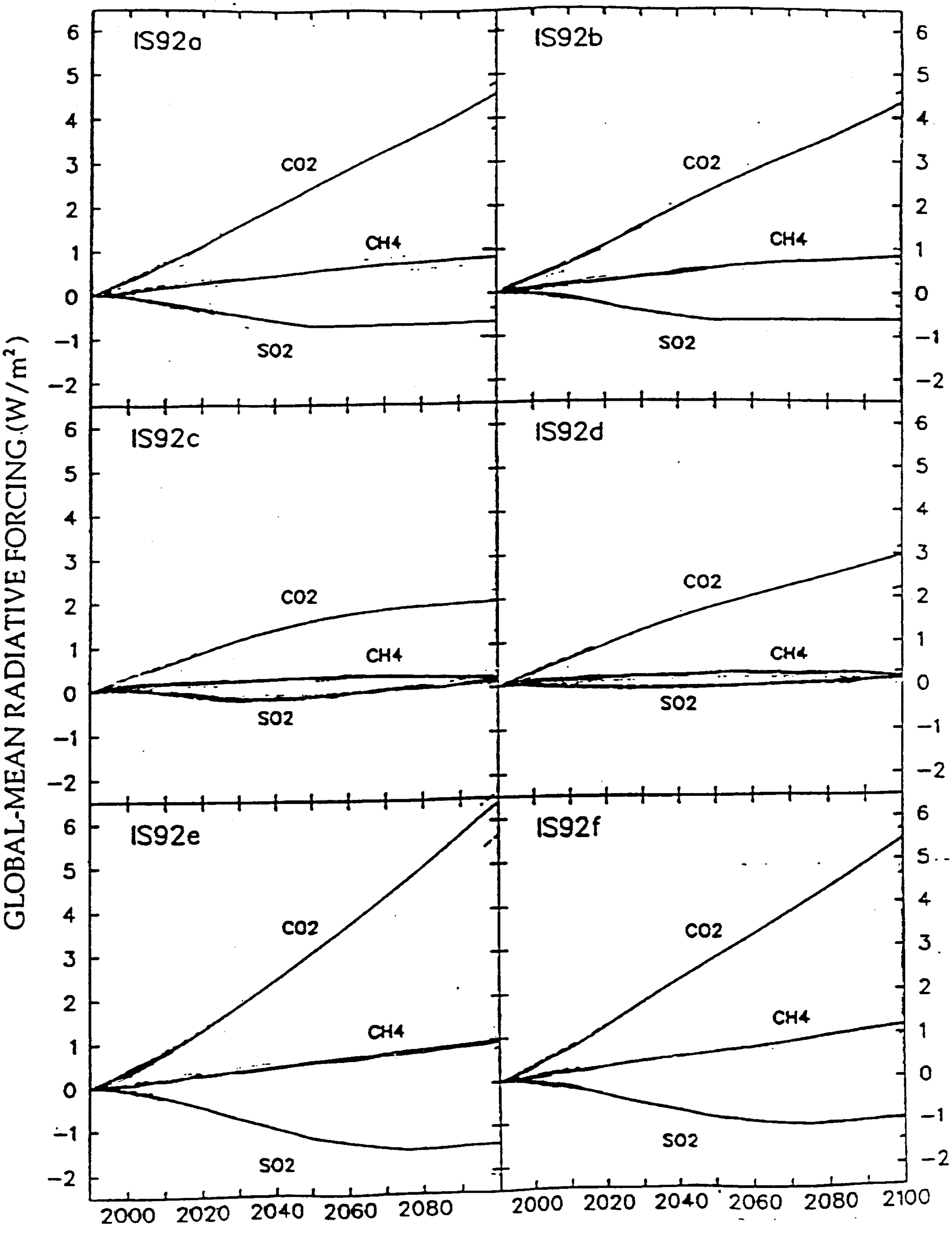
Stage 1: Parameterized Transport Module

Stage 2: Predicted 2-D Transport Module

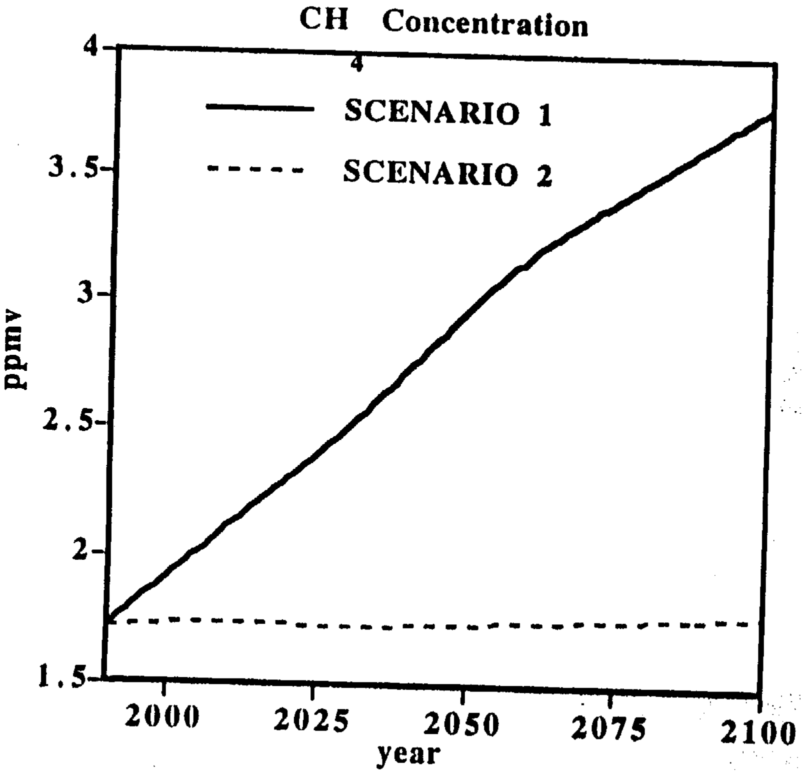
Change in Radiative Forcing

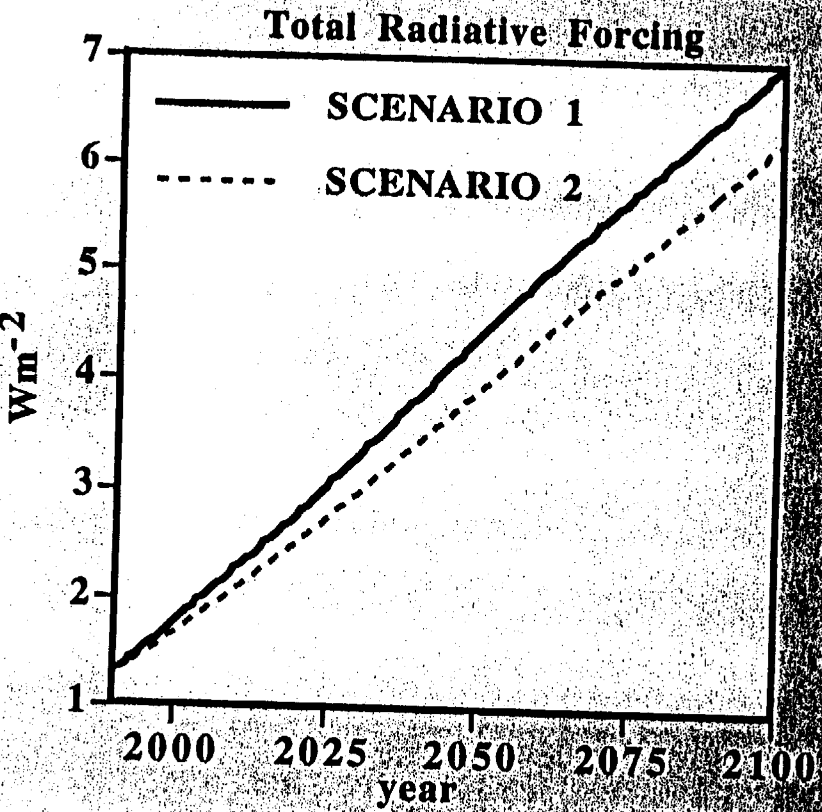
		1750-1994	1993-1994
Greenhouse	*gases*	*2.45* Wm^{-2}	*0.047* $Wm^{-2}yr^{-1}$
	CO_2	1.56	0.03
	CH_4	0.47	0.008
	N_2O	0.14	0.002
	CFC-11	0.057	0.0018
	CFC-12	0.12	0.003
	CFC-113	0.027	0.0016
	CFC-114	0.009	0.0002
	CFC-115	0.002	0.0002
	Other	0.065	< 0.0001
	SF_6	0.0024	0.0002

Radiative Forcing for CO_2, CH_4, and Sulphate Aerosols for IS92 Scenarios

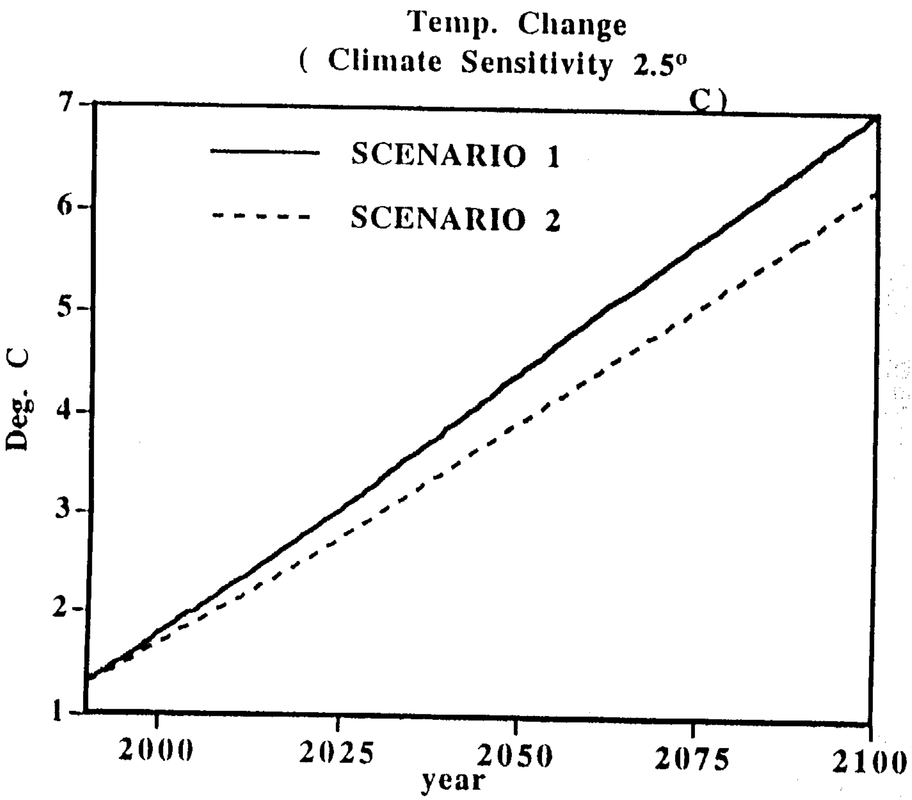


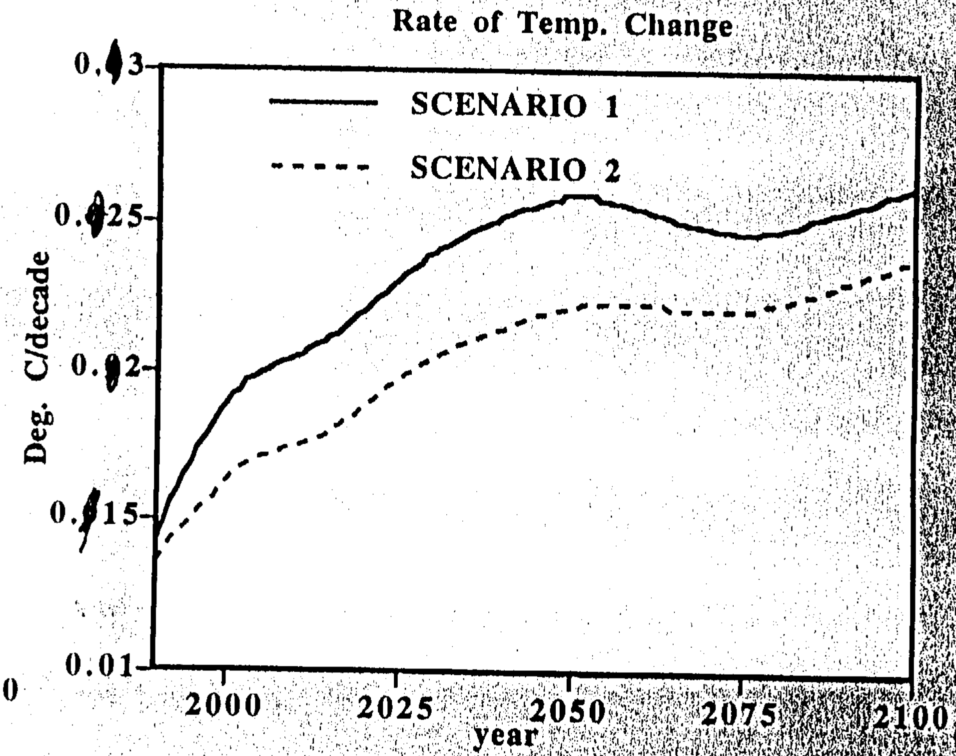
Effect of CH_4 Emission Reduction on Concentration and Radiative Forcing



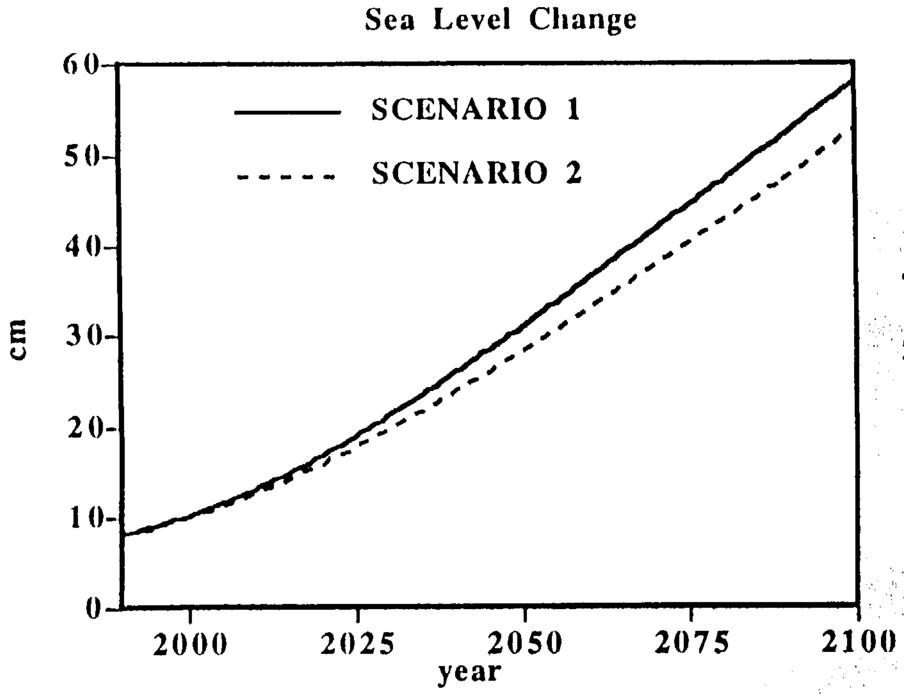


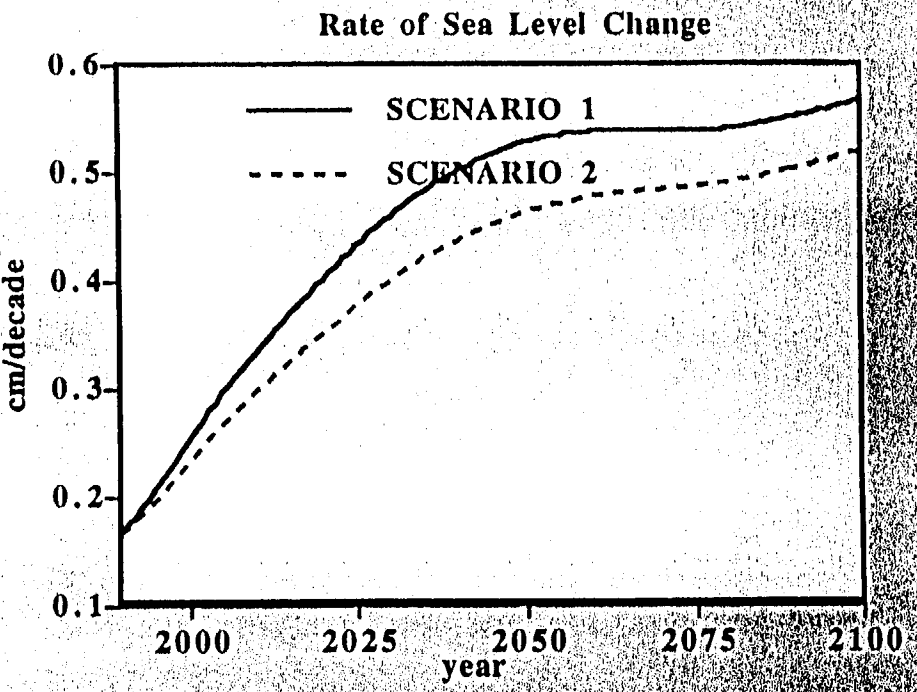
Effect of CH_4 Emission Reduction on Temp. Change and Rate of Temp. Change


Temp. Change (Climate Sensitivity 2.5° C)

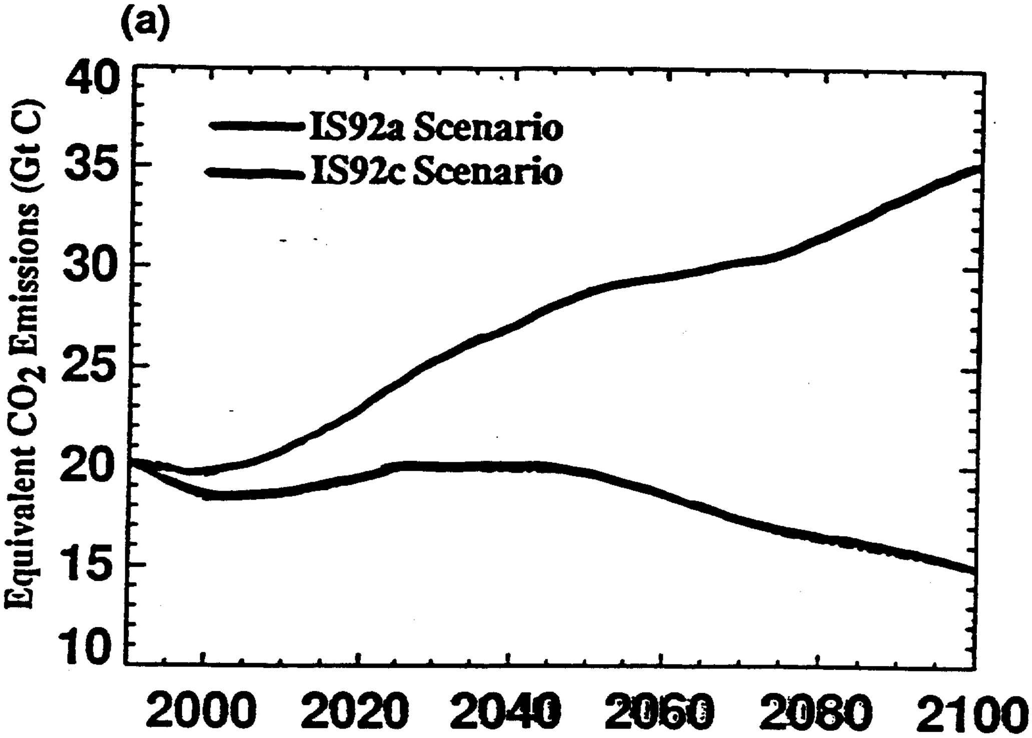

Rate of Temp. Change

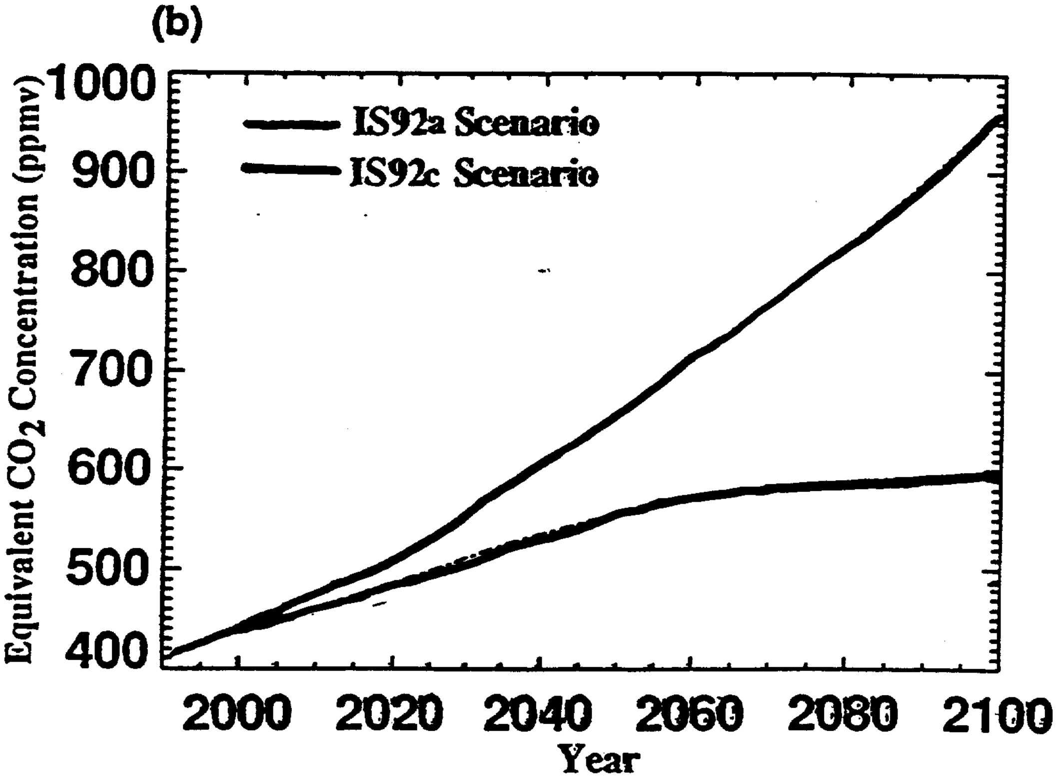
Effect of CH_4 Emission Reduction on Sea Level Change and Rate of Sea Level Change



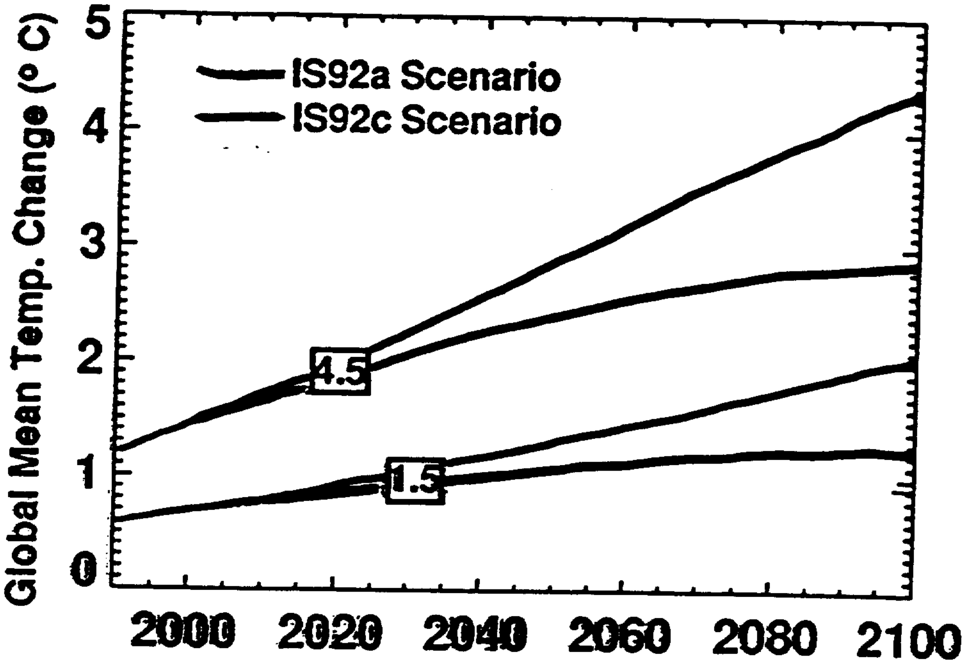


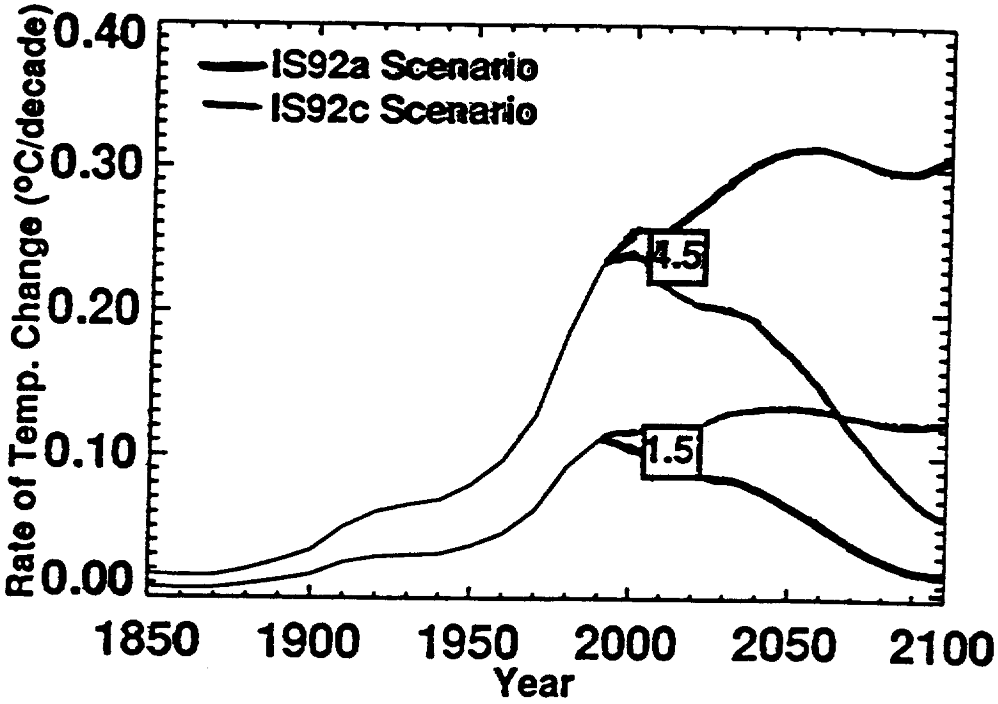
Equivalent CO_2 (a) Emissions and (b) Concentrations for IPCC Scenarios



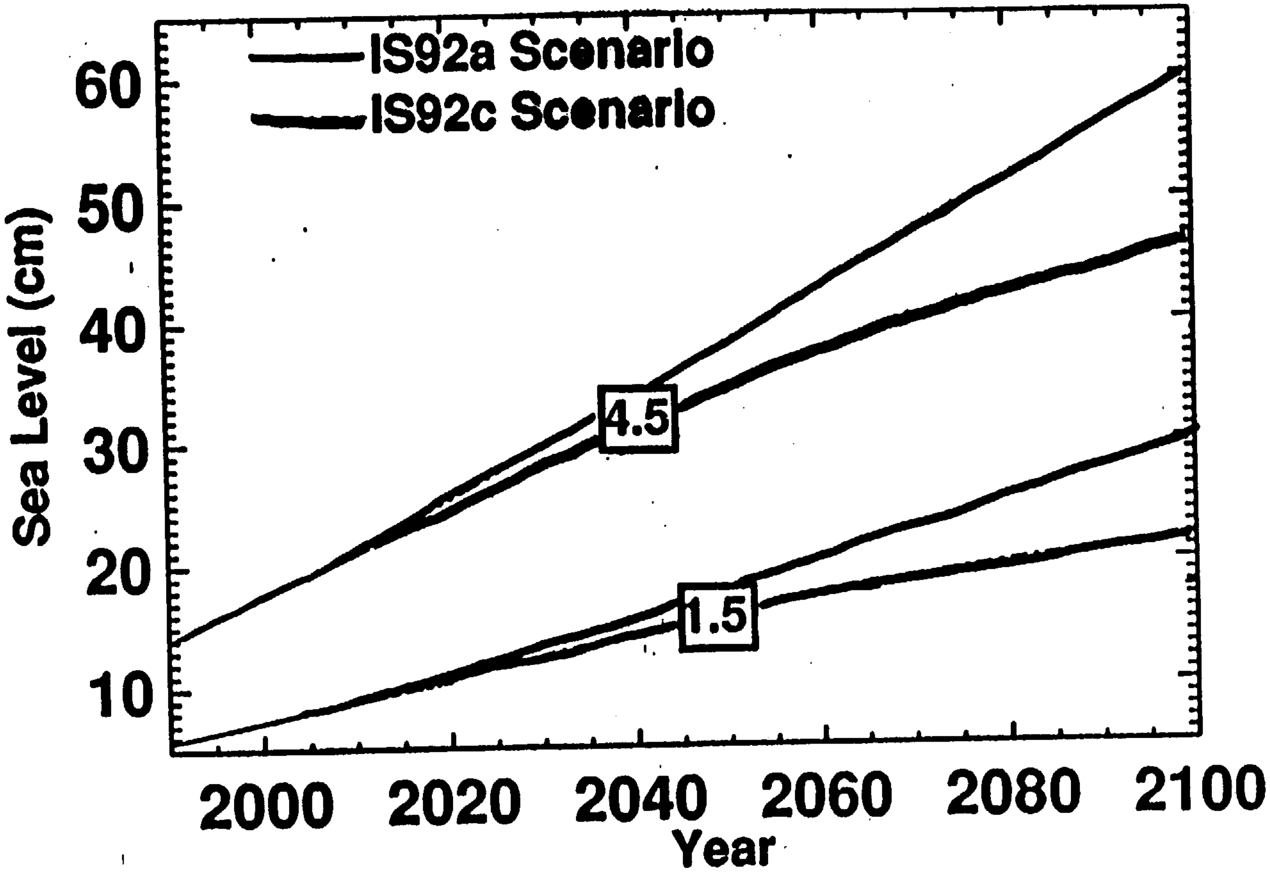


Model Estimated Global Mean Temperature Change and Rate of Temperature Change For IPCC Scenarios





Model Estimated Global Mean Sea Level Change For IPCC Scenarios



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Methane Modeling and Abatement Studies

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Research Programs

1. Modeling of methane sinks & sources for ISAM
2. Evaluation of the Economic Greenhouse Gas Abatement Model
3. Analysis of emissions associated with fuel switching

1. Methane Model

- parameterization of:
  - A . Tropospheric sinks of CH_4
    - reactions with OH
    - transport to the stratosphere
    - soil uptake
  - B . Sources of CH_4
    - anthropogenic
    - natural

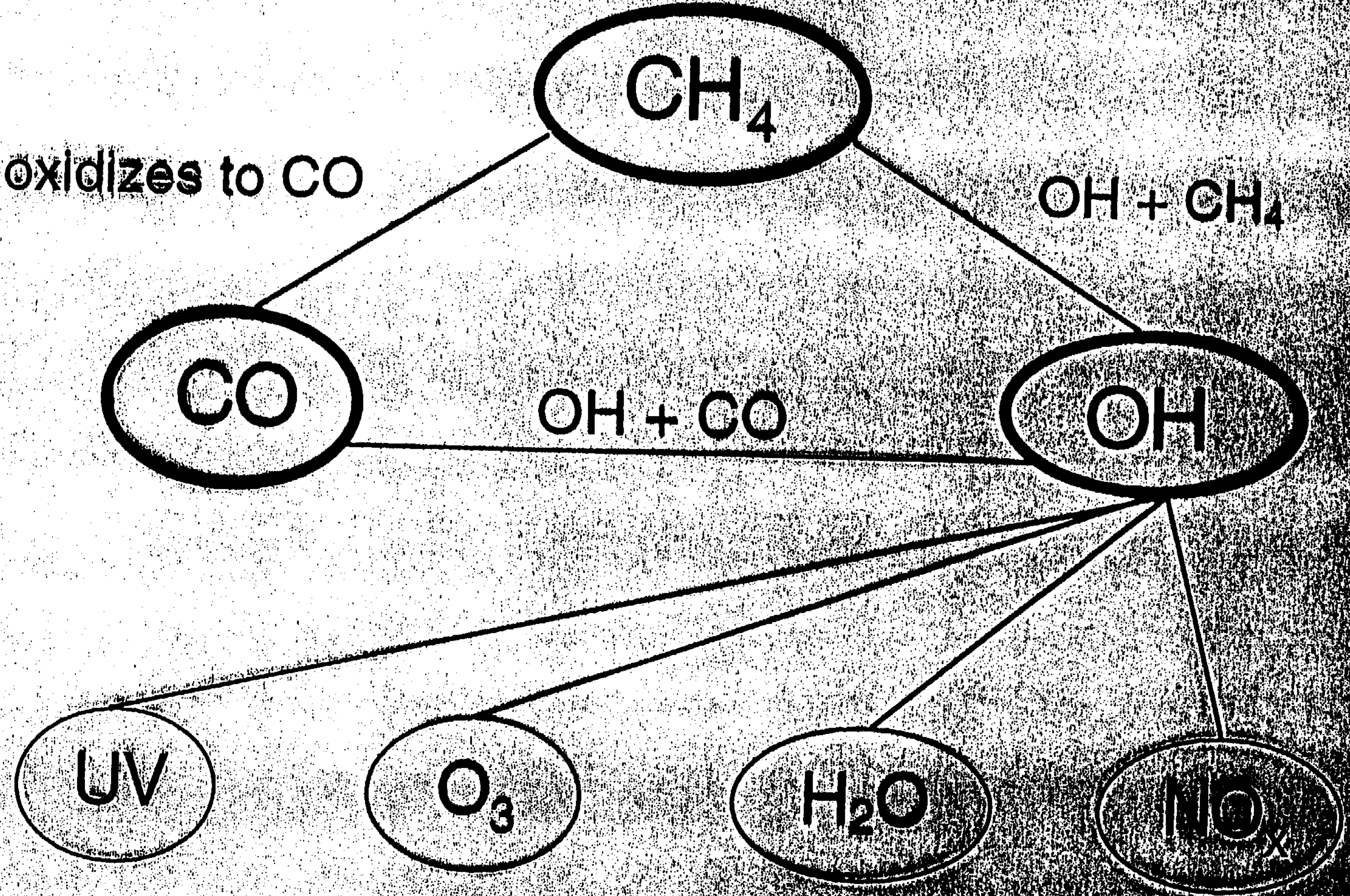
A. Methane Sinks

- almost 90% of CH_4 is removed in troposphere through reactions with OH
- remainder removed by transport to the stratosphere (~6%) & by soil reactions (~4%)
- OH is a spatially variable radical with a lifetime of a few seconds
- detailed modeling of OH is crucial

OH concentrations

- OH depends non-linearly on atmospheric concentrations of many tropospheric gases
- most important gases: CH_4, CO, NO_x, tropospheric O_3, NMHCs
- other factors: tropospheric water vapor, uv radiation flux which depends on stratospheric ozone

Simplified CH_4/OH/CO Chemistry



Simple models of OH concentration

Method: use 1D or 2D chemical transport model to parameterize dependence of OH on other gases

Examples of one-equation models:

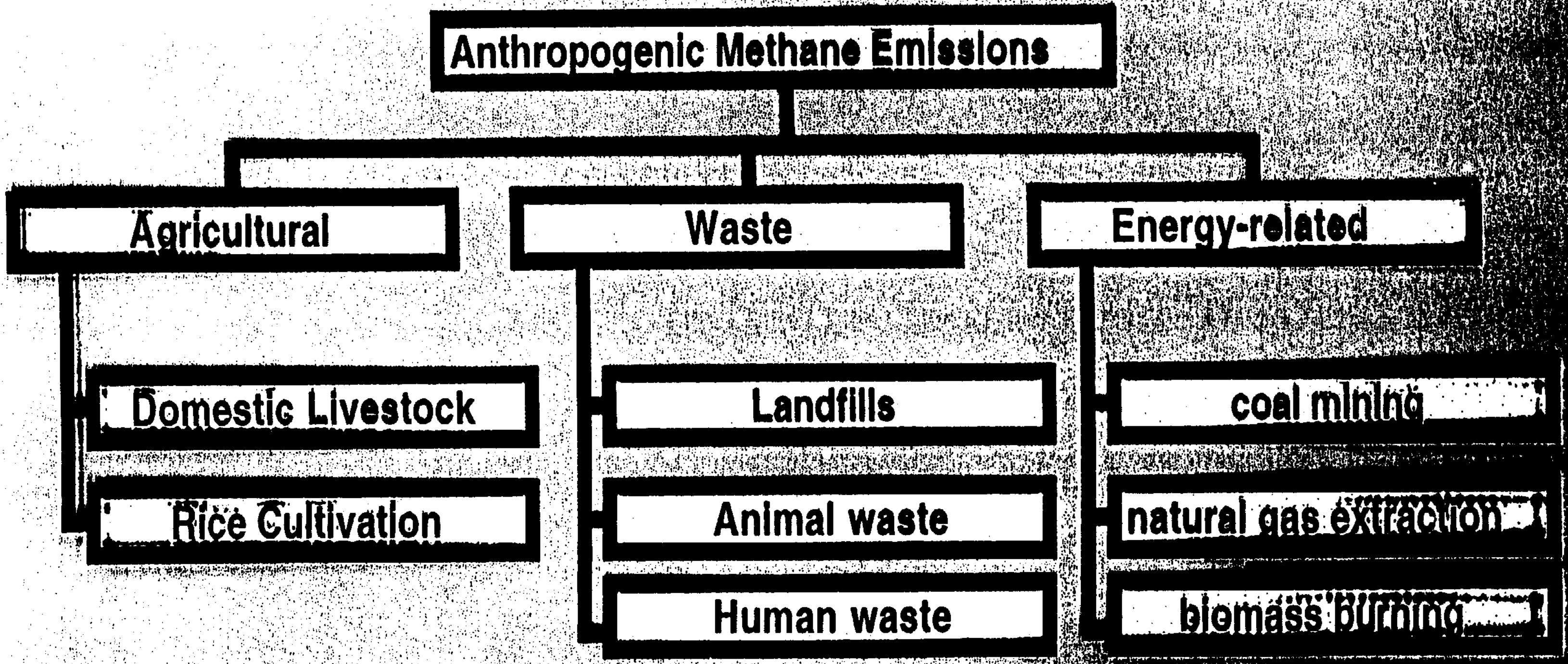
- Wigley & Osborn, 1994: CH_4, CO, NO_x, NMHCs
- Thompson et al., 1990: CH_4, CO, O_3, NO_x, wv, uv
- Rotmans & Eggink, 1989: CH_4, CO

Modeling tropospheric OH

Use our 2D chemical model to derive relation of **latitudinal** OH concentrations to key factors:

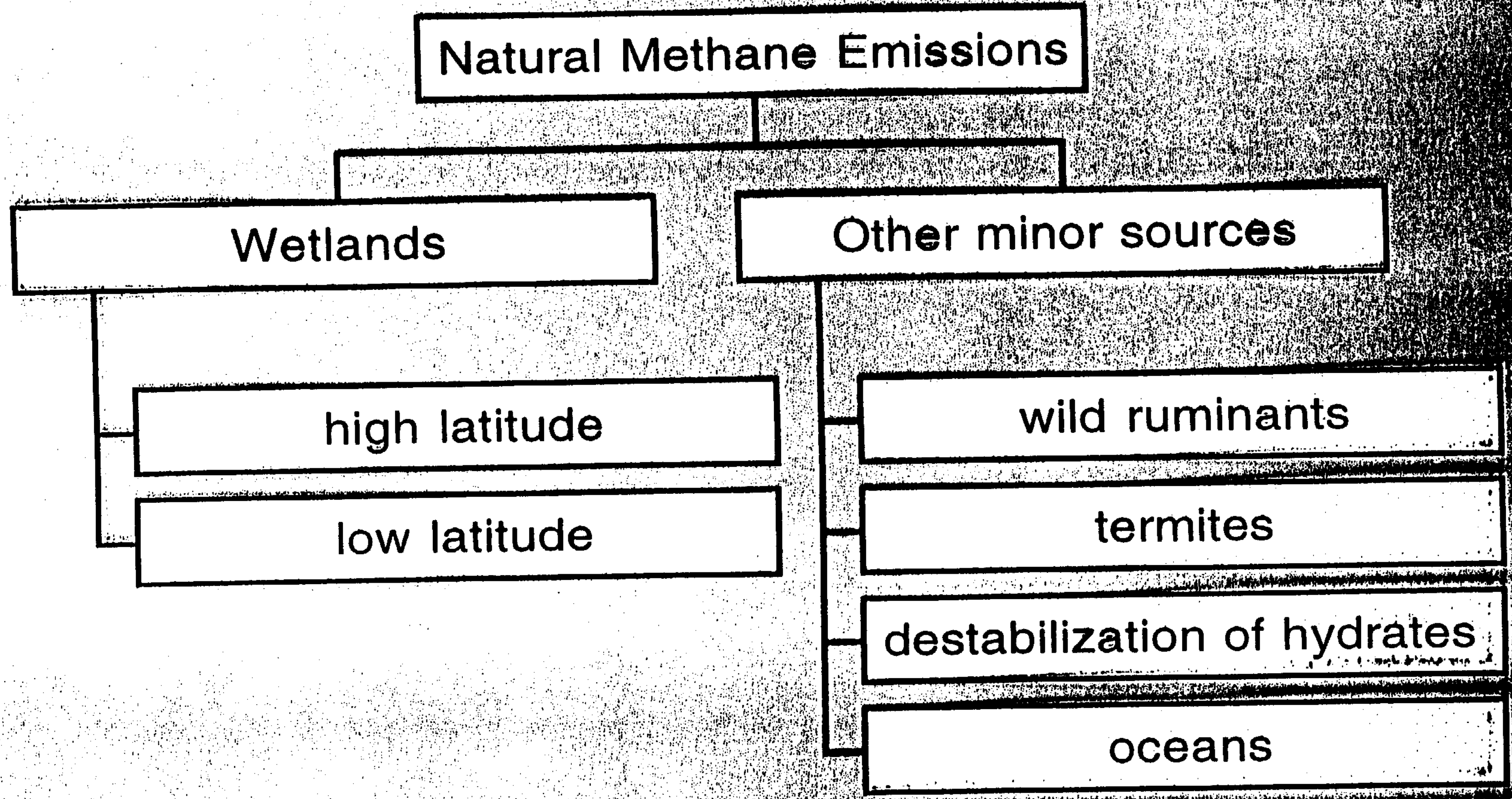
- gases affected by anthropogenic activities - CH_4, CO, NO_x, O_3, NMHCs
- tropospheric water vapor, determined by temperature
- UV radiation flux, dependent on stratospheric O_3 concentrations

B. Anthropogenic Sources of Methane



- Anthropogenic Methane Emissions
  - Agricultural
    - Domestic Livestock
    - Rice Cultivation
  - Waste
    - Landfills
    - Animal waste
    - Human waste
  - Energy-related
    - coal mining
    - natural gas extraction
    - biomass burning

Natural Methane Sources



Natural Methane Emissions

- Wetlands
  - high latitude
  - low latitude
- Other minor sources
  - wild ruminants
  - termites
  - destabilization of hydrates
  - oceans

Modeling sources of CH_4

Prediction of methane emissions from scenarios of basic variables including:

- temperature changes
- population growth
- evolution of land use patterns
- future energy demand and sources
- technological improvements

Future efforts

Improve parameterization of CH_4 sinks through:

- use of 3D chemical model (under development)
- incorporation of NMHC and other chemistry
- more complete modeling of temperature effects on water vapor & reaction rates

Combine detailed modeling of CH_4 sources with isotopic ratio analyses to study uncertainties in current methane budget.

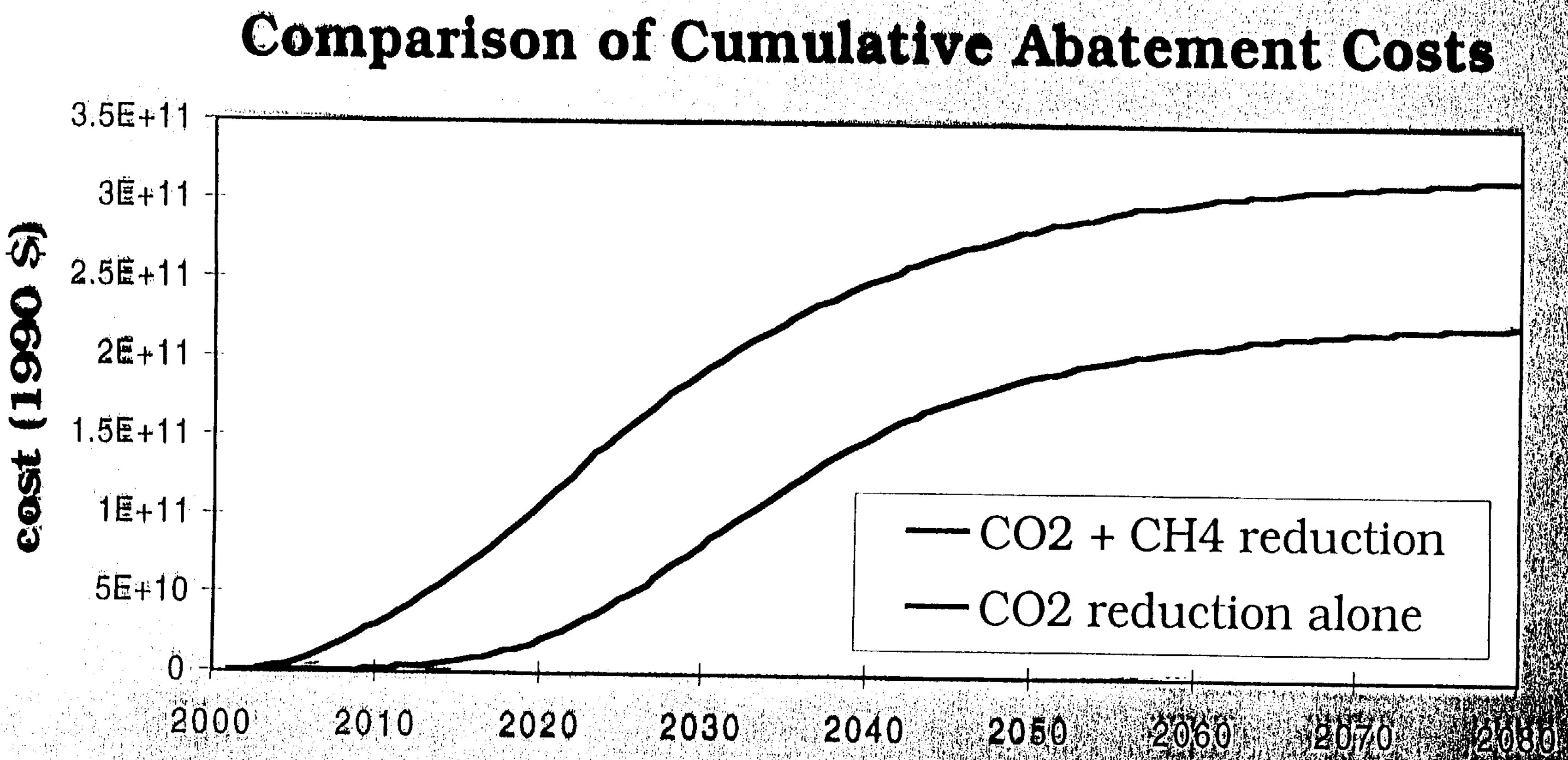
2. Economic GHG Abatement Model

Comparison of costs associated with reducing CO_2 emissions vs. simultaneous reduction of CO_2 & CH_4 emissions

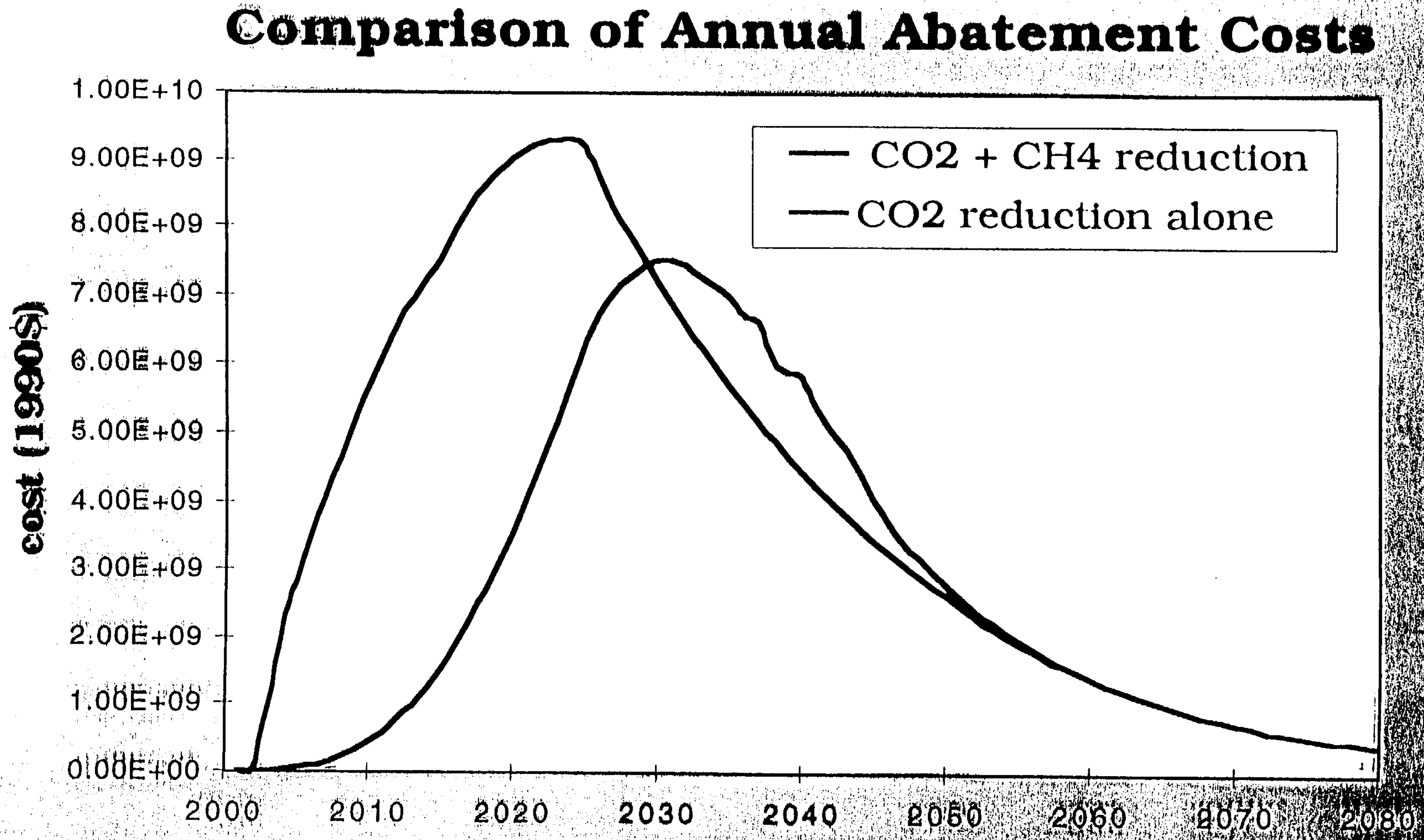
... to comply with IPCC greenhouse gas reduction scenarios.

Preliminary results

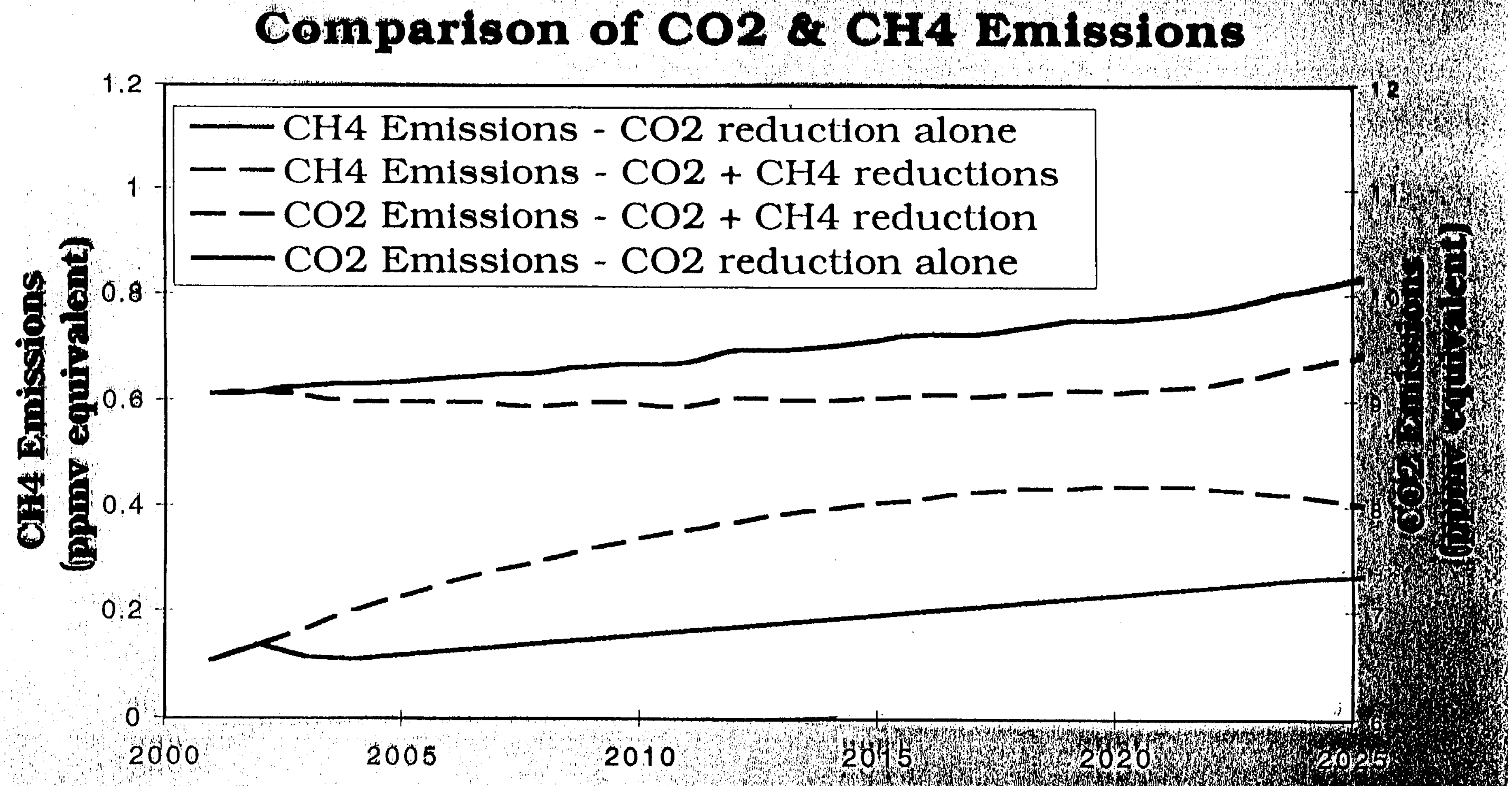
1. Simultaneous reduction of CO_2 and CH_4 results in **lower costs** when compared to CO_2 abatement alone



2. CH_4 provides a **short-term** option to reduce greenhouse gas emissions at a **low price**

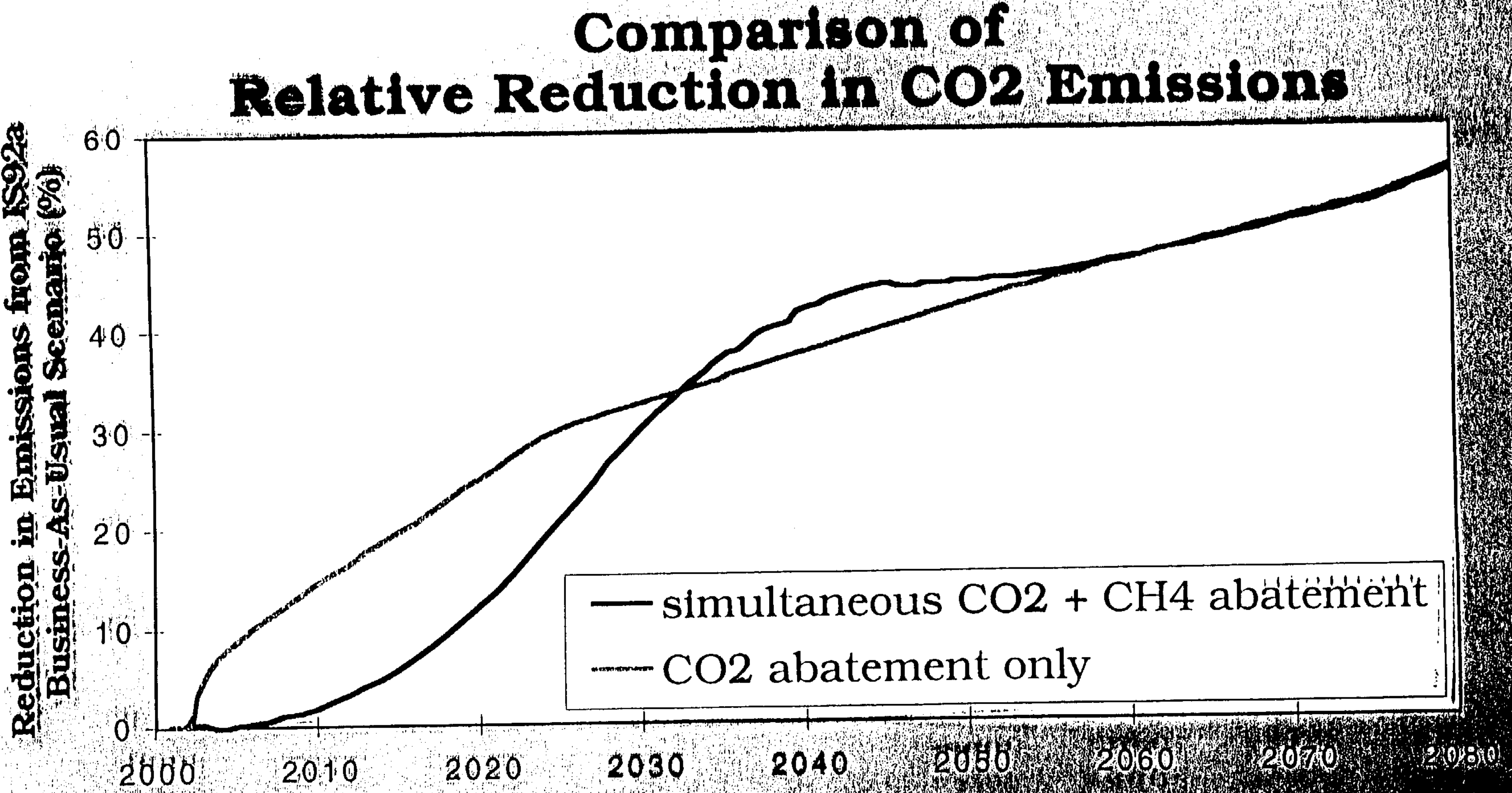


2. CH_4 provides a **short-term** option to **reduce greenhouse gas emissions** at a low price



Comparison of CO2 & CH4 Emissions

3. CO_2 reduction is the only method to comply with **long-term** climate goals



Future efforts

- conduct sensitivity analysis of model to uncertainties inherent to abatement cost estimates
- incorporate other important greenhouse gases and aerosols into model
- develop improved abatement cost functions for non-CO_2 greenhouse gases

3. Climatic Effects of Fuel Switching

Fuel Switching: the replacement of a high carbon fuel source (such as coal or oil) with a less carbon intensive fuel (natural gas).

Can fuel switching reduce total CO_2-equivalent greenhouse gas emissions significantly?

From fuel switching . . .

- **CO_2** emissions from energy production **decrease** due to lower carbon content and higher efficiency of natural gas
- **CH_4** emissions from natural gas extraction **grow** due to increased production
- **CH_4** emissions from coal mining **decrease** due to decline in coal demand
- **sulfate aerosol** emissions **decrease** due to cleaner fuel use

Future efforts

- quantify the sensitivity of climate impacts to uncertainties in energy-related emissions
- examine the complete impact on climate of the replacement of coal and oil use by natural gas in each sector of the economy
- estimate costs of climate protection obtained by fuel switching

Guy Brasseur

NCAR

The IMAGES Model

1. 3-D Global Chemical Transport model
2. Domain : Surface to 50 mb (20 km)
3. Detailed surface emissions
4. Relatively comprehensive chemical scheme (50 species)
5. Advection : Semi-Lagrangian transport scheme
6. Parameterization of sub-scale transport (convection, mixing)
7. Dry and wet deposition
8. Large time steps (1 day) except 3 days | month (1 hour)
9. Input data (Temp, winds, precip., etc...) from observations

Table 1. Chemical species included in the model.

1/ Fixed species :
O_2: 20.95%
N_2: 79.05%
H_2O: climatological distribution from ECMWF
H_2: 550 ppbv
N_2O: 305 ppbv

2/ Long-lived species (for which transport is considered)

inorganic species

O_3	ozone
H_2O_2	hydrogen peroxide
HNO_3	nitric acid
$NO_x \equiv NO+NO_2+HNO_4+NO_3+2N_2O_5$	nitrogen oxides (family)

organic species (non oxygenated)

CH_4	methane
C_2H_6	ethane
C_2H_4	ethylene
C_3H_6	propylene
C_5H_8	isoprene
$C_{10}H_{16}$	α-pinene
OTHC	other hydrocarbons

organic species (oxygenated)

CO	carbon monoxide
CH_2O	formaldehyde
PAN ($CH_3CO_3NO_2$)	peroxy-acetyl nitrate
MPAN ($CH_2CCH_3CO_3NO_2$)	peroxymethacrylic nitrate
CH_3OOH	methyl peroxide
C_2H_5OOH	ethyl peroxide
C_3H_6OHOOH	peroxide from propylene
CH_3COOOH	peracetic acid

3/ Short-lived species (for which transport is not considered)

inorganic species

$O(^1D)$	oxygen atom (excited state)
O or $O(^3P)$	oxygen atom (fundamental state)
OH	hydroxyl radical
HO_2	hydroperoxyl radical
NO	nitrogen monoxide
NO_2	nitrogen dioxide
HNO_4	pernitric acid
NO_3	nitrogen trioxide
N_2O_5	nitrogen hemipentoxide

carbonyls

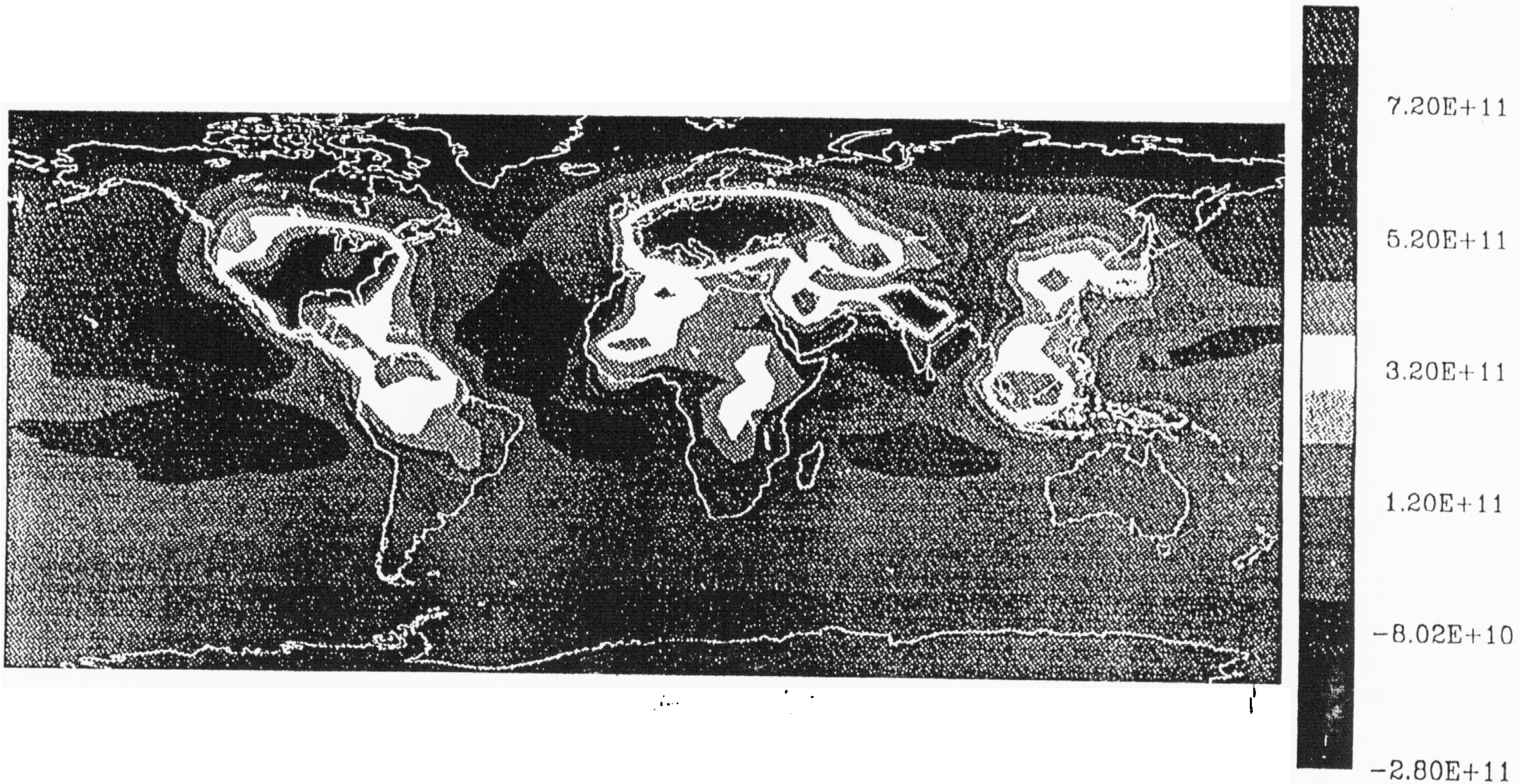
CH_3CHO	acetaldehyde
CH_2OHCHO	glycolaldehyde
$CHOCHO$	glyoxal
CH_3COCHO	methylglyoxal
MVK ($CH_2CHCOCH_3$)	methylvinylketone
MACR (CH_2CCH_3CHO)	methacrolein
peroxy radicals	
CH_3O_2	methylperoxy radical
$C_2H_5O_2$	ethylperoxy radical
$C_3H_6OHO_2$	peroxy radical from propylene
$C_5H_8OHO_2$	peroxy radical from isoprene
$MOHO_2$	peroxy radical from MVK and MACR
CH_3CO_3	acetylperoxy radical
MCO_3 ($CH_2CCH_3CO_3$)	peroxymethacrylic radical

Sulfur

DMS
COS
CS_2
H_2S
SO_2
$SO_4^=$

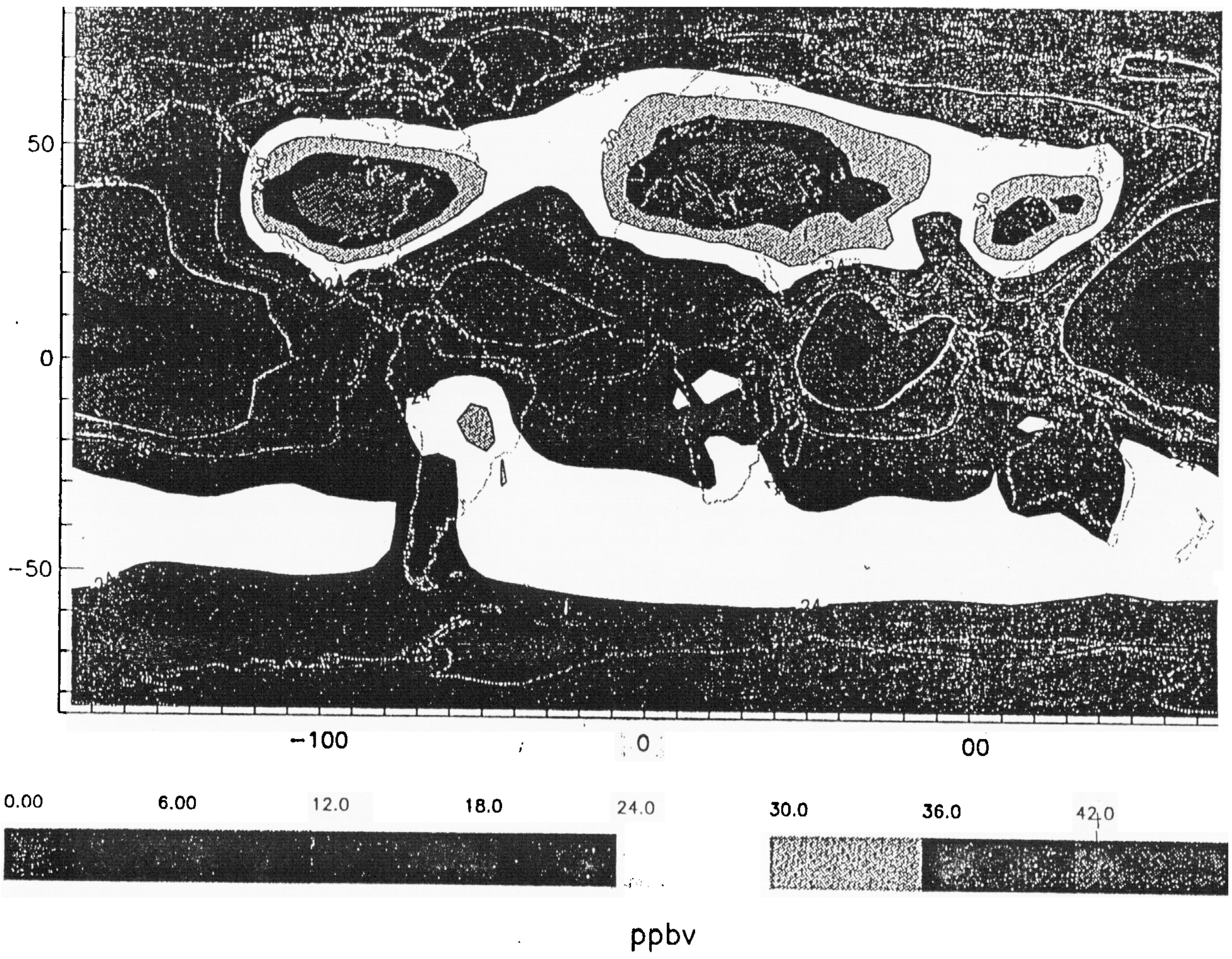
Also (tracers)

CFC-11
N_2O
CH_3CCl_3
Rn
Krypton



O3 Integrated Net Production

IMAGES model on day 546.0

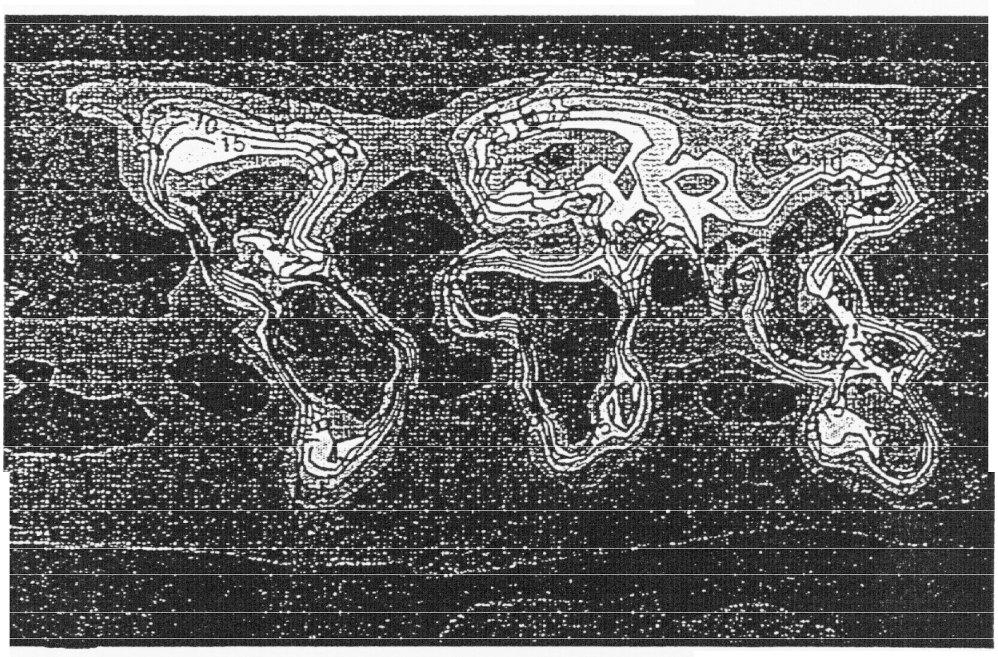


O3 (ppbv)   0.995 sigma   aua_toz92

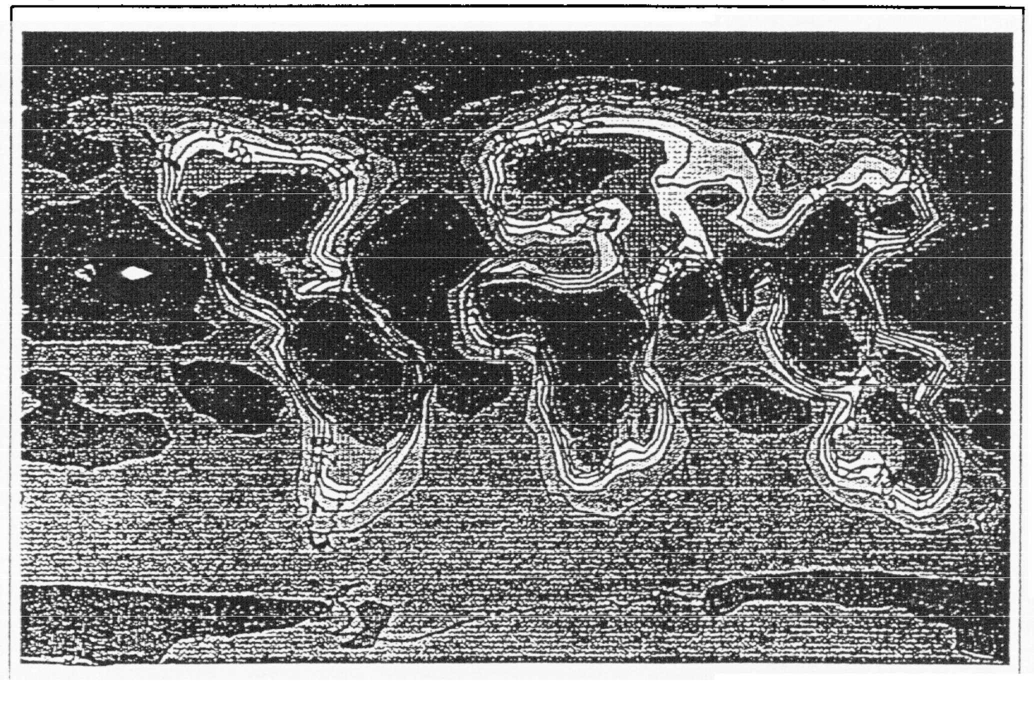
Evolution of the CH_4 Budget

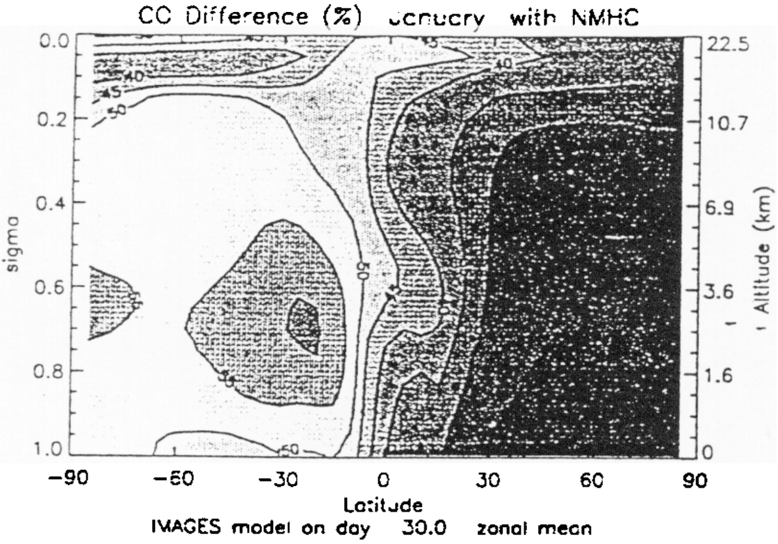
	Pre-Industrial	Present	Yr 2050
Burden (Tg CH_4)	1760	4467	6848
Emission (Tg CH_4/yr)	~ 208 (s.s)	487	>625
Photochemical Loss (Tg CH_4/yr)	205	431	613
Dry Deposition (Tg CH_4/yr)	3	8	12
Photochemical Lifetime (years)	8.6	10.4	11.2
Global Lifetime (years)	8.4	10.2	10.9

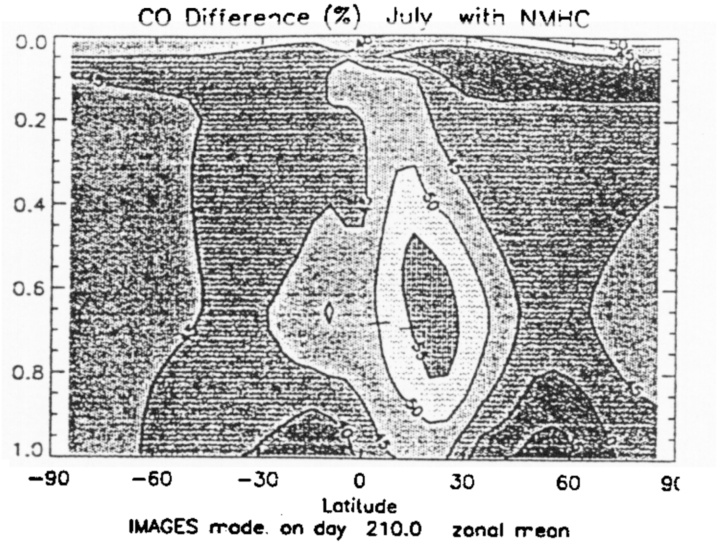
-O Integrated Net Production (10+10 molec./cm2/s) no NMHC

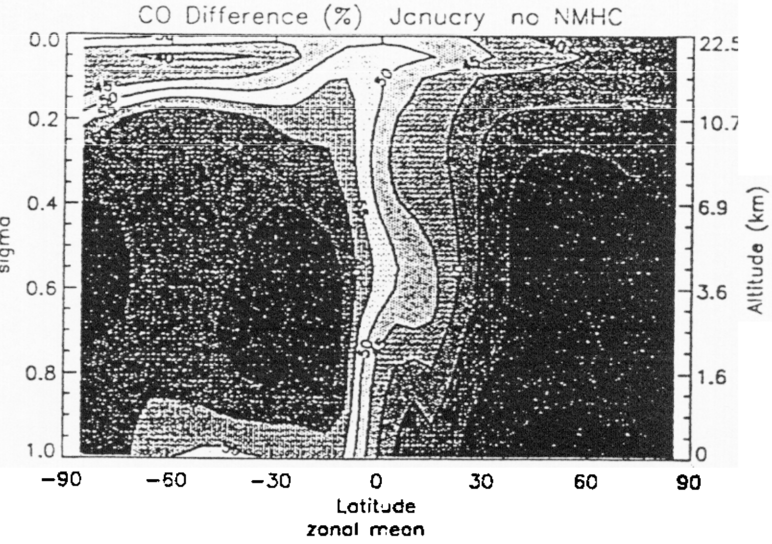


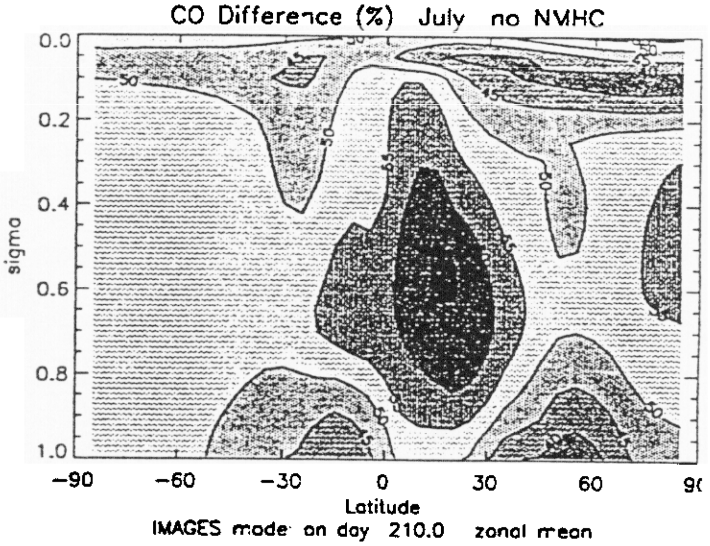
O3 Integrated Net Production (10+10 molec./cm2/s) no NMHC, CH4*2

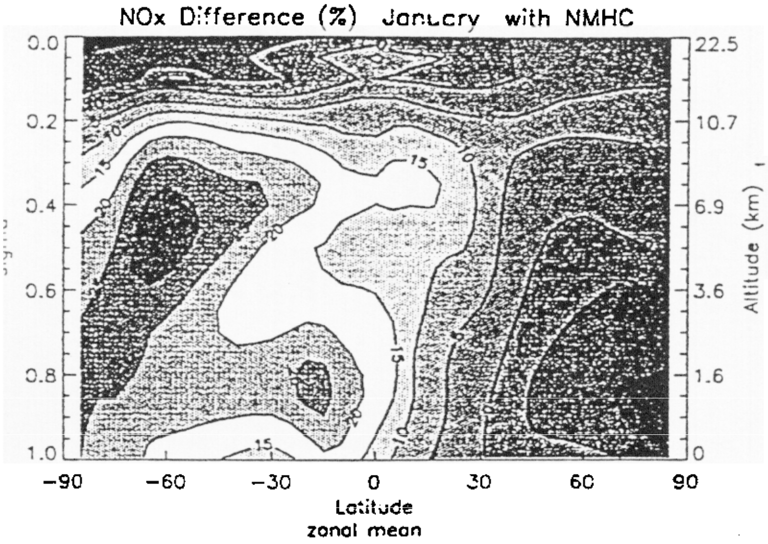


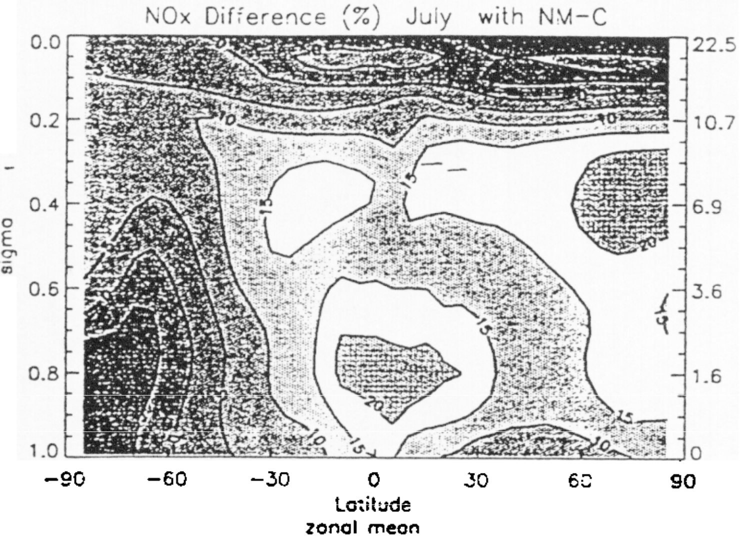

CO Difference (%) January with NMHC

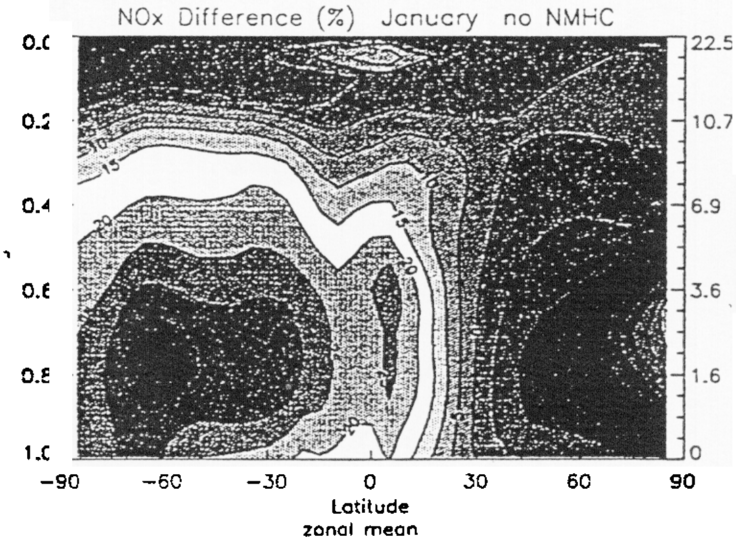

CO Difference (%) July with NMHC

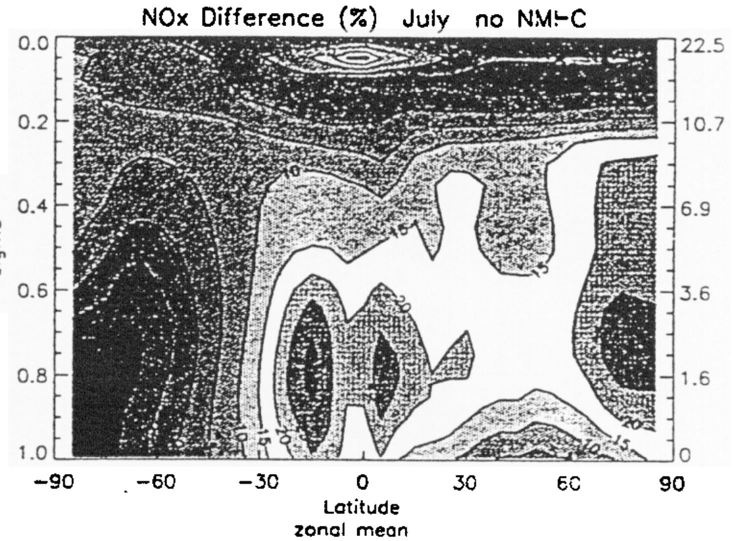

CO Difference (%) January no NMHC


CO Difference (%) July no NMHC

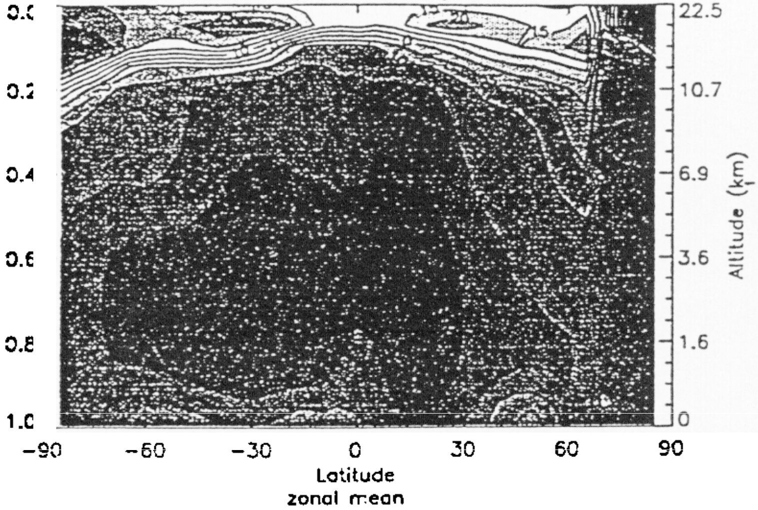

NOx Difference (%) January with NMHC


NOx Difference (%) July with NM-C

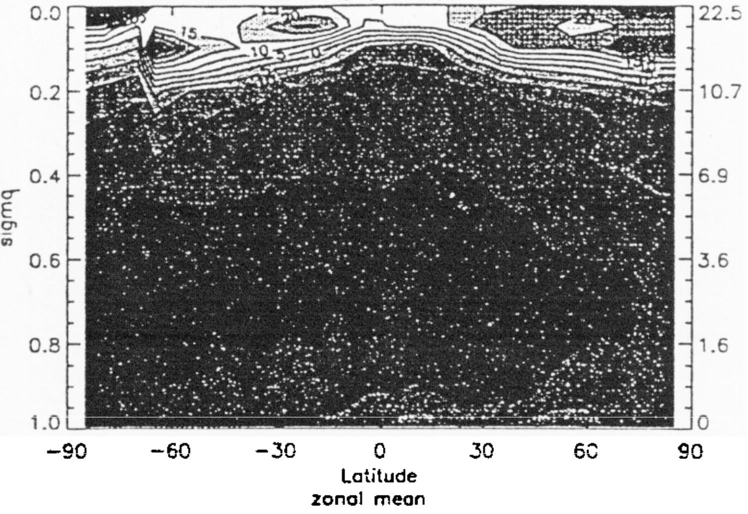

NOx Difference (%) January no NMHC


NOx Difference (%) July no NMHC

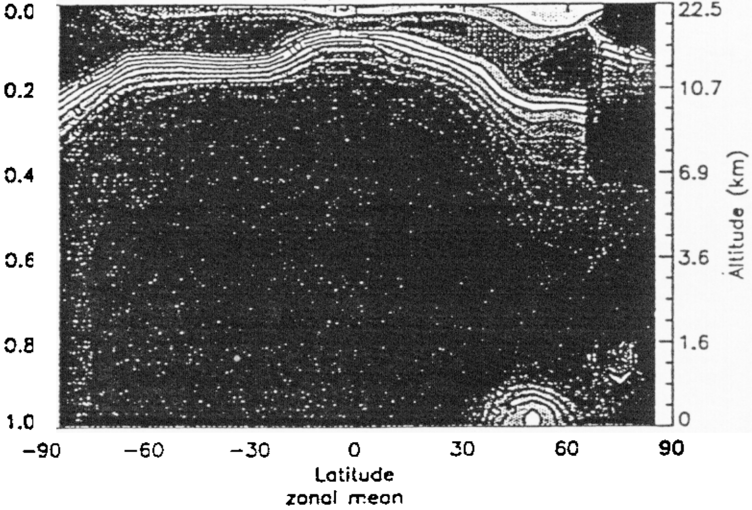
OH Difference (%) January with NMHC



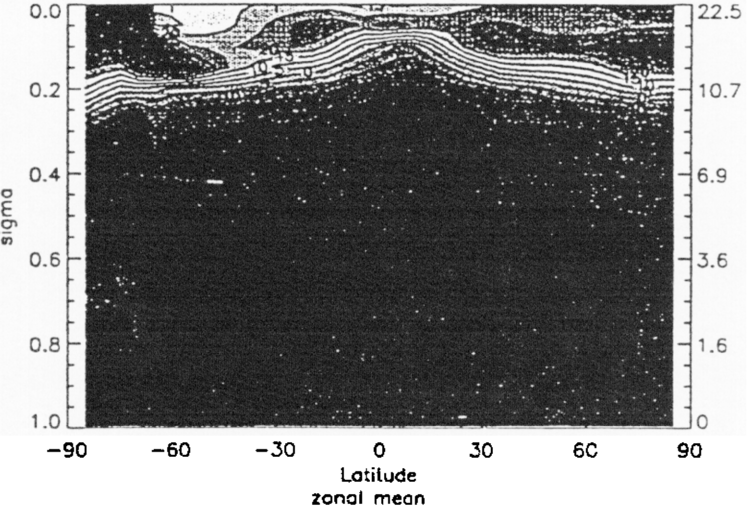
OH Difference (%) July with NMHC

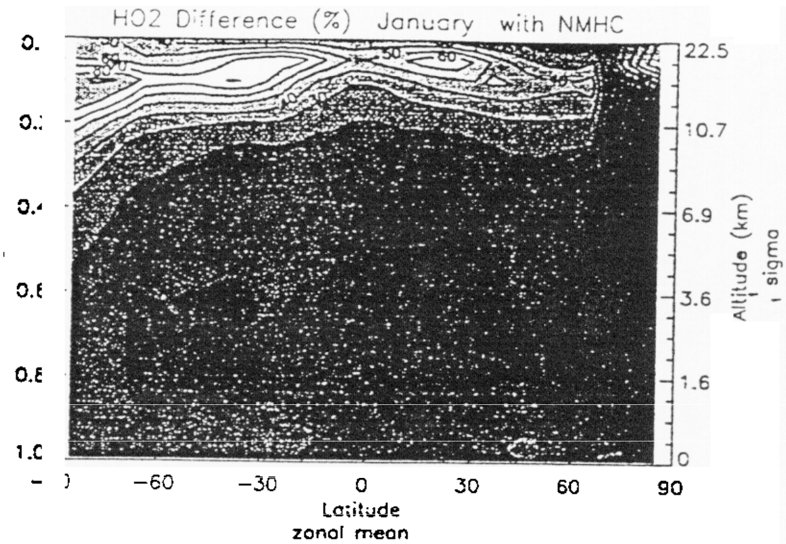


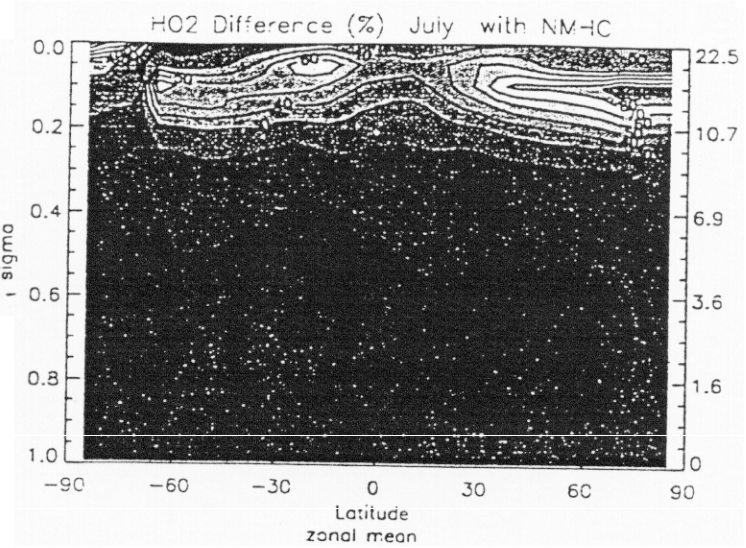
OH Difference (%) January no NMHC

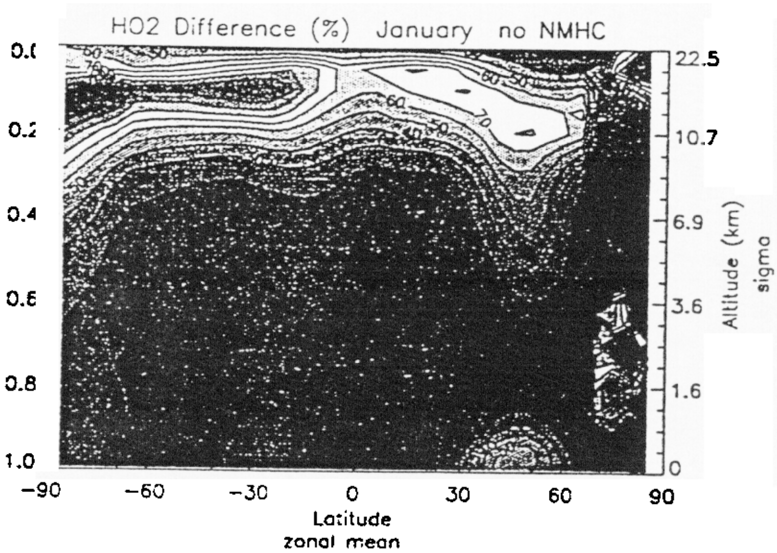


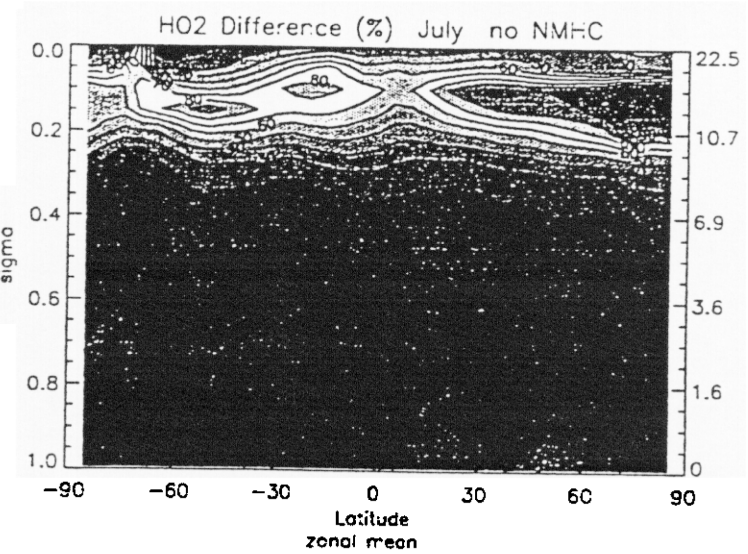
OH Difference (%) July no NMHC



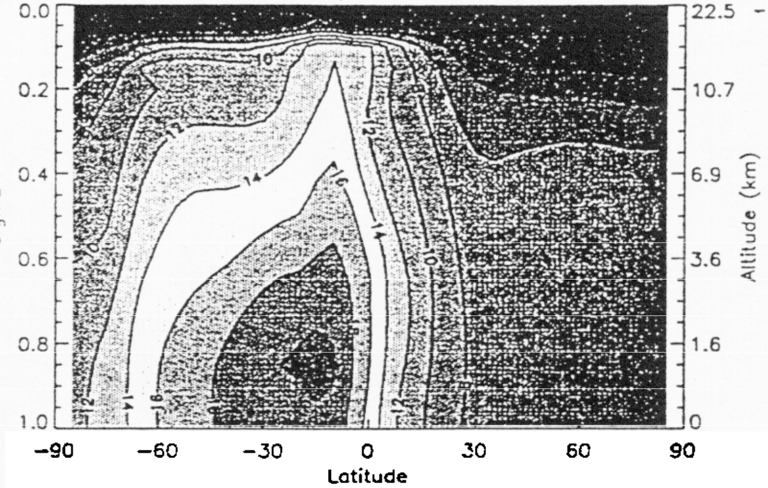

HO2 Difference (%) January with NMHC
Altitude (km)
sigma
Latitude
zonal mean
22.5
10.7
6.9
3.6
1.6
0
-60
-30
0
30
60
90
50
60
70
40
1.0


HO2 Difference (%) July with NMHC
0.0
0.2
0.4
0.6
0.8
1.0
22.5
10.7
6.9
3.6
1.6
0
-90
-60
-30
0
30
60
90
Latitude
zonal mean
60
50
40


HO2 Difference (%) January no NMHC
Altitude (km)
sigma
0.0
0.2
0.4
0.6
0.8
1.0
22.5
10.7
6.9
3.6
1.6
0
-90
-60
-30
0
30
60
90
Latitude
zonal mean
60
70
50

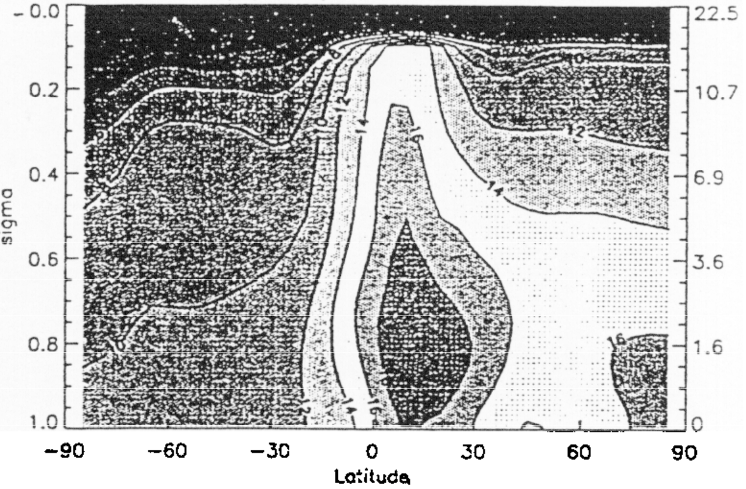

HO2 Difference (%) July no NMHC
0.0
0.2
0.4
0.6
0.8
1.0
22.5
10.7
6.9
3.6
1.6
0
-90
-60
-30
0
30
60
90
Latitude
zonal mean
80
70
60

O3 Difference (%) January CH4*2 – CH4*1, with NMHC



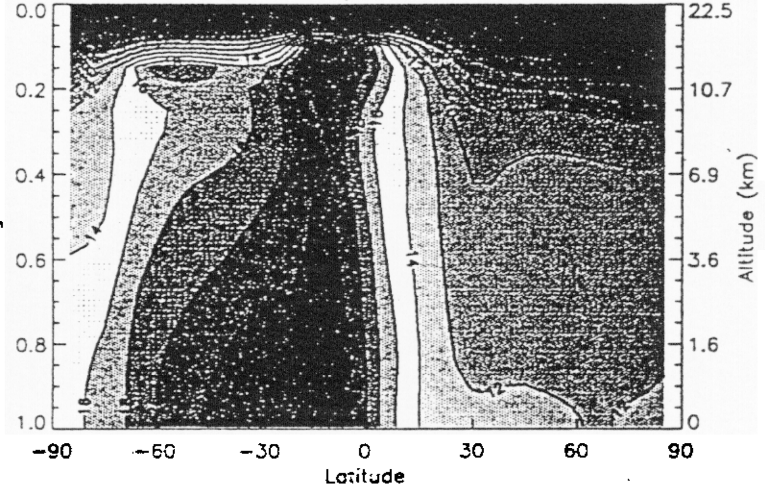
IMAGES model on day 30.0 zonal mean

O3 Difference (%) July CH4*2 – CH4*1, with NMHC



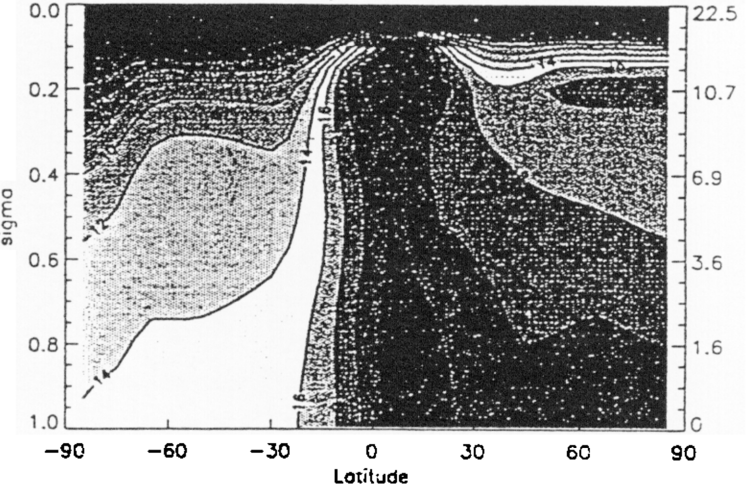
IMAGES model on day 210.0 zonal mean

O3 Difference (%) January CH4*2 – CH4*1, no NMHC



IMAGES model on day 30.0 zonal mean

O3 Difference (%) July CH4*2 – CH4*1, no NMHC



IMAGES model on day 210.0 zonal mean

Model Exercise and Intercomparison

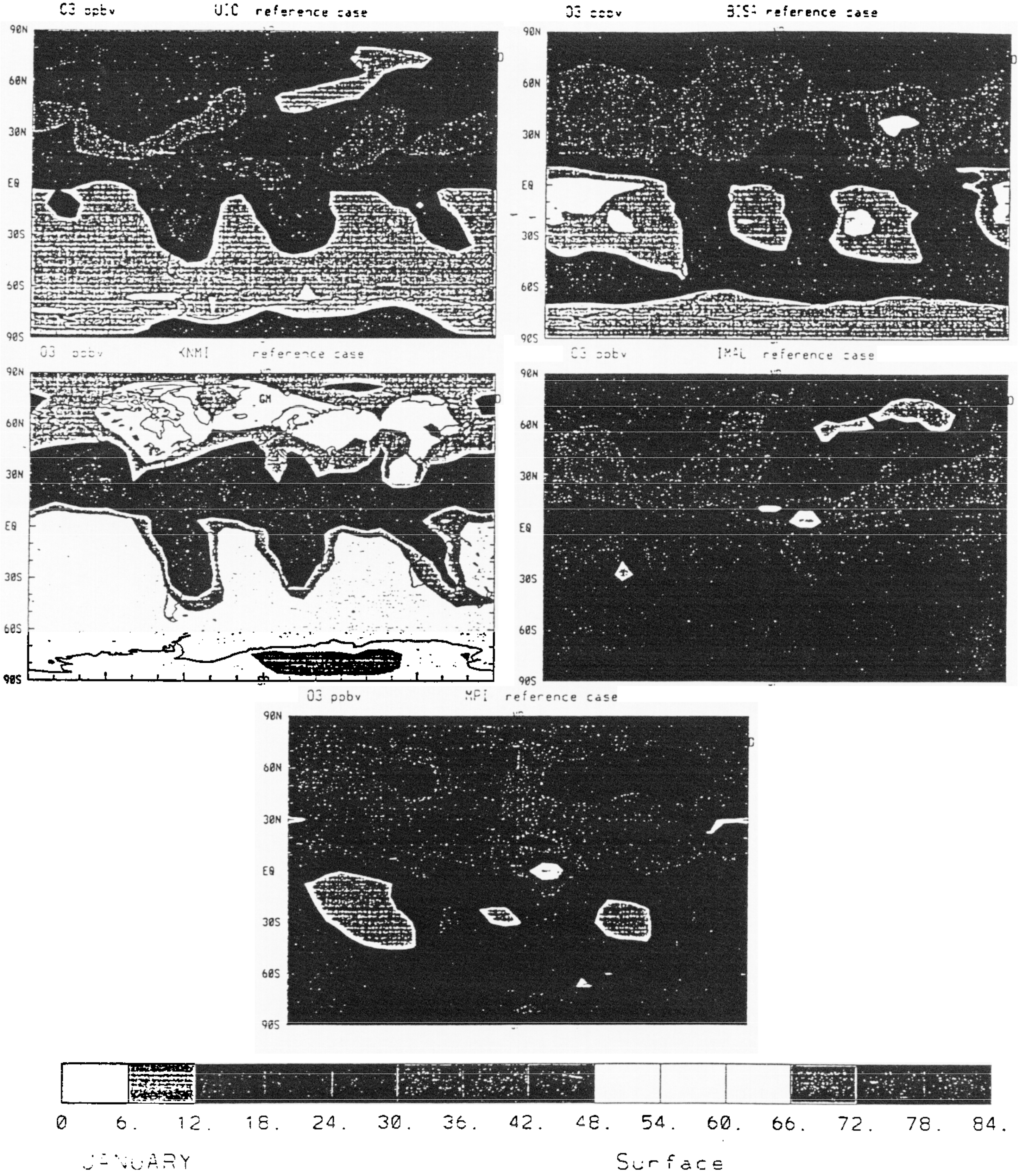
5 Participants:

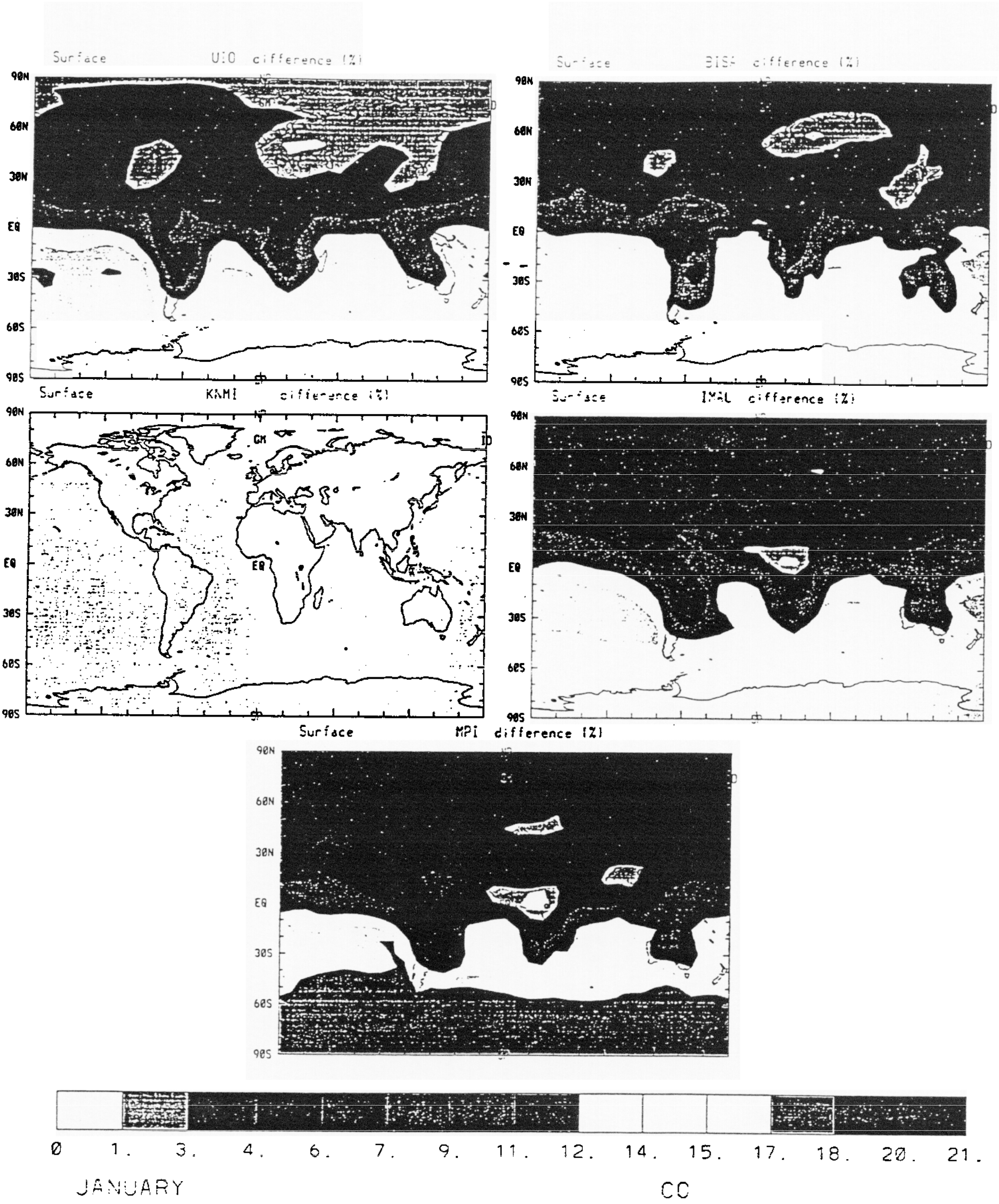
- BiSA → IMAGES (NCAR + Belgium)
- IMAU → TM2 with VOC (The Netherlands)
- UiO → CTM1 (U. of Oslo)
- MPi → TM2 (Germany)
- KNMi → CTM K (The Netherlands)

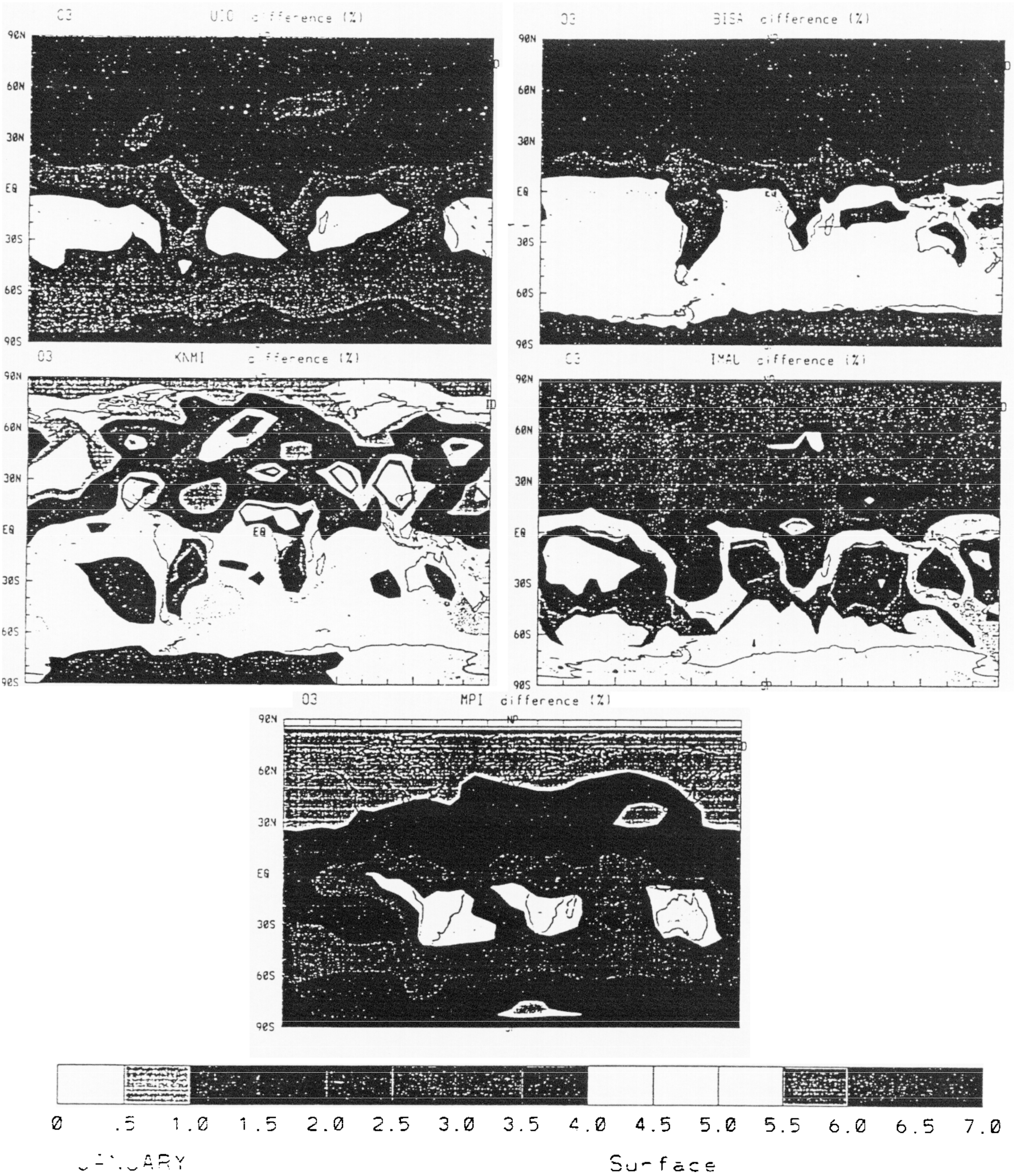
Purpose:

Assess the response of the models (O_3, CO, OH) to a 20% increase in methane

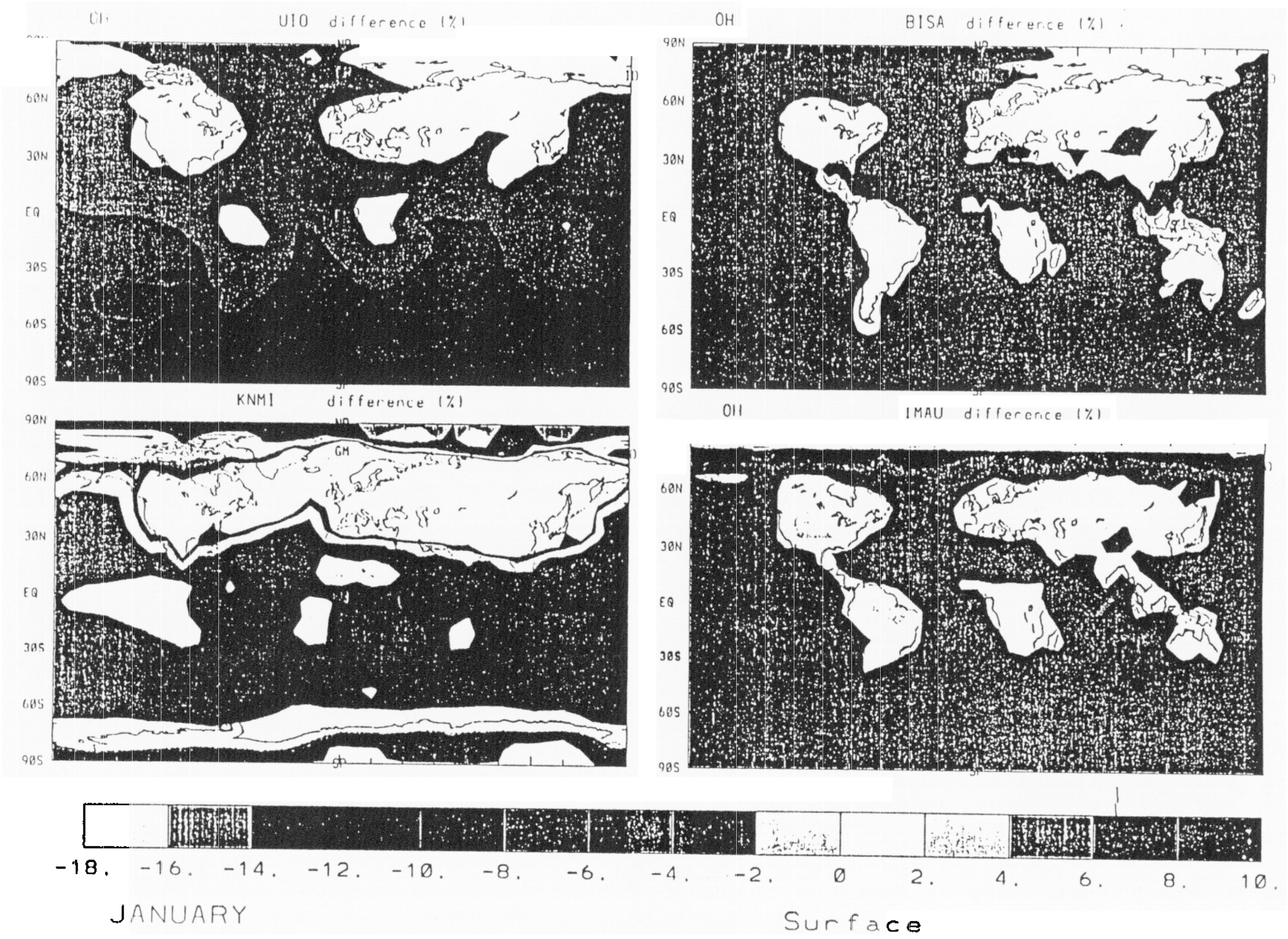
(Note: KMNi has no CO emission!)


O3 ppbv UiO reference case
O3 ppbv BISA reference case
O3 ppbv KNMI reference case
O3 ppbv IMAL reference case
O3 ppbv MPI reference case
90N
60N
30N
EQ
30S
60S
90S
GM
0
6.
12.
18.
24.
30.
36.
42.
48.
54.
60.
66.
72.
78.
84.
JANUARY
Surface


Surface UIO difference (%)
Surface BISA difference (%)
Surface KNMI difference (%)
Surface IMAL difference (%)
Surface MPI difference (%)
90N
60N
30N
EQ
30S
60S
90S
NP
GM
ID
SP
0
1.
3.
4.
6.
7.
9.
11.
12.
14.
15.
17.
18.
20.
21.
JANUARY
CO


O3 UIO difference (%)
O3 BISA difference (%)
O3 KNMI difference (%)
O3 IMAU difference (%)
O3 MPI difference (%)
90N
60N
30N
EQ
30S
60S
90S
NP
0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
JANUARY
Surface

I


OH
UIO difference (%)
OH
BISA difference (%)
KNMI difference (%)
OH
IMAU difference (%)
90N
60N
30N
EQ
30S
60S
90S
NP
GM
SP
-18.
-16.
-14.
-12.
-10.
-8.
-6.
-4.
-2.
0
2.
4.
6.
8.
10.
JANUARY
Surface

Nonlinear Response of Methane Change

	O Standard	A CH_4 x 2	A–O	B no NMHC	C CH_4 x 2 no NMHC	C–B
O_3 production	6005	6927	922	5100	6144	1044
loss	5133	5790	657	4522	5250	728
net productivity	872	1137	265	578	894	316
dry deposition	1218	1362	144	1005	1184	179
top flux	346	225	-121	427	290	-137
CH_4 lifetime	8.71	10.92	+25.4%	8.163	10.629	+30.2%
CH_3CCl_3 lifetime	4.815	5.822	+20.9%	4.540	5.586	+23.0%

Feedback Factor: 1.25 1.30

With NMHC | No NMHC

- 2-D NCAR Model (SOCRATES)
  → Theresa Huang

- Inverse Modeling
  - Use observations at surface stations
  - "Adjust" emissions to best fit these observations

$$[CH_4]_{observ.} = \sum_i \alpha_i \, E_i(CH_4)$$

- Use $\delta^{13}CH_4$ (also measured)

Theresa Huang

NCAR

NCAR troposphere/middle atmosphere 2-D Model- SOCRATES (Simulation Of Chemistry, Radiation And Transport of Environmentally important Species).

Major features:

- Model domain: 0 - 120 km. -85 to 85 degs lat.
- UV radiative transfer with absorption and scattering by aerosols and clouds.
- IR radiative effect for CO_2, H_2O, O_3, CH_4, N_2O, CFC11, CFC12, aerosols, and clouds.
- Planetary wave model and gravity wave parameterization.
- Option of stratospheric QBO forcing.
- Over 60 chemical species and 140 chemical reactions
- Tropospheric chemistry and water vapor transport.
- Diurnal variation of chemical species.

Table 4a Long-lived species

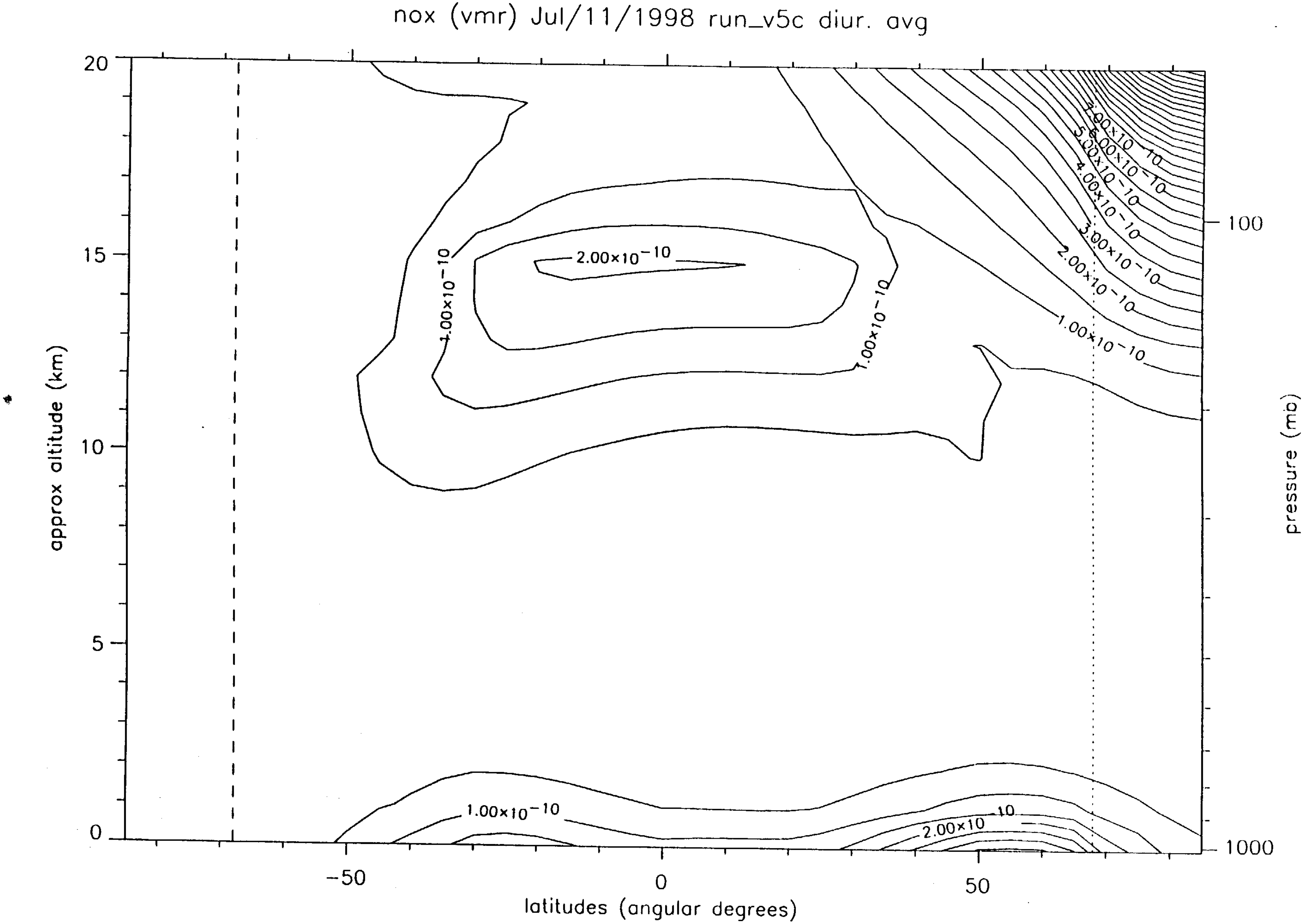
1............N_2O
2............CH_4
3............H_2O
4............$NO_y=NO+NO_2+HNO_3+$
$2*N_2O_5+HO_2NO_2+NO_3+N+$
$ClONO_2+BrONO_2+ClNO_2$
5............HNO_3
6............$N2O_5$
7............$Cl_y=ClO+OClO+$
$2*Cl_2O_2+HCl+ClONO_2+HOCl+$
$2*Cl_2+ClNO_2$
8............$O_x=O_3+O(3P)+O(1D)$
9............CO
10..........OClO
11..........TRACER
12..........AEROSOLS
13..........HCl
14..........$ClONO_2$
15..........HOCl
16..........Cl_2
17..........H_2O_2
18..........$ClNO_2$
19..........HBr
20..........$BrONO_2$
21..........$NO_x=NO+NO_2$
22..........HO_2NO_2
23..........$ClO_x=Cl+ClO$
24..........$BrO_x=Br+BrO$
25..........Cl_2O_2
26..........HOBr
27..........CO_2
28..........C_2H_6
29..........C_2H_4
30..........C_3H_6
31..........CH_2O
32..........PAN (${CH_3CO_3NO_2}$)
33..........H_2
34..........HO_x
35..........CFC-10 (CCl_4)
36..........CFC-11 (CCl_3F)
37..........CFC-12 (CCl_2F_2)
38..........CFC-113 ($C_2Cl_3F_3$)
39..........CFC-114 ($C_2Cl_2F_4$)
40..........CFC-115 (C_2ClF_5)
41..........HCFC-22 ($CHClF_2$)
42..........CH_3CCl_3
43..........CH_3Cl
44..........CCl_2O
45..........CClFO
46..........CF_2O
47..........Ha-1211 (CF_2ClBr)
48..........Ha-1301 (CF_3Br)
49..........HF
50..........CH_3Br
51..........$Br_y=Br+BrO+HOBr+$
$HBr+BrONO_2+BrCl$

Table 4b Intermediate lifetime species

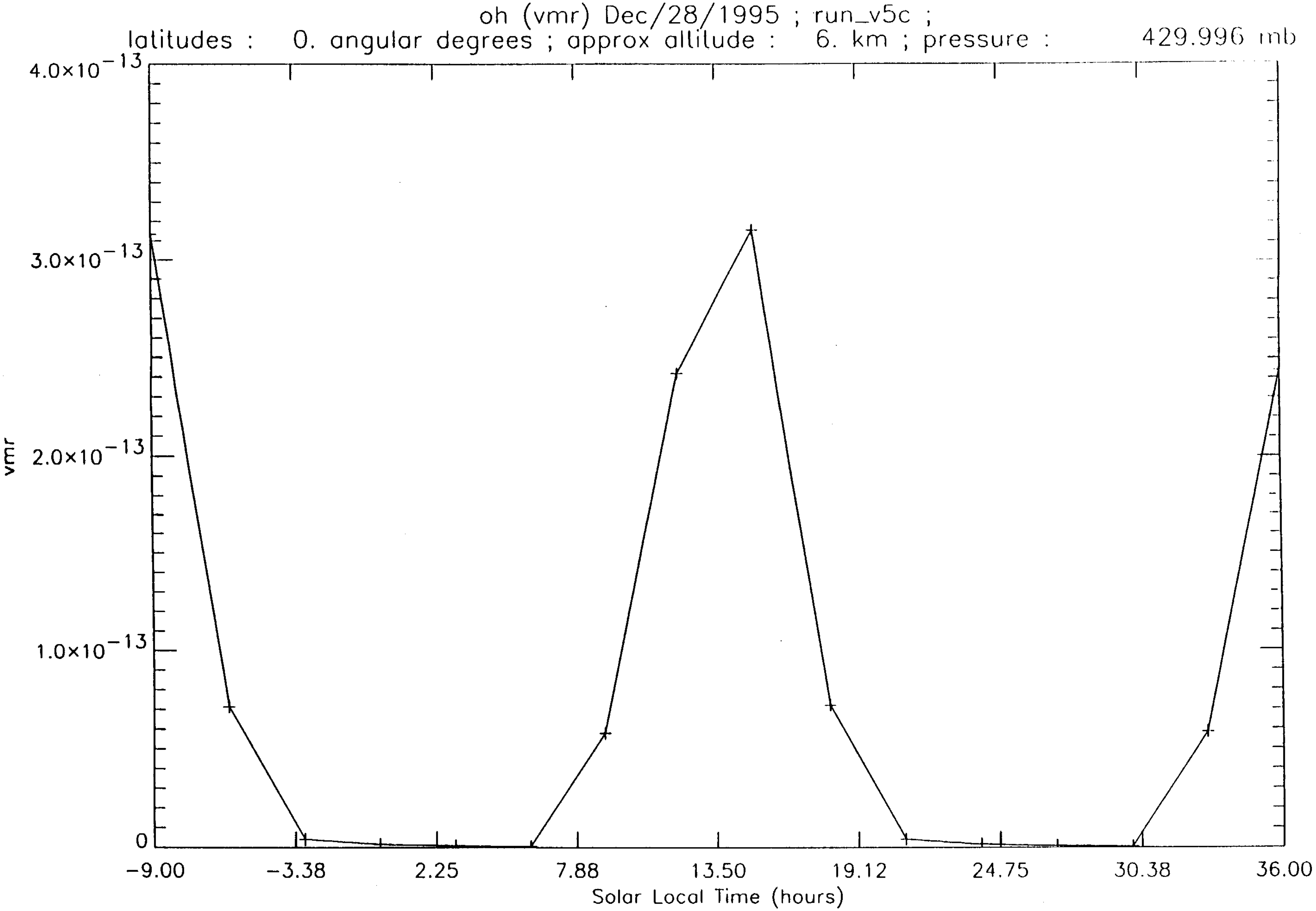
1..........CH_3O_2
2..........CH_3OOH
3..........$C_2H_5O_2$
4..........C_2H_5OOH
5..........CH_3CHO
6..........CH_3CO_3
7..........CH_3COOOH
8..........$C_3H_6OHO_2$
9..........C_3H_6OHOOH
10..........BrCl

Table 4c Short-lived species

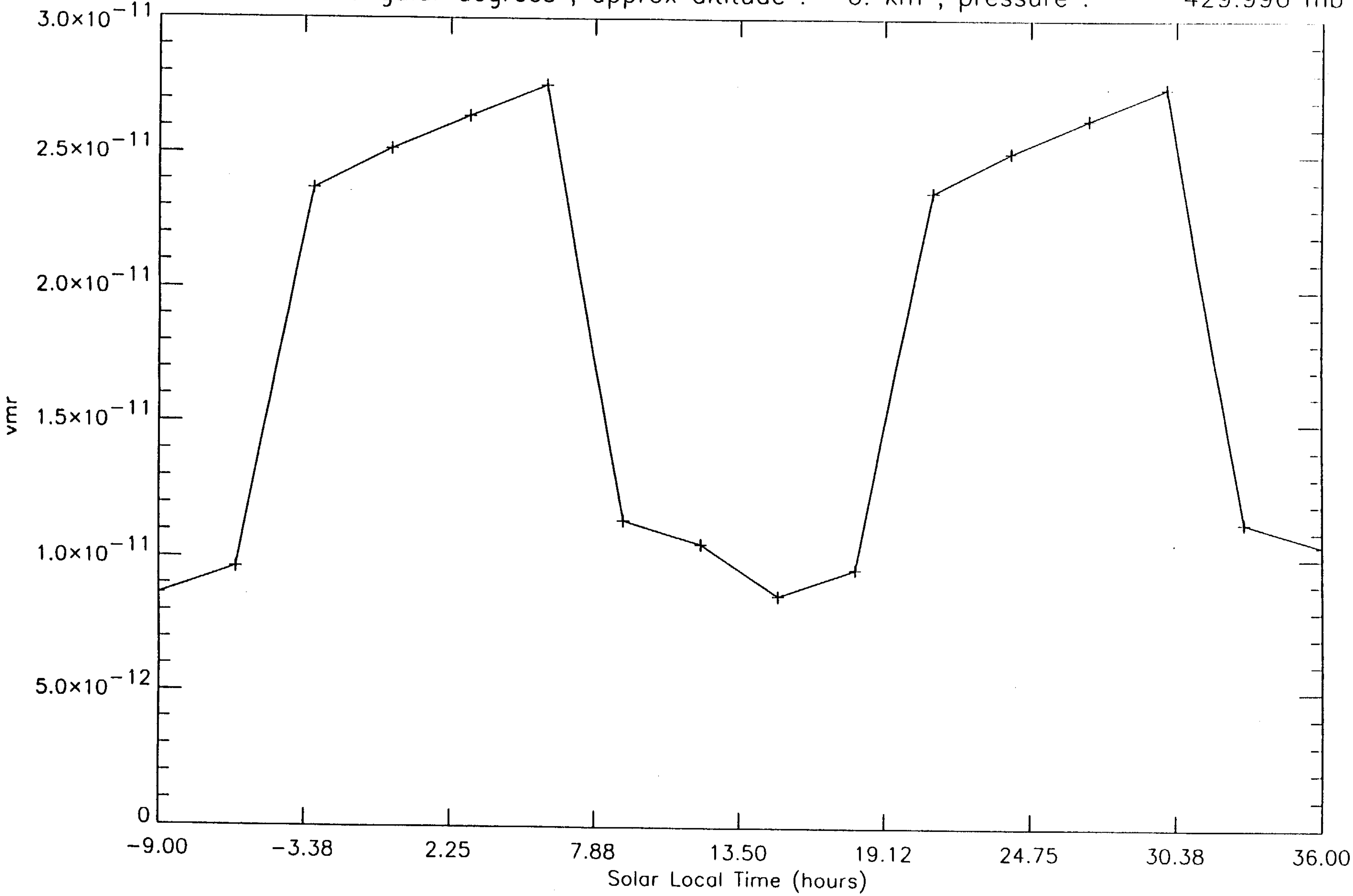
1..........O(1D)
2..........OH
3..........Cl
4..........O(3P)
5..........O_3
6..........HO_2
7..........NO_2
8..........NO
9..........Br
10..........N
11..........ClO
12..........BrO
13..........NO_3
14..........H

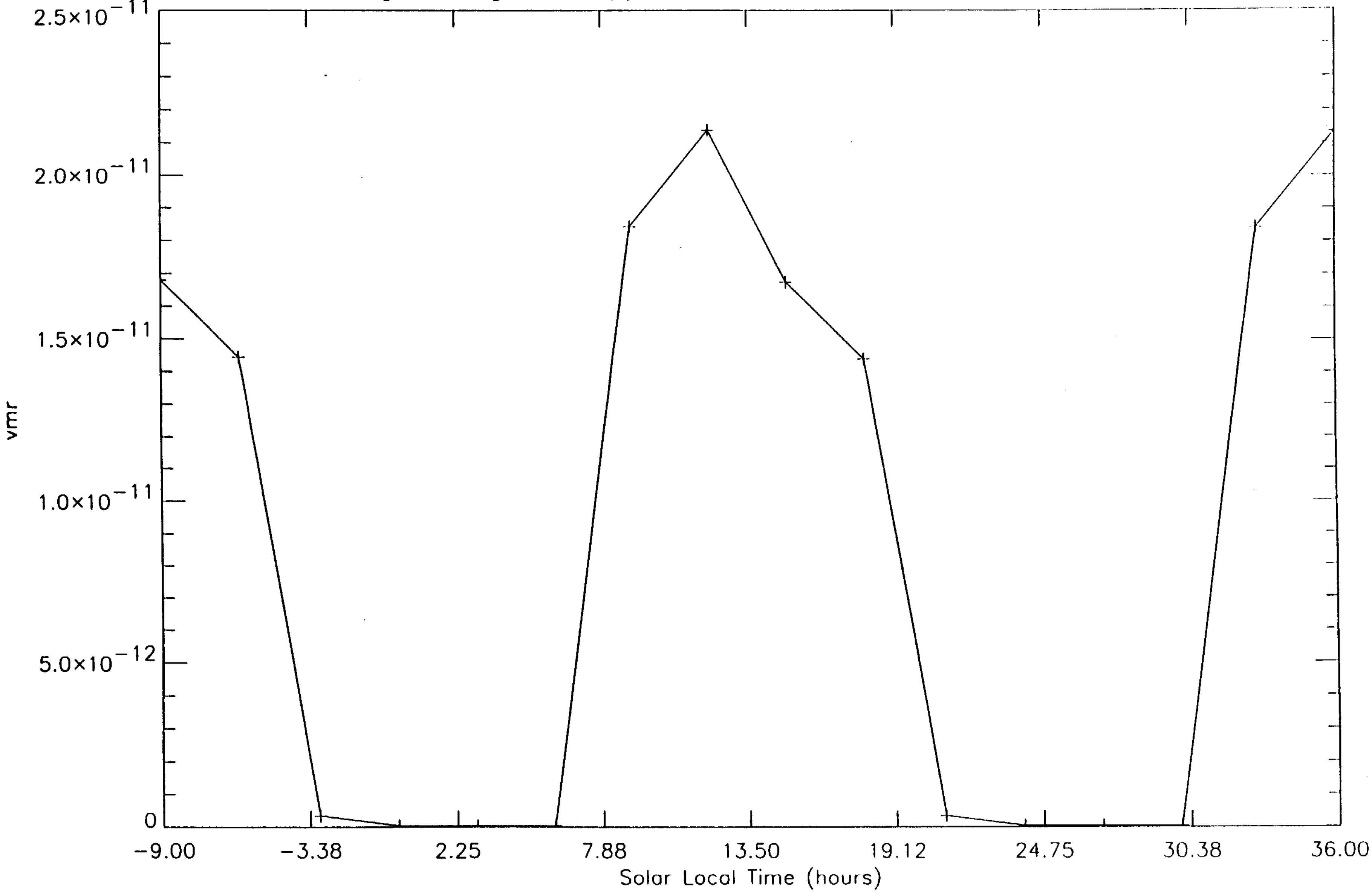


Contour from 0.00000 to 1.45000e-09 by 5.00000e-11

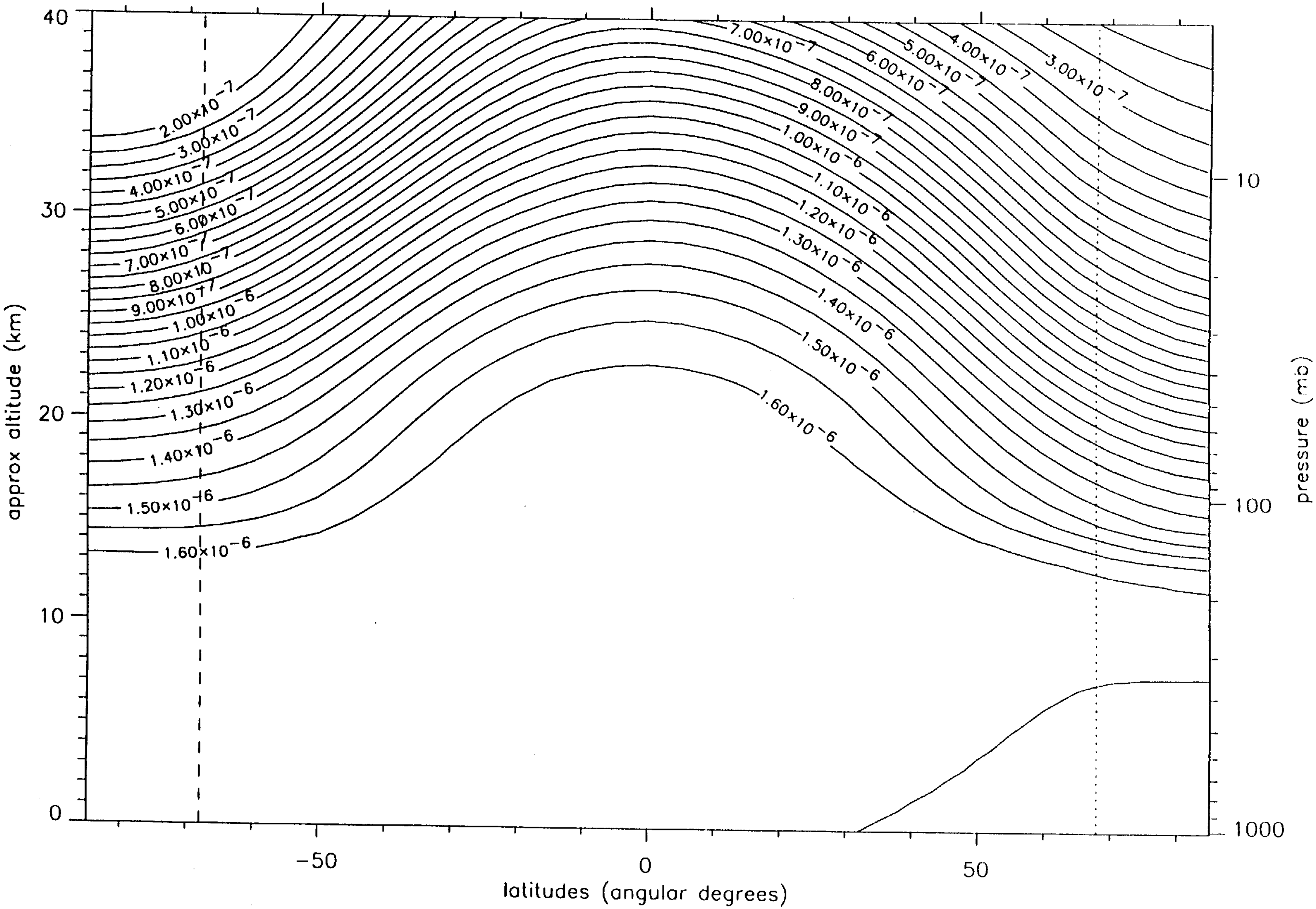

oh (vmr) Dec/28/1995 ; run_v5c ;
latitudes : 0. angular degrees ; approx altitude : 6. km ; pressure : 429.996 mb
4.0×10⁻¹³
3.0×10⁻¹³
2.0×10⁻¹³
1.0×10⁻¹³
0
vmr
-9.00
-3.38
2.25
7.88
13.50
19.12
24.75
30.38
36.00
Solar Local Time (hours)

no2 (vmr) Dec/28/1995 ; run_v5c ;
latitudes : 0. angular degrees ; approx altitude : 6. km ; pressure : 429.996 mb



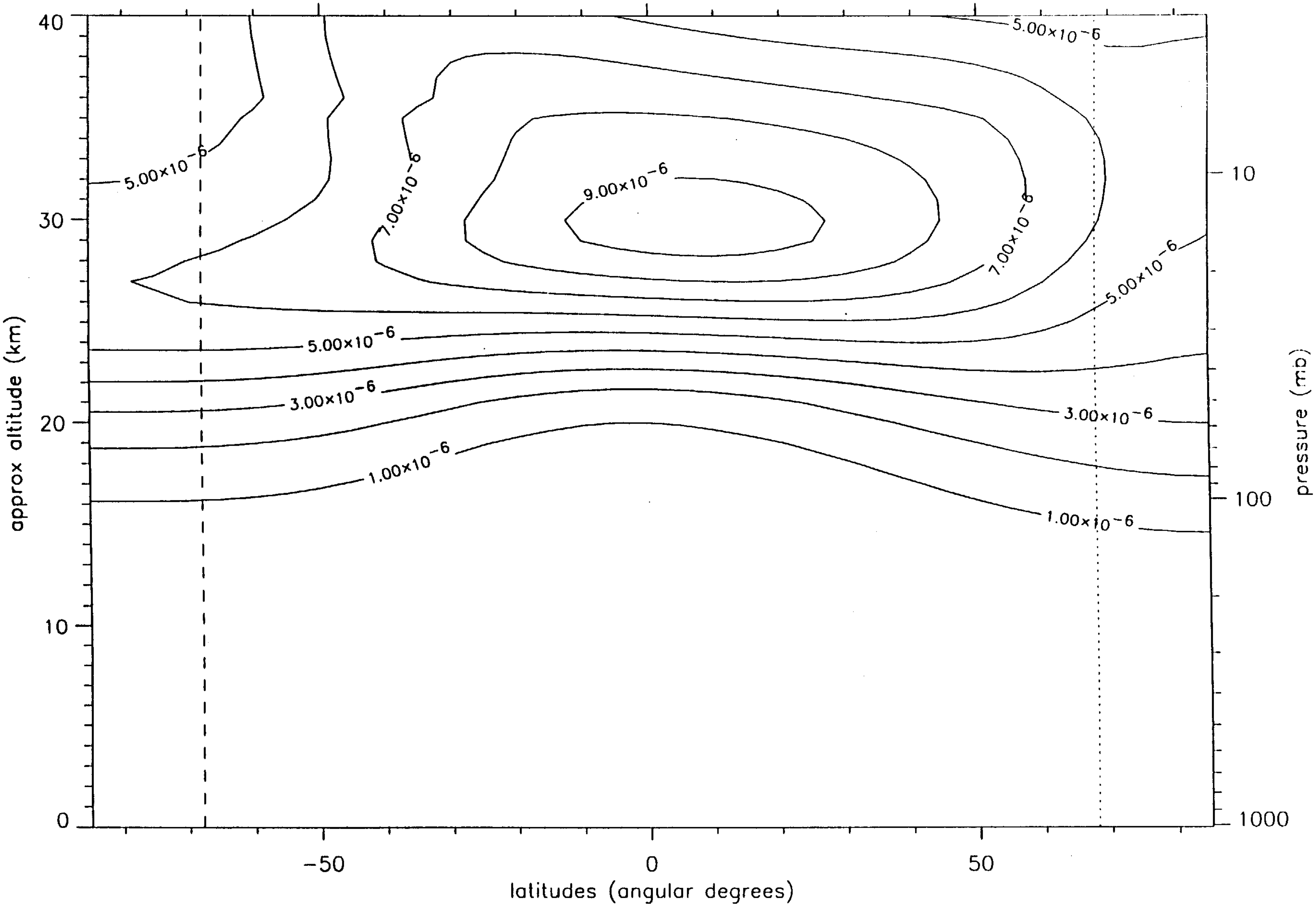


no (vmr) Dec/28/1995 ; run_v5c ;
latitudes : 0. angular degrees ; approx altitude : 6. km ; pressure : 429.996 mb

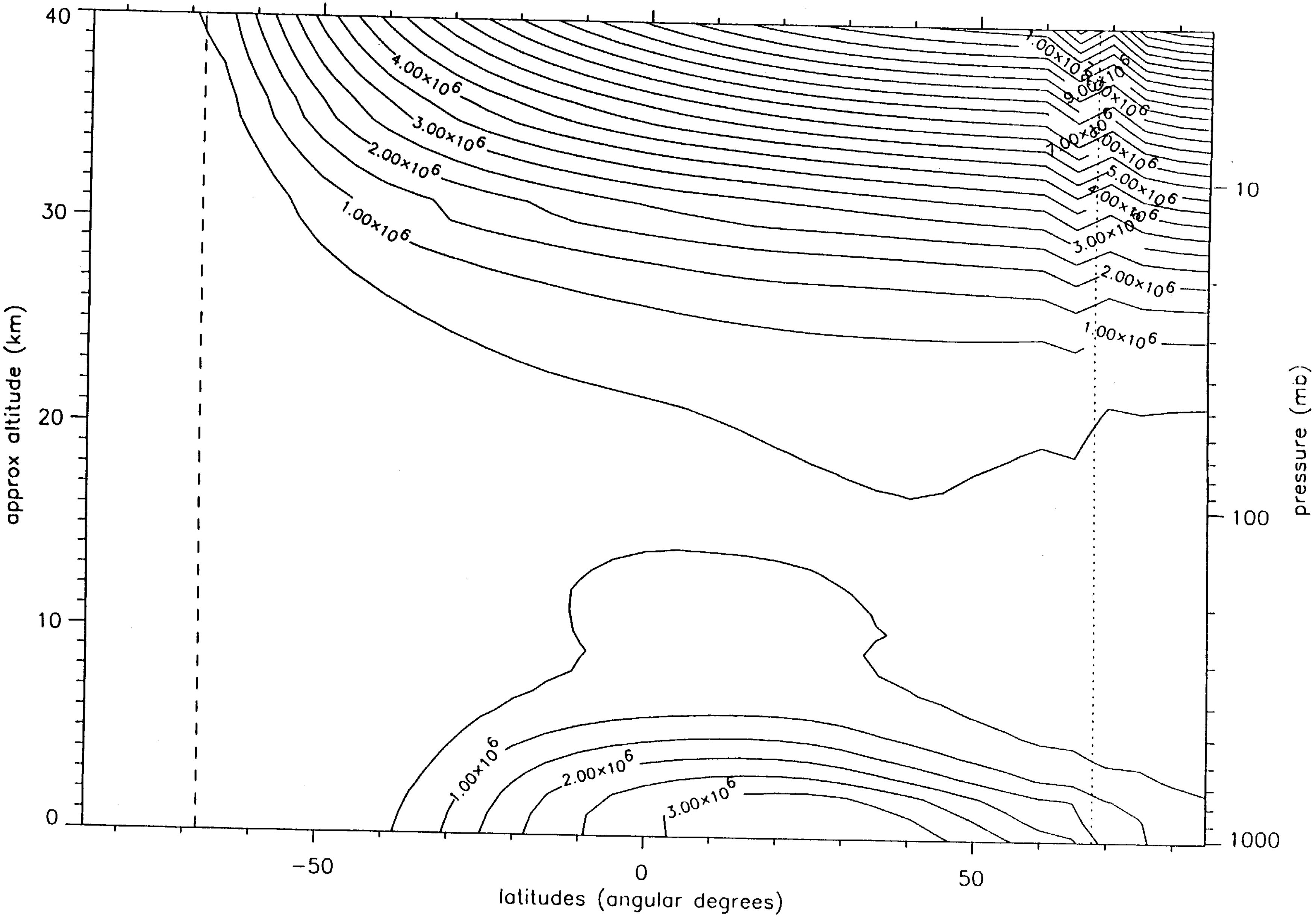


ch4 (vmr) Jul/11/1998 run_v5c diur. avg

Contour from 2.00000e-07 to 1.65000e-06 by 5.00000e-08 o3 (vmr) Jul/11/1998 run_v5c diur. avg

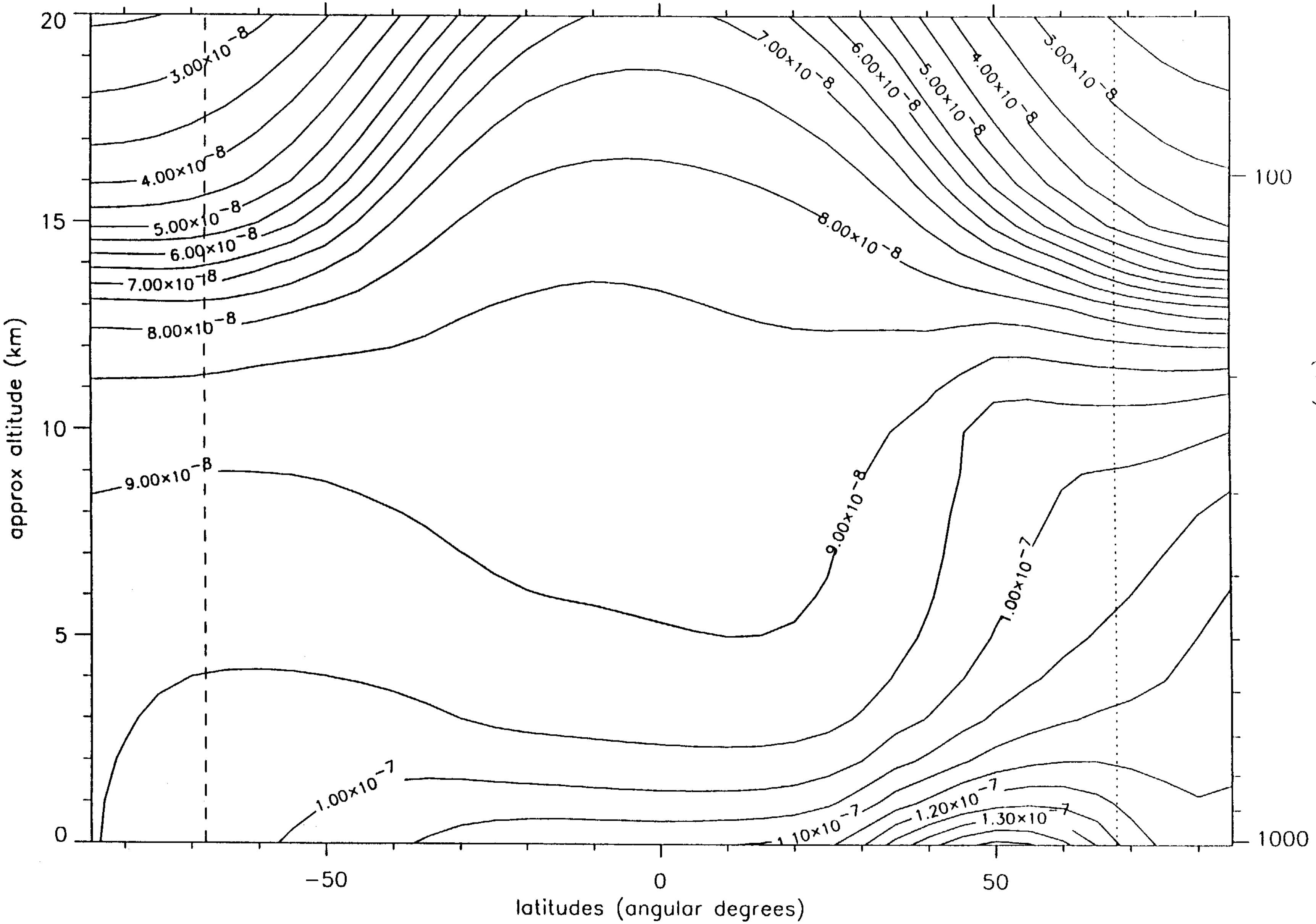


Contour from 1.00000e-06 to 9.49167e-06 by 1.00000e-06 oh (molec/cm3) Jul/11/1998 run_v5c diur. avg

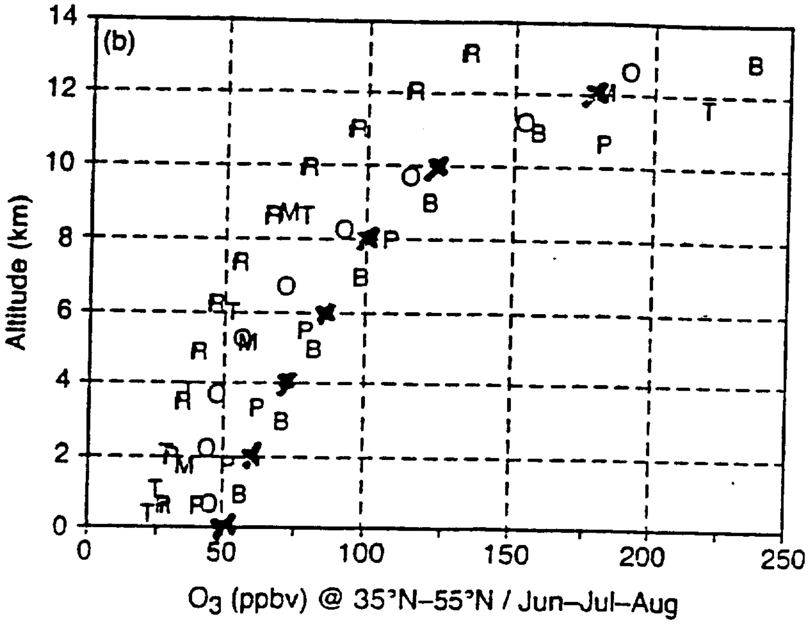


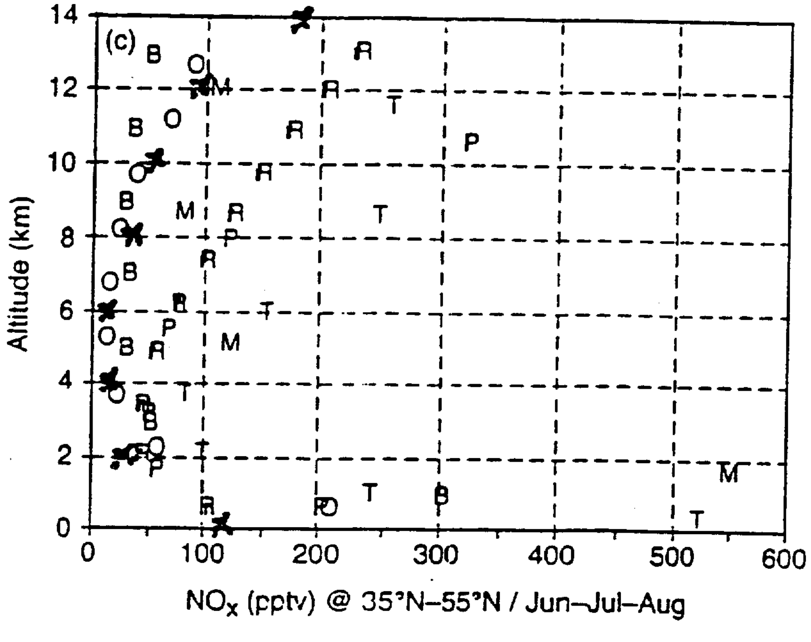
Contour from 0.00000 to 1.45000e+07 by 500000.

co (vmr) Jul/11/1998 run_v5c diur. avg



Contour from 0.00000 to 1.45000e-07 by 5.00000e-09


(b)
Altitude (km)
0
2
4
6
8
10
12
14
0
50
100
150
200
250
O$_3$ (ppbv) @ 35°N–55°N / Jun–Jul–Aug


(c)
Altitude (km)
0
2
4
6
8
10
12
14
0
100
200
300
400
500
600
NO$_x$ (pptv) @ 35°N–55°N / Jun–Jul–Aug

SOCRATES as a tool in studies of CH4 radiative and chemical effect

1. CH4 response time.

   a. Effect of CH4 perturbation on OH and its dependency on perturbation size under steady-state condition.

   b. Apply actual CH4 pulse to the model and obtain CH4 response time. Sensitivity of the response time to pulse size and pulse duration.

2. Calculation of CH4 GWP (exact formulation needs to be discussed):

   a. Changes in CH4 residence time.

   b. Production of stratospheric H2O

   c. Changes in tropospheric and stratospheric O3.

   d. Time dependent calculations?

3. Impact of NMHC on indirect CH4 GWP.

- Changes in tropospheric ozone.

Model experiments -

Model Run 1 (Control run) - 4 year steady-state run.

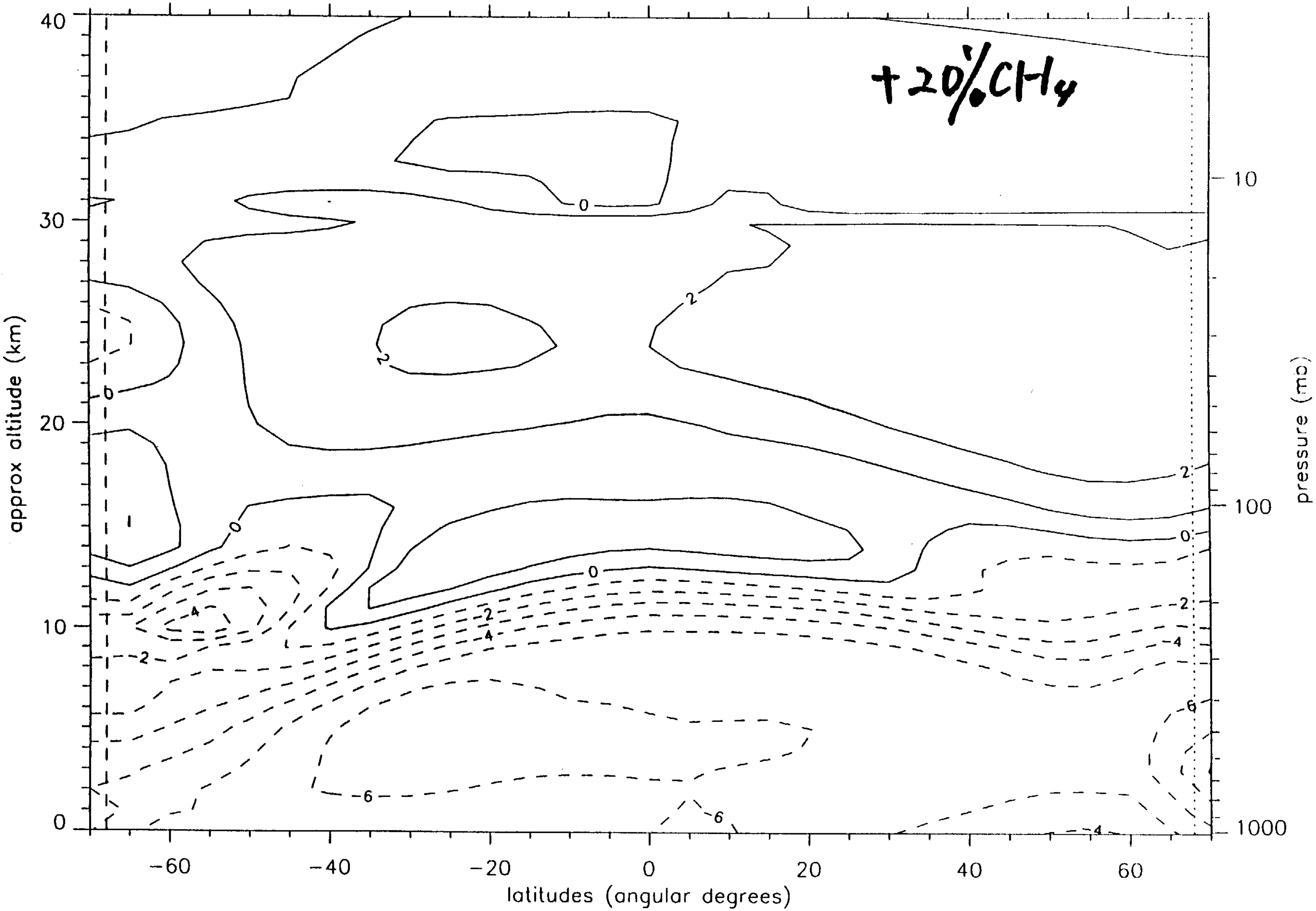
Model Run 2 (120% CH4 perturbation run) -

(CH4 results from control run) * 1.2

Model Run 3 (150% CH4 perturbation run) -

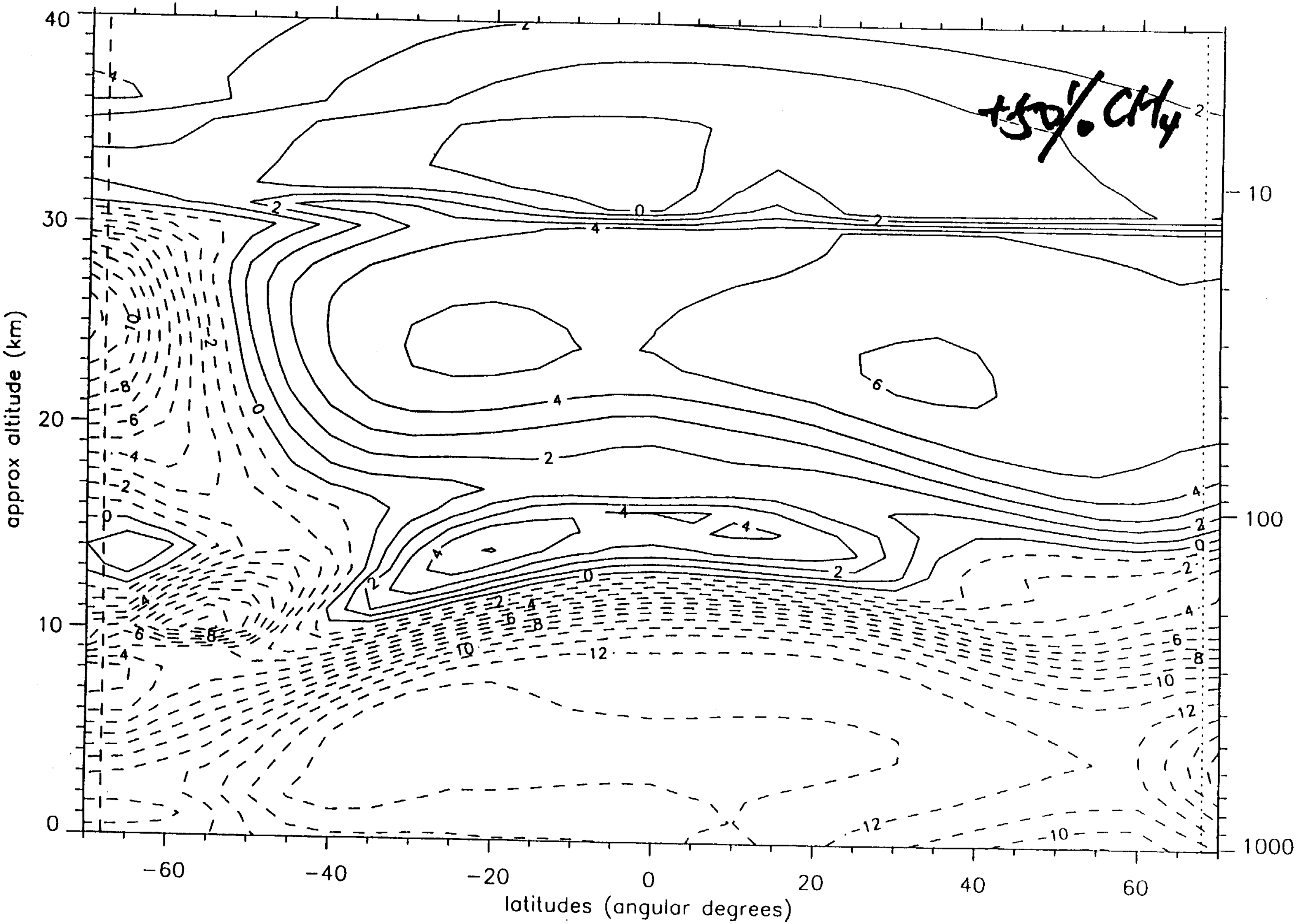
(CH4 results from control run) *1.5

oh relative difference (%) Jul/11/1998 run_v5c diur. avg



+20% CH4

Contour from −10.0000 to 19.0000 by 1.00000 oh relative difference (%) Jul/11/1998 run_v5c diur. avg



+50% CH_4

Contour from −16.0000 to 13.0000 by 1.00000

F Feedback factor: relative change (%) in the globally averaged OH amount for a 1% increase in CH_4 concentration.

AT/LT CH_4 adjustment time/ CH_4 lifetime

$= 1 / [1 + d(\ln OH)/d(\ln CH_4)]$

$= 1 / (1 + \boldsymbol{F})$

Run 2

20% increase in CH_4 -> 6 % decrease in OH

$\boldsymbol{F} = -6\%/20\% = -0.3$

AT/LT = 1.42

Run 3

50% increase in CH_4 -> 12% decrease in OH

$\boldsymbol{F} = -12\%/50\% = -0.24$

AT/LT = 1.31

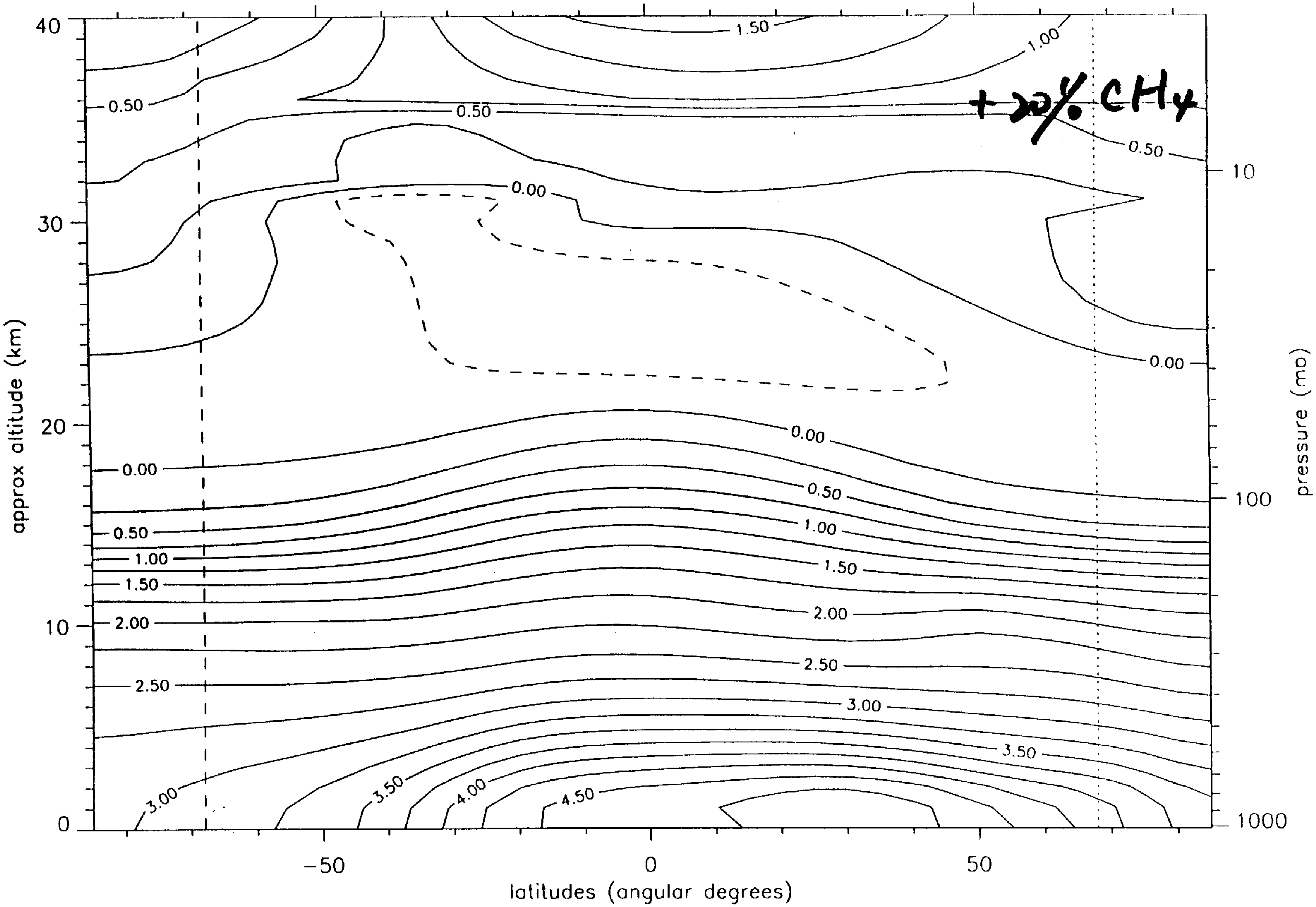
Table 2.9: Inferred CH_4 response time from the CH_4 perturbation simulations.

Model code	Feedback factor	Adjustment time/lifetime
B	-0.20%	1.29
M	-0.17%	1.23†
O	-0.35%	1.62
P	-0.22%	1.32
R	-0.26%	1.39
(R)	-0.18%	1.26†
T	-0.34%	1.61
NCAR	-0.3%	1.42

Note: Feedback factor = relative change (%) in the globally averaged CH_4 loss frequency (i.e., [OH]) for a +1% increase in CH_4 concentrations.

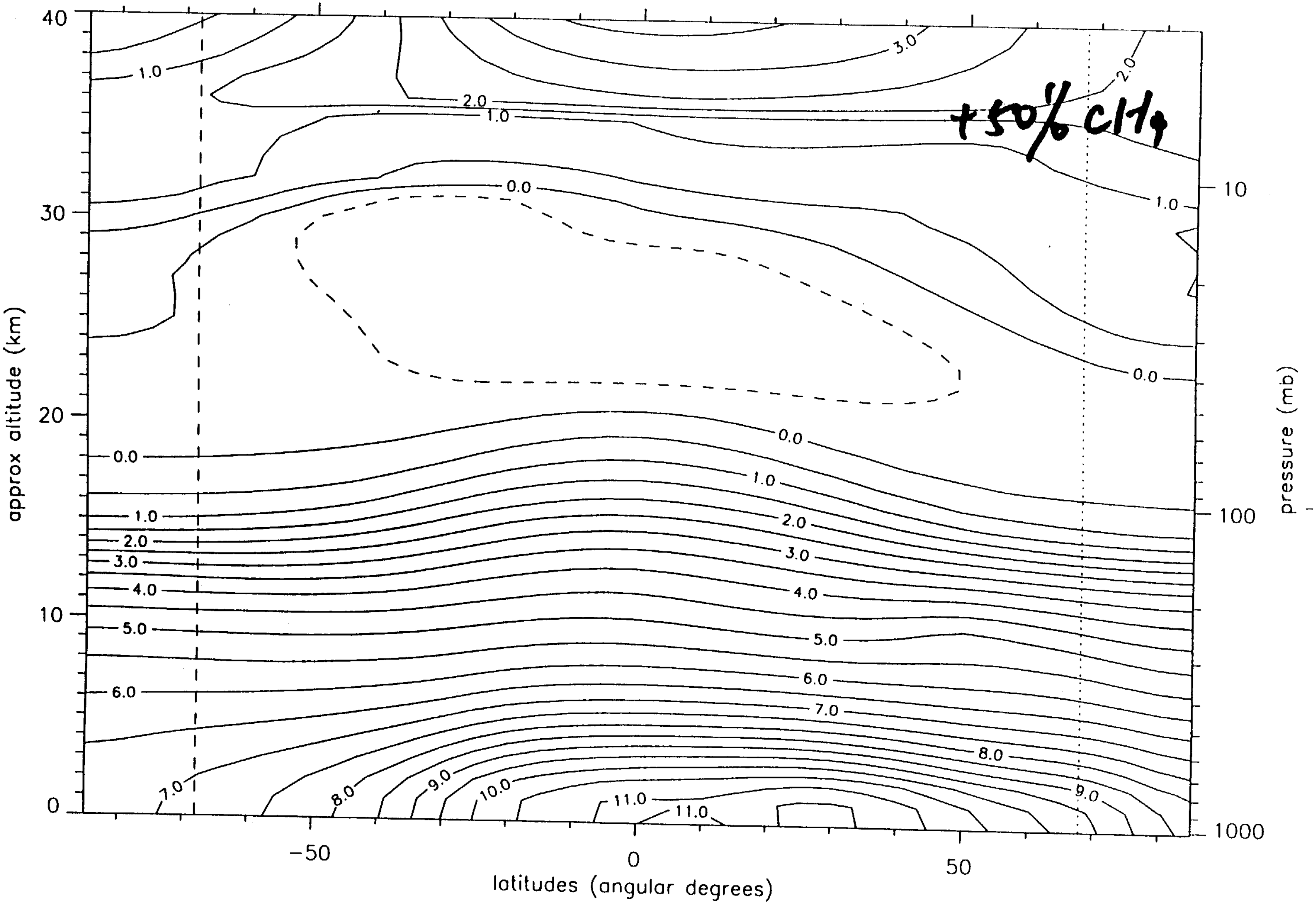
† These models use fixed CO concentrations and so underestimate this ratio.

o3 relative difference (%) Jul/11/1998 run_v5c diur. avg



+20% CH$_4$

Contour from -0.500000 to 6.75000 by 0.250000 o3 relative difference (%) Jul/11/1998 run_v5c diur. avg



+50% CH4

Contour from -1.00000 to 13.5000 by 0.500000

Sasha Madronich

NCAR

30-90°S

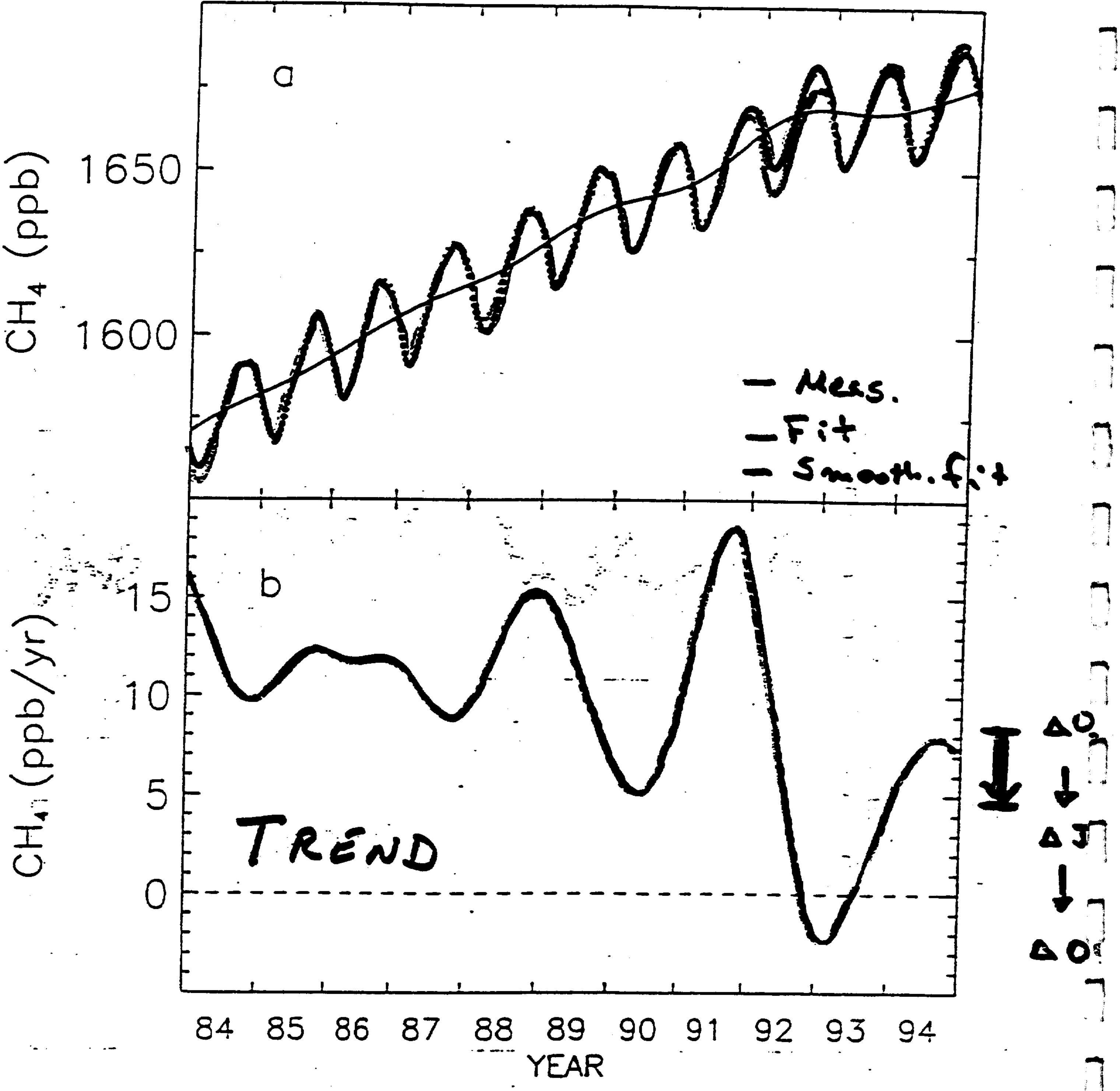


Figure 1

E.J. Dlugokencky, E.G. Dutton, P.C. Novelli, P.P. Tans, K.A. Masarie
NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado

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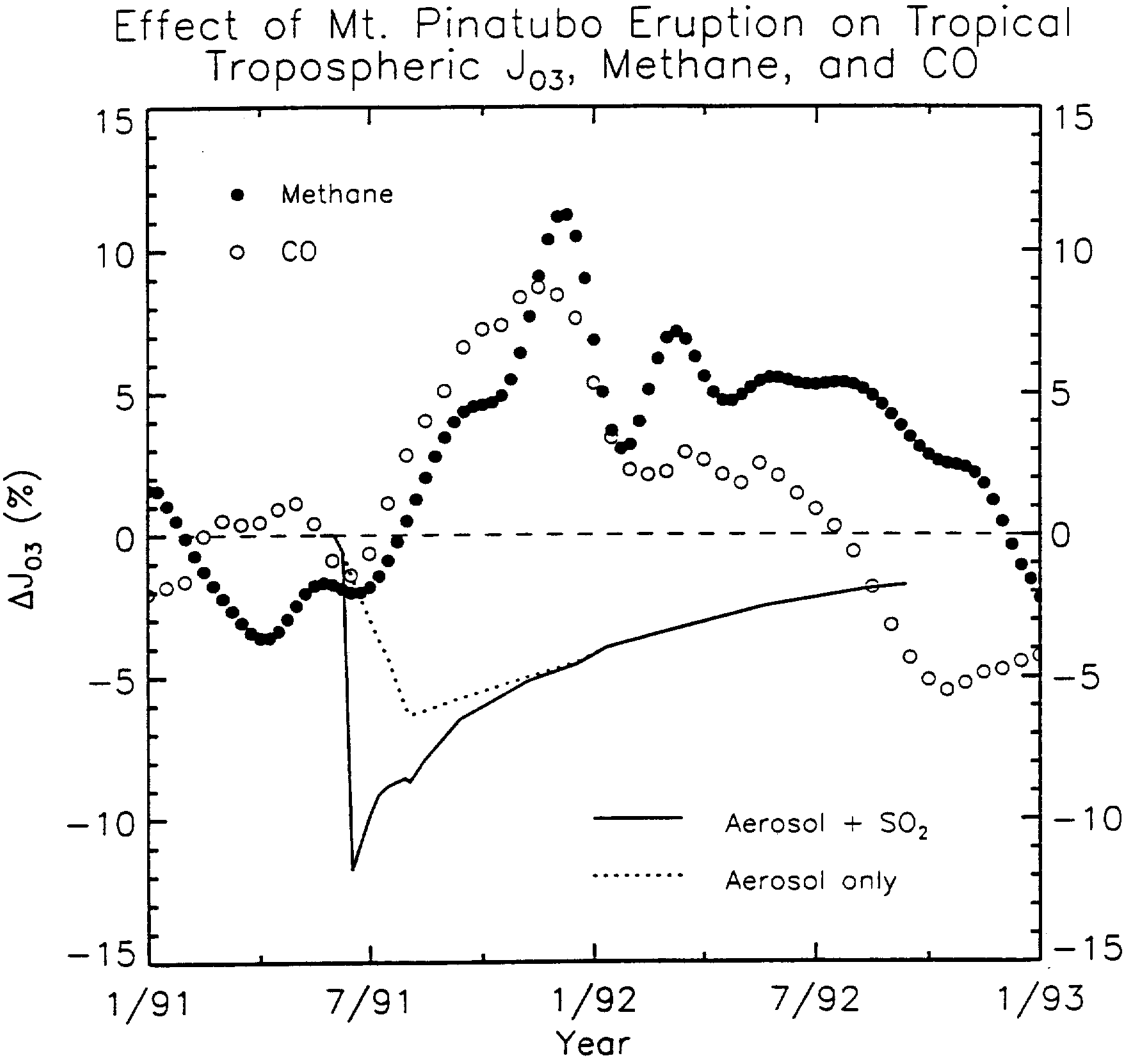
National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, Colorado



Dlugokencky, Dutton, Novelli, Tans, Masarie, Lantz, and Madronich, 1996

EXPLORATORY STUDIES

- Response of tropospheric O_3 to CO (and RH) increases, at low NOx
  - increase [O_3] if HO_x loss mostly from HO_2
  - decrease [O_3] if HO_x loss mostly from HO_2
- Tropospheric chemical oscillations
  - discover and describe
  - robust (CO, CH_4, isoprene)
  - identify two-variable oscillating kernel
  - analytic derivation of oscillation period
  - chaotic behavior dampened by $HO_2 + HO_2$
- Relative role of CH4 and NMHCs
  - large pool of oxygenated and nitrogenated species, Cy
  - long lifetime, long-range transport
- Scavenging of oxygenated organics by PBL aerosols
  - major loss for Cy and NOy?
  - less O3 production?

Table 1: Solutions for current state:

Species	Sensitivity (%/%)				
	F_{CH4}	F_{CO}	F_{NO}	F_{O3}	F_{H2}
CH_4	1.33	0.26	-0.49	-0.01	0.03
CO	0.53	0.97	-0.46	-0.01	0.03
H_2	0.33	0.07	-0.13	0.00	0.76
O_3	0.30	0.15	0.19	0.07	0.02
NO	-0.02	0.09	0.41	-0.07	0.01
NO_2	0.03	0.24	0.55	-0.01	0.02
HNO_3	-0.01	-0.01	1.02	0.00	0.00
H_2O_2	0.58	0.54	-0.29	0.03	0.06
CH_3OOH	1.42	0.29	-0.71	0.06	0.03
CH_2O	1.07	0.06	-0.10	-0.01	0.01
CH_3OH	1.96	-0.20	-0.67	0.11	-0.02
OH	-0.35	-0.28	0.53	0.01	-0.03
HO_2	0.23	0.22	-0.06	0.02	0.02
CH_3OO	0.92	-0.14	-0.25	0.06	-0.02

Response of tropospheric O_3 to CO (and RH) increases, at low NO_x

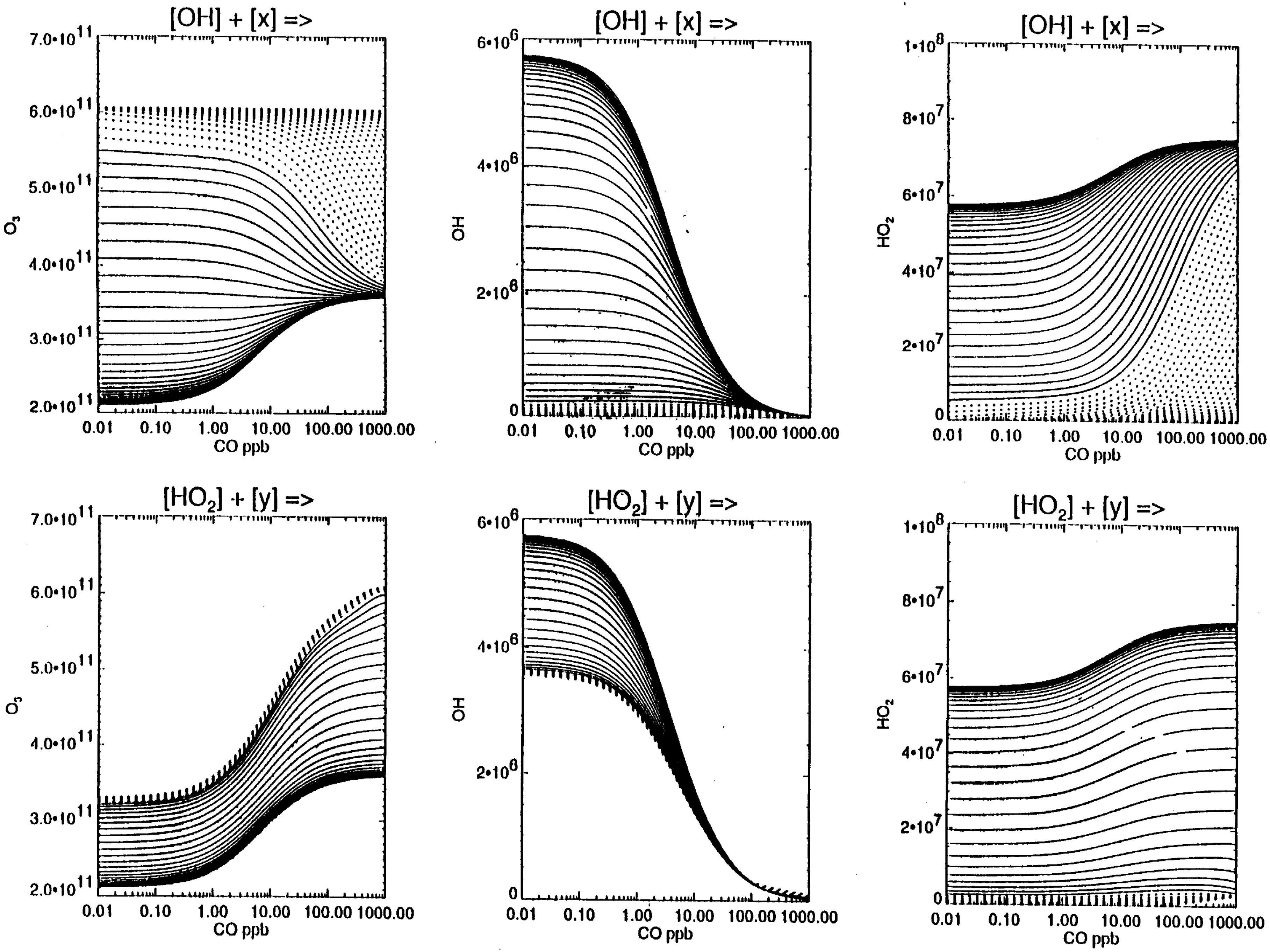
Crutzen, 1987:

$CO + OH \rightarrow HO_2 + CO_2$ $(-O_2)$
$HO_2 + O_3 \rightarrow OH + 2\,O_2$

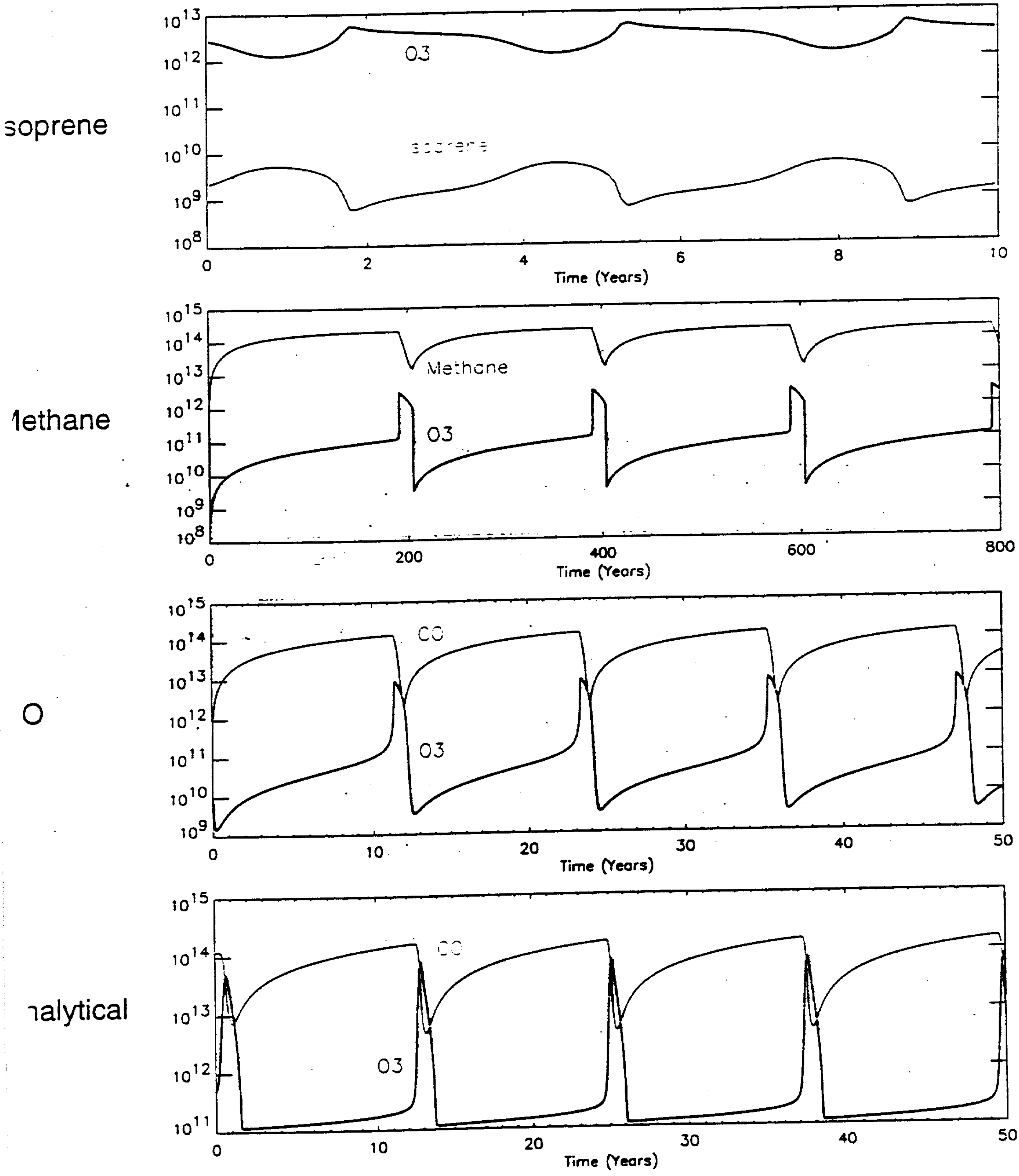
NET: $CO + O_3 \rightarrow CO_2 + O_2$

But this neglects many other important reactions, e.g.:

$OH + O_3 \rightarrow HO_2 + O_2$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$


[OH] + [x] =>
O_3
7.0•10^{11}
6.0•10^{11}
5.0•10^{11}
4.0•10^{11}
3.0•10^{11}
2.0•10^{11}
0.01
0.10
1.00
10.00
100.00
1000.00
CO ppb
[OH] + [x] =>
OH
6•10^{6}
4•10^{6}
2•10^{6}
0
0.01
0.10
1.00
10.00
100.00
1000.00
CO ppb
[OH] + [x] =>
HO_2
1•10^{8}
8•10^{7}
6•10^{7}
4•10^{7}
2•10^{7}
0
0.01
0.10
1.00
10.00
100.00
1000.00
CO ppb
[HO_2] + [y] =>
O_3
7.0•10^{11}
6.0•10^{11}
5.0•10^{11}
4.0•10^{11}
3.0•10^{11}
2.0•10^{11}
0.01
0.10
1.00
10.00
100.00
1000.00
CO ppb
[HO_2] + [y] =>
OH
6•10^{6}
4•10^{6}
2•10^{6}
0
0.01
0.10
1.00
10.00
100.00
1000.00
CO ppb
[HO_2] + [y] =>
HO_2
1•10^{8}
8•10^{7}
6•10^{7}
4•10^{7}
2•10^{7}
0
0.01
0.10
1.00
10.00
100.00
1000.00
CO ppb

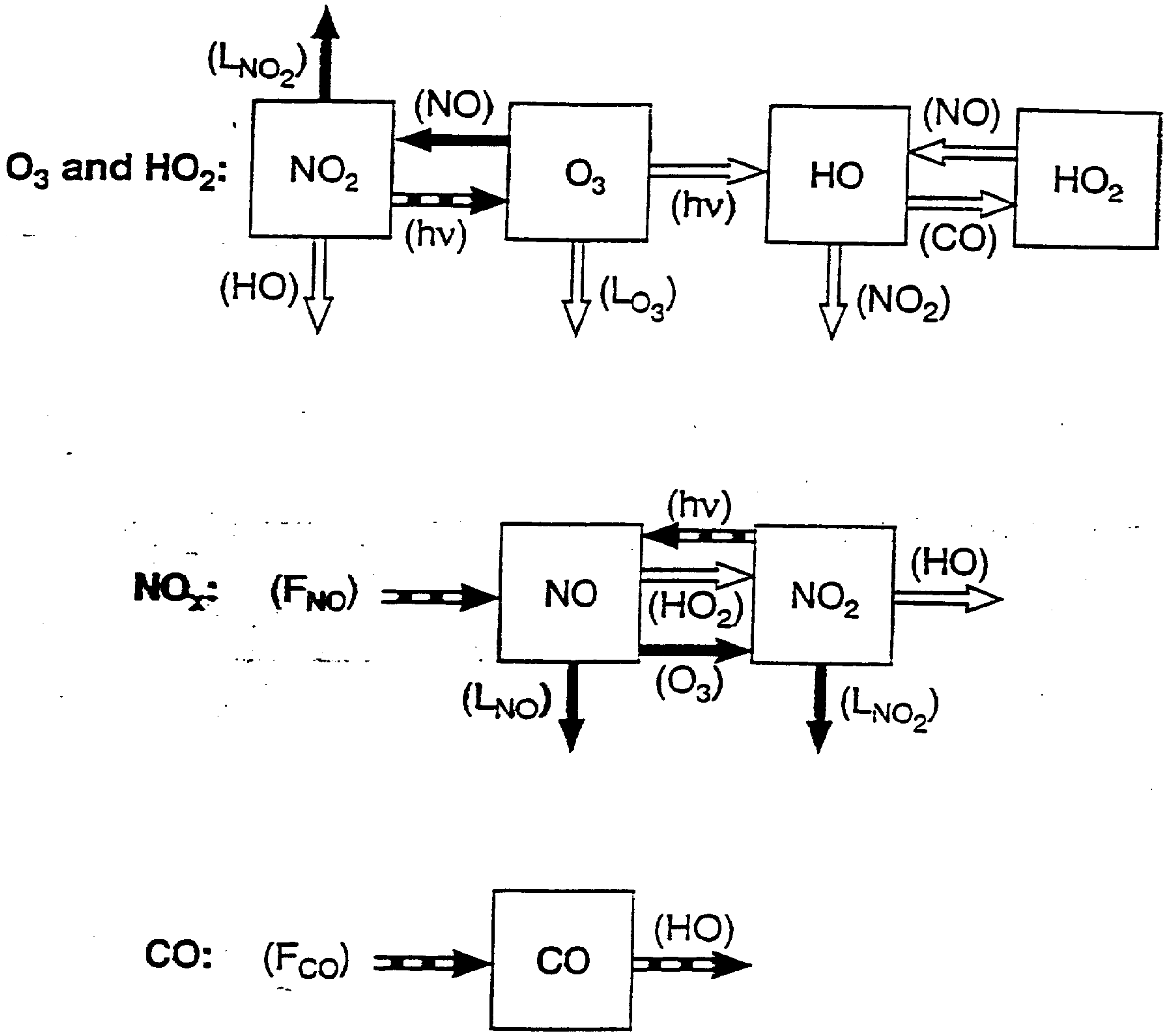
Different Oscillating Chemical Mechanisms Numerical Results and Analytical Solution



P.Hess, S.Madronich, 1995

REACTION NETWORK N_2

Reaction Pathways for O_3 and HO_x, NO_x, and CO



KEY:

⇒ Important Reaction Pathway for P_1

➡ Important Reaction Pathway for P_2

▭➡ Important Reaction Pathway for P_1 and P_2

Fig 1

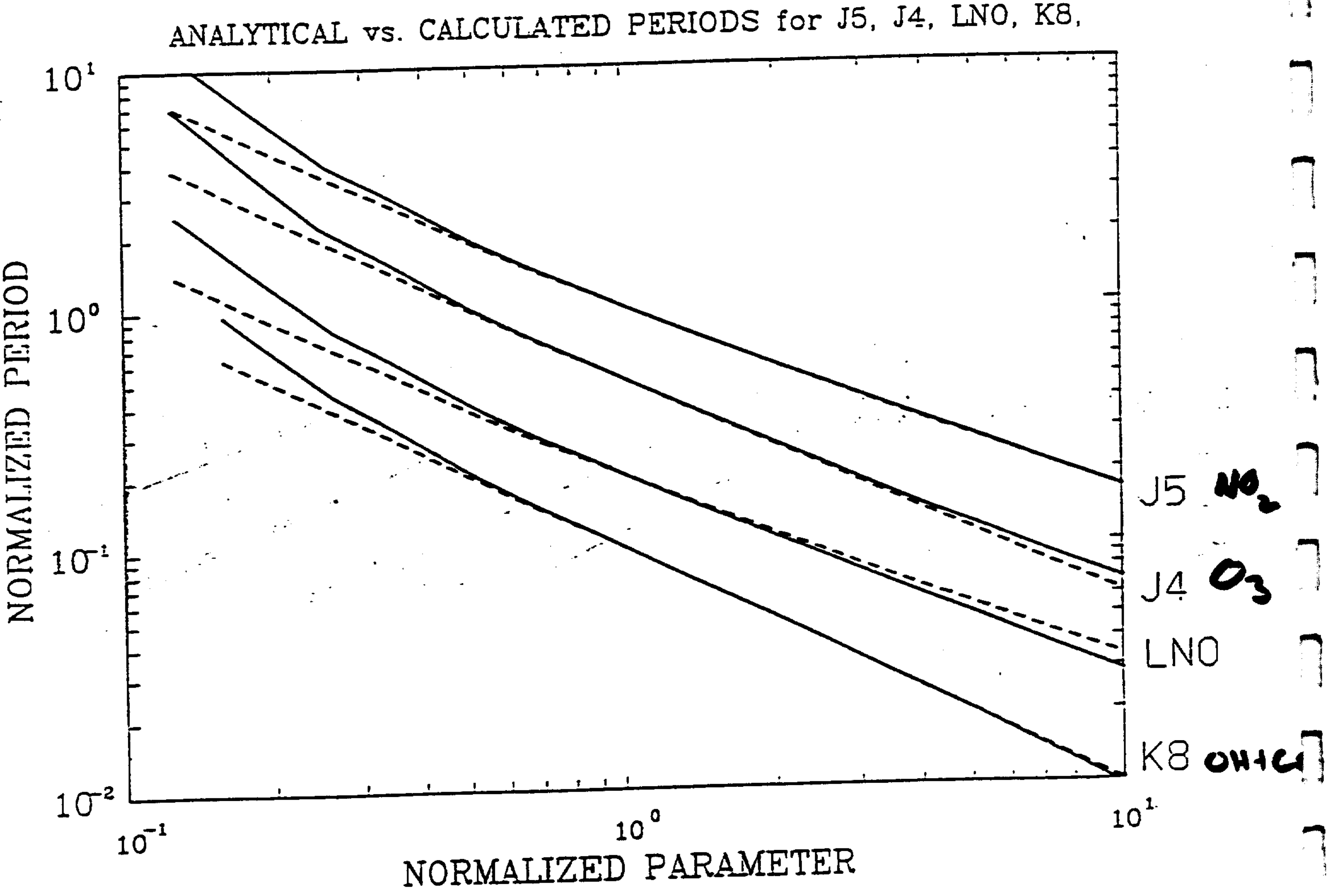

ANALYTICAL vs. CALCULATED PERIODS for J5, J4, LNO, K8.
NORMALIZED PERIOD
NORMALIZED PARAMETER
10^1
10^0
10^{-1}
10^{-2}
10^{-1}
10^0
10^1
J5 NO_2
J4 O_3
LNO
K8 OH+Cl

Fig 8a

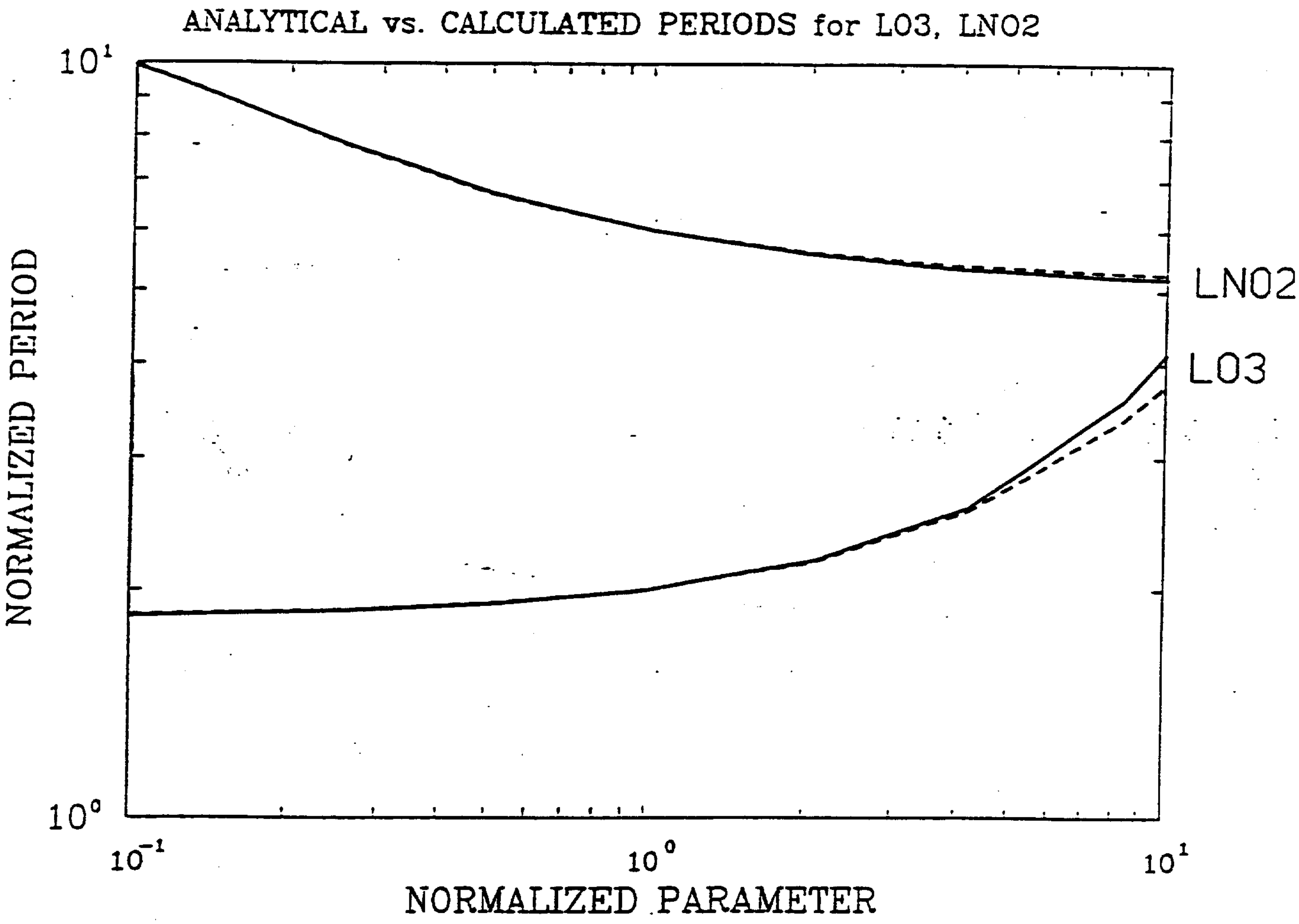
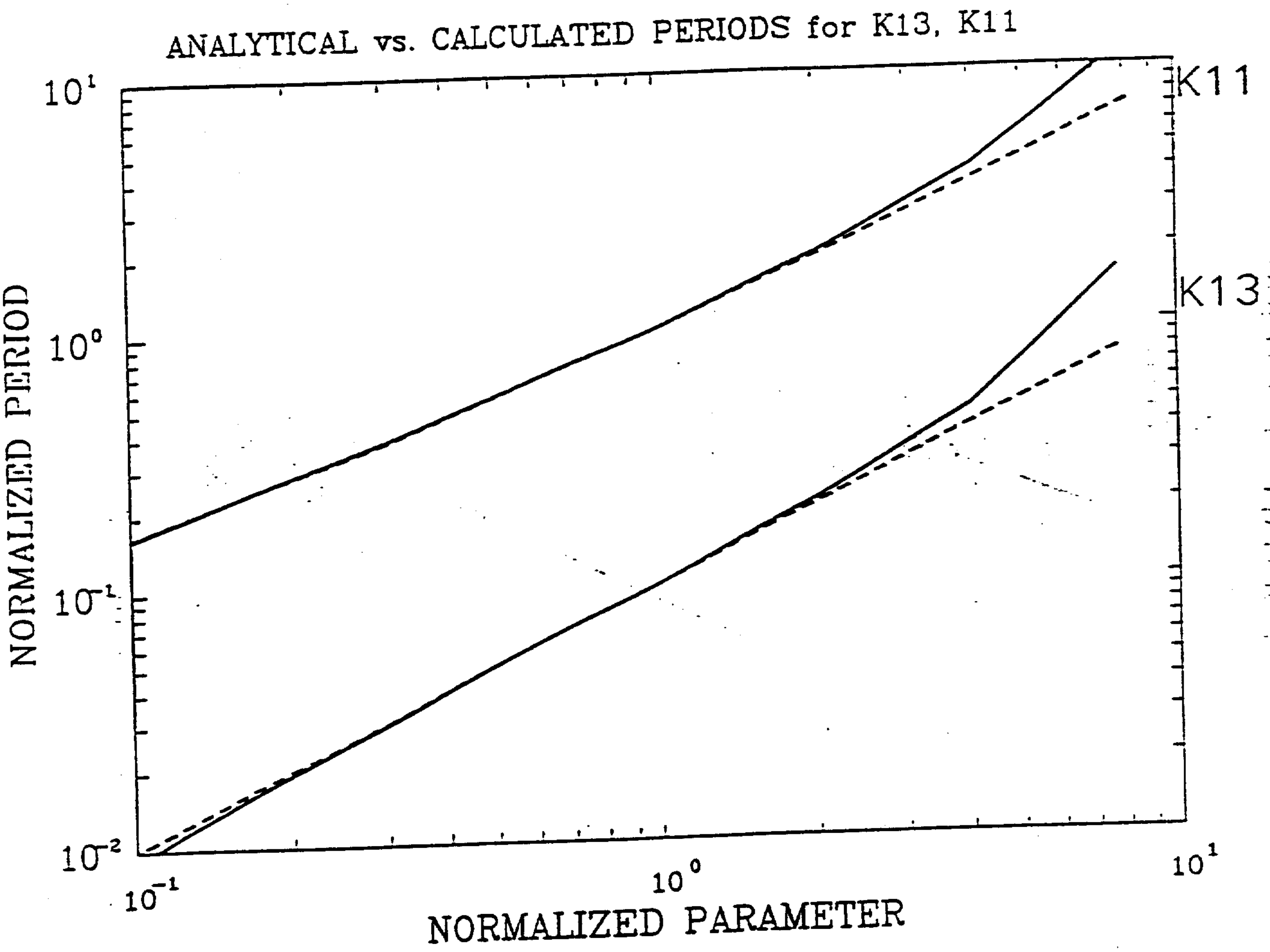
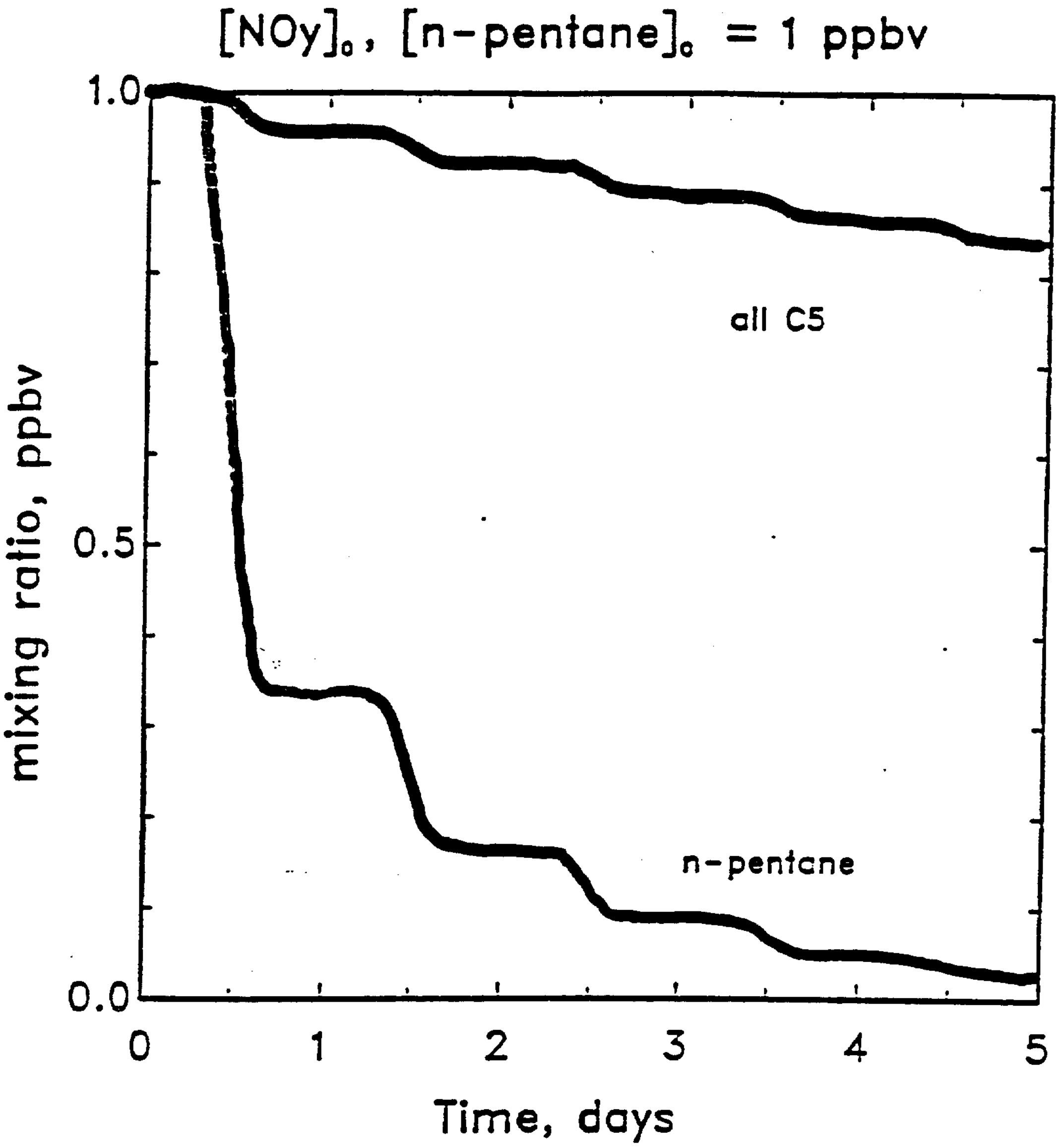

ANALYTICAL vs. CALCULATED PERIODS for L03, LN02
10^1
10^0
NORMALIZED PERIOD
10^-1
10^0
10^1
NORMALIZED PARAMETER
LN02
L03

Fig 8


ANALYTICAL vs. CALCULATED PERIODS for K13, K11
K11
K13
NORMALIZED PERIOD
10^1
10^0
10^{-1}
10^{-2}
10^{-1}
10^0
10^1
NORMALIZED PARAMETER

Fig

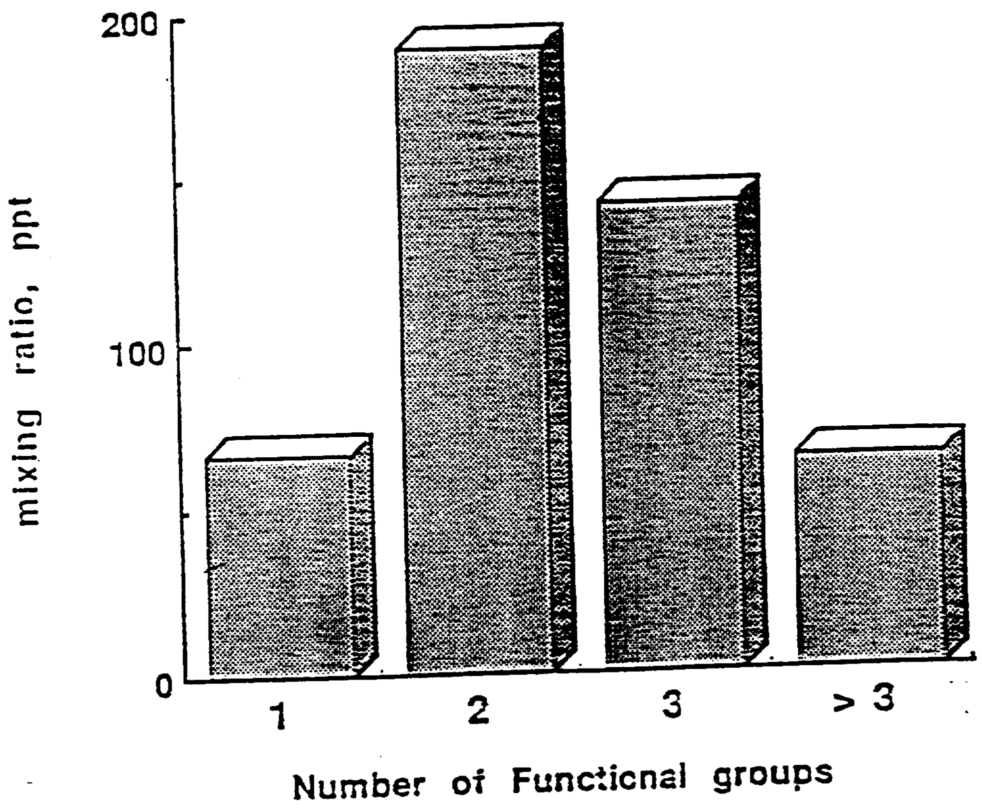


1. Box model simulation of n-pentane photodegradation. Initial conditions are $[NO_2]_0$ = 1 ppbv, $[\text{n-pentane}]_0$ = 1 ppbv. Dashed line gives concentration of n-pentane, solid line is concentration of all five-carbon species including remaining n-pentane and intermediate organic compounds.

Table 3: A Few Intermediate, Partly Oxygenated Organics from the Oxidation of Hydrocarbons

Aldehydes:	CH_2O	formaldehyde
	CH_3CHO	acetaldehyde
	CH_3CH_2CHO	propionaldehyde
Ketones:	CH_3COCH_3	acetone
	$CH_3COCH_2CH_3$	methyl ethyl ketone
	$CH_3COCH{=}CH_2$	methyl vinyl ketone
Alcohols:	CH_3OH	methanol
	CH_3CH_2OH	ethanol
Hydroperoxides:	CH_3OOH	methyl hydroperoxide
	CH_3CH_2OOH	ethyl hydroperoxide
Organic acids:	$HCOOH$	formic acid
	CH_3COOH	acetic acid
	$CH_3CO(OOH)$	peracetic acid
Organic nitrates:	$CH_3(ONO_2)$	methyl nitrate
	$CH_3CO(OONO_2)$	peroxy acetyl nitrate (PAN)

Organic nitrates, [NOy]o = 1 ppbv [NMHC]o = 10 ppbv

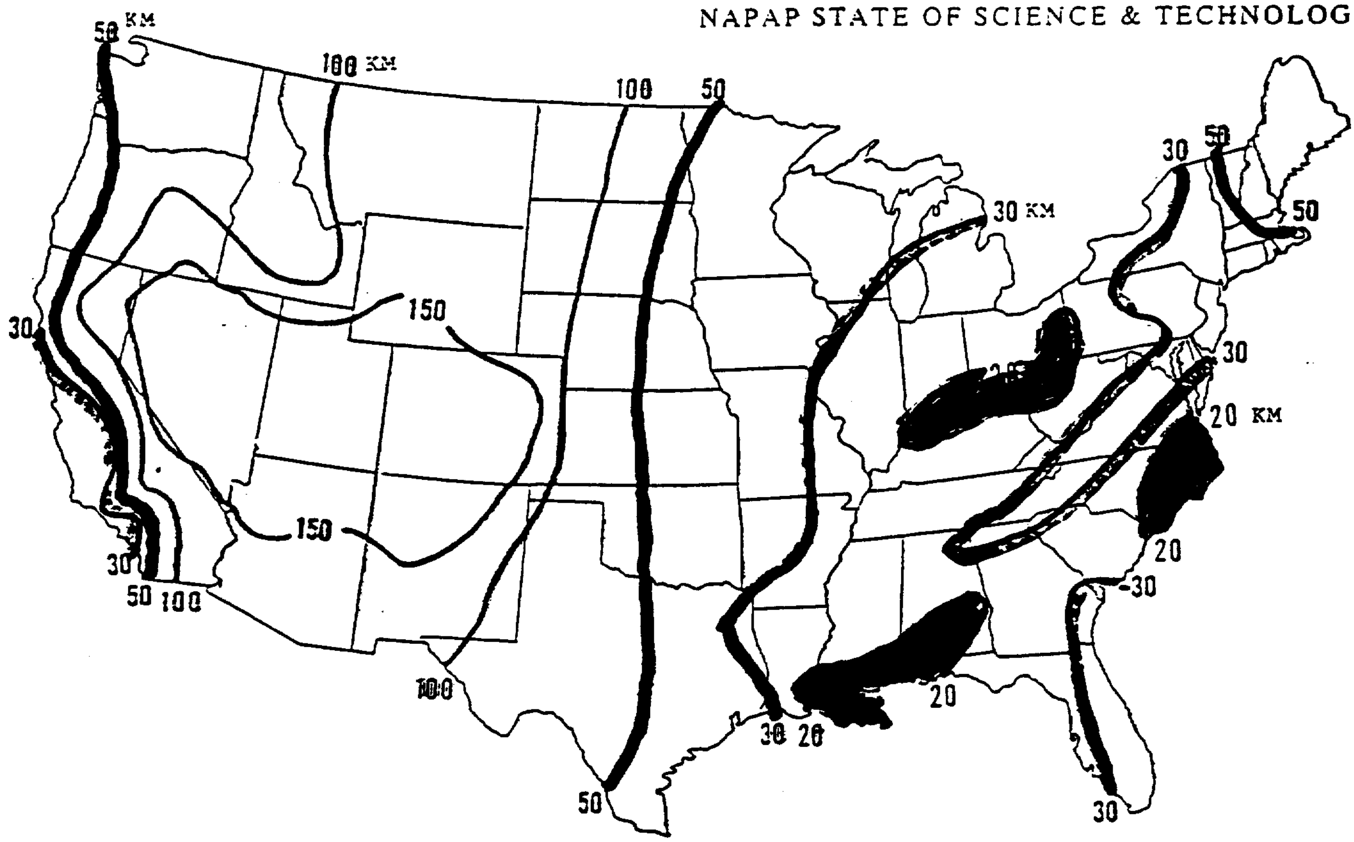


$CH_2(ONO_2)CHO$

$CH_3COCH_2(ONO_2)$

$CH_3COCH(ONO_2)CH_2(OH)$

$CH_2{=}C(CH_3)CH((OOH)CH_2(ONO_2)$



$$\text{VISIBLE RANGE} = \frac{3.9}{\beta_{650}} \text{ km}$$

AEROSOLS AS SCAVANGERS OF OXYGENATED ORGANICS ?

Collision rate = $n \gamma v S / 4$

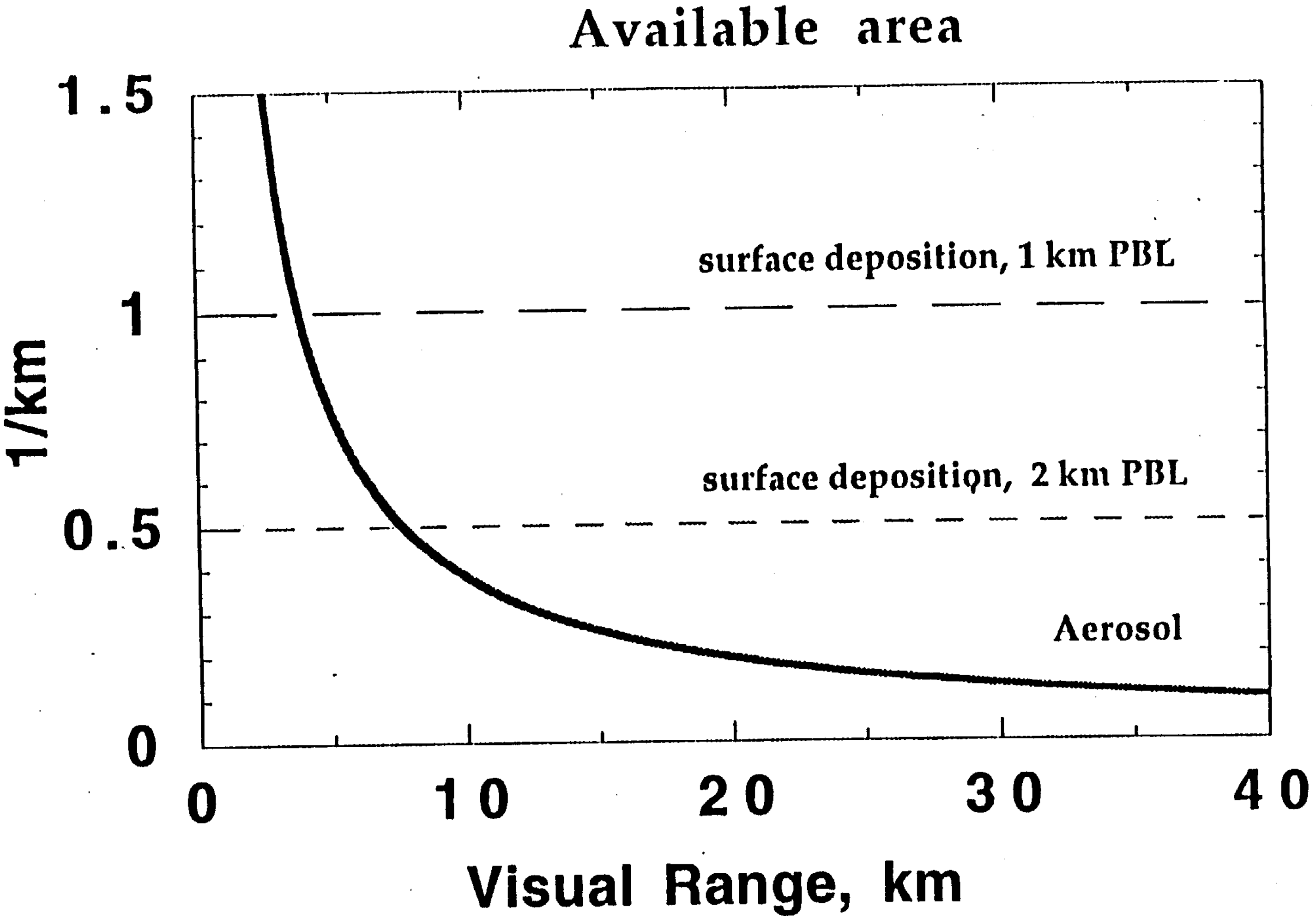
n = concentration of gas molecules
γ = sticking coefficient
v = molec. speed ~ 3×10^4 cm s^{-1}
S = aerosol specific surface area ~ β
β = aerosol optical depth, km^{-1} ~ 3.9 / (visible range)

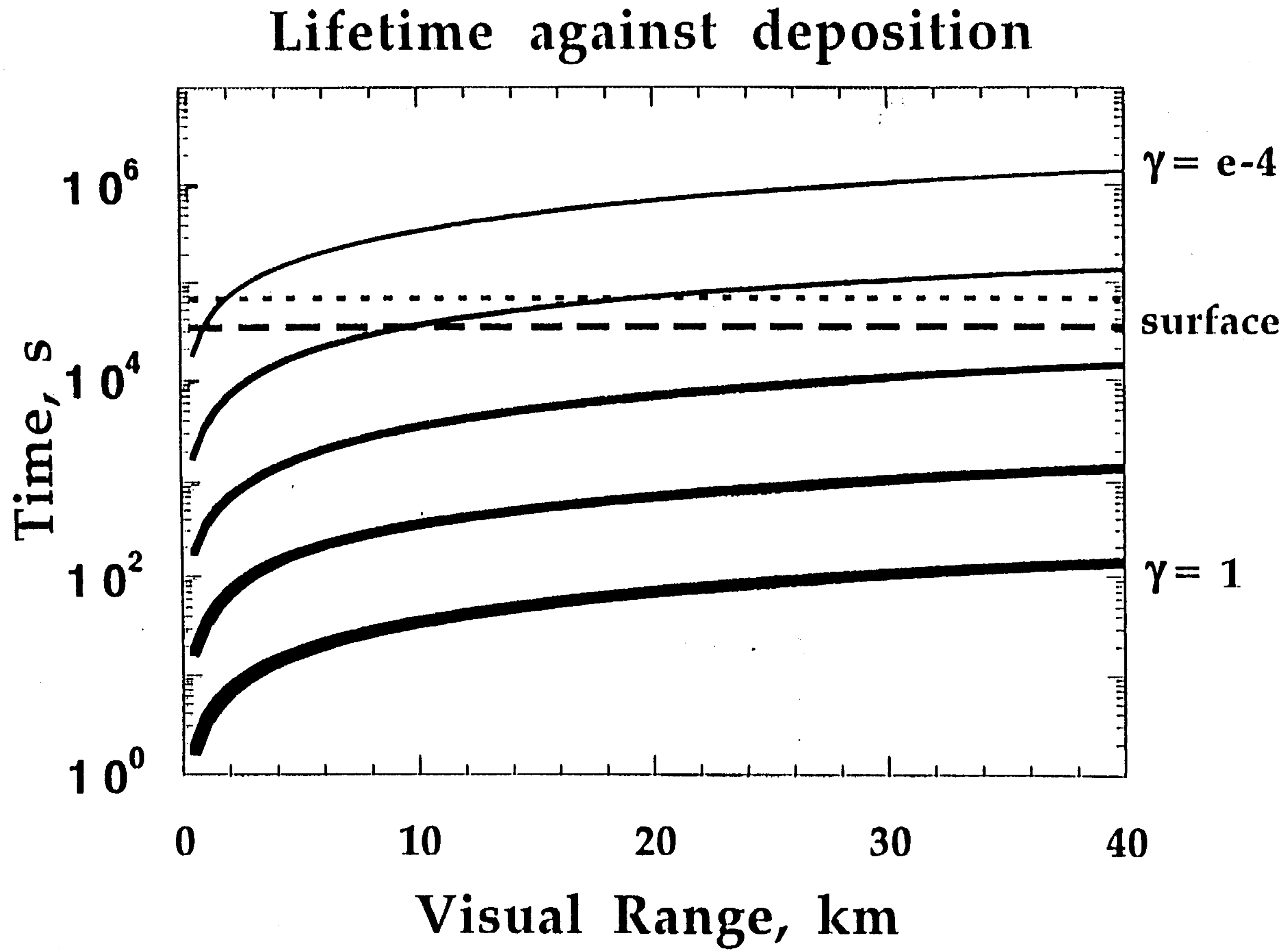
Time for molecule-aerosol collision ~ 13 sec / (β γ)

For visible range = 25 km, β ~ 0.15 km^{-1}

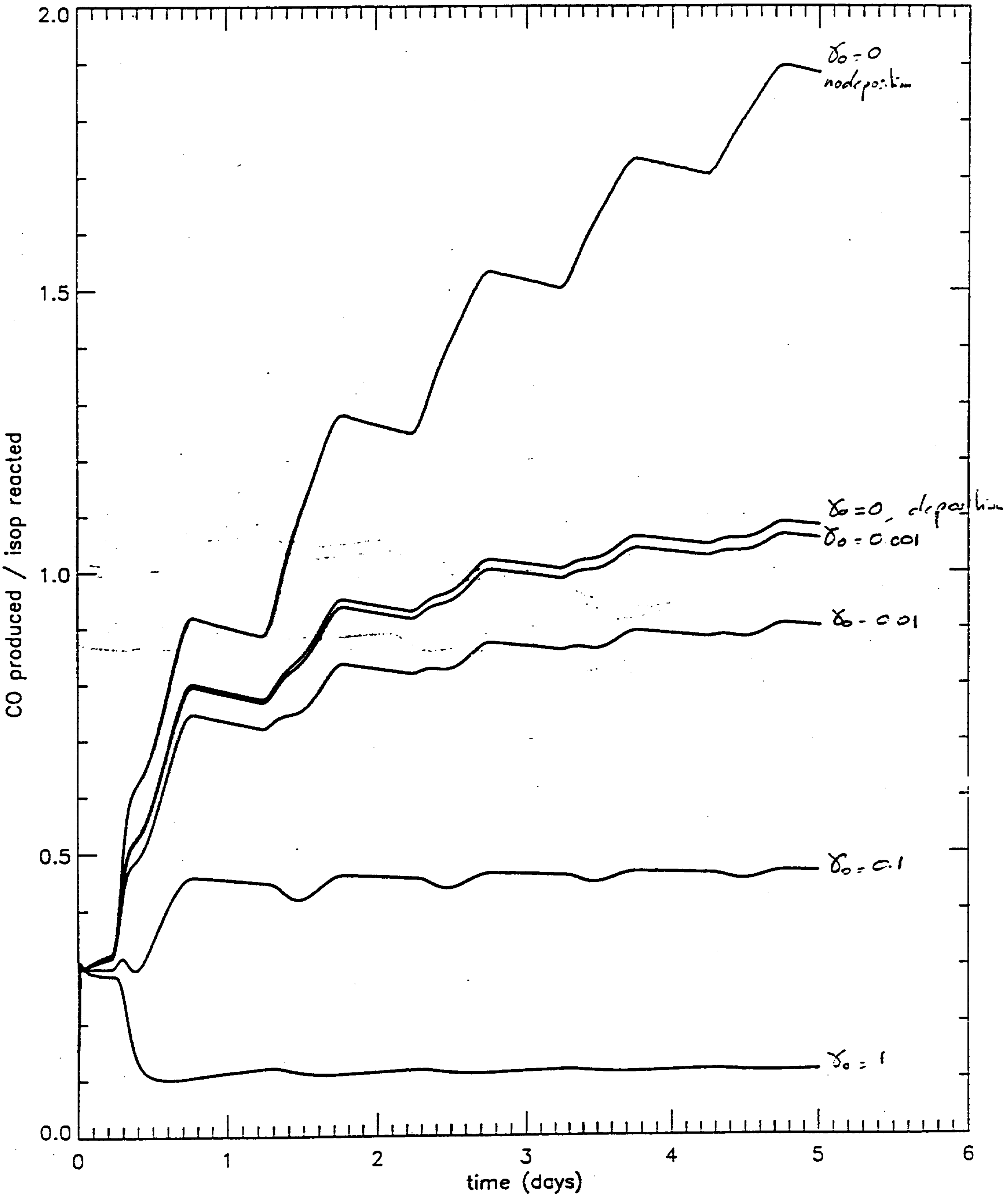
so collision time ~ 80 sec / γ .

e.g. γ for N_2O_5 0.1 on $(NH_4)HSO_4$ aerosol
> 0.005 on water

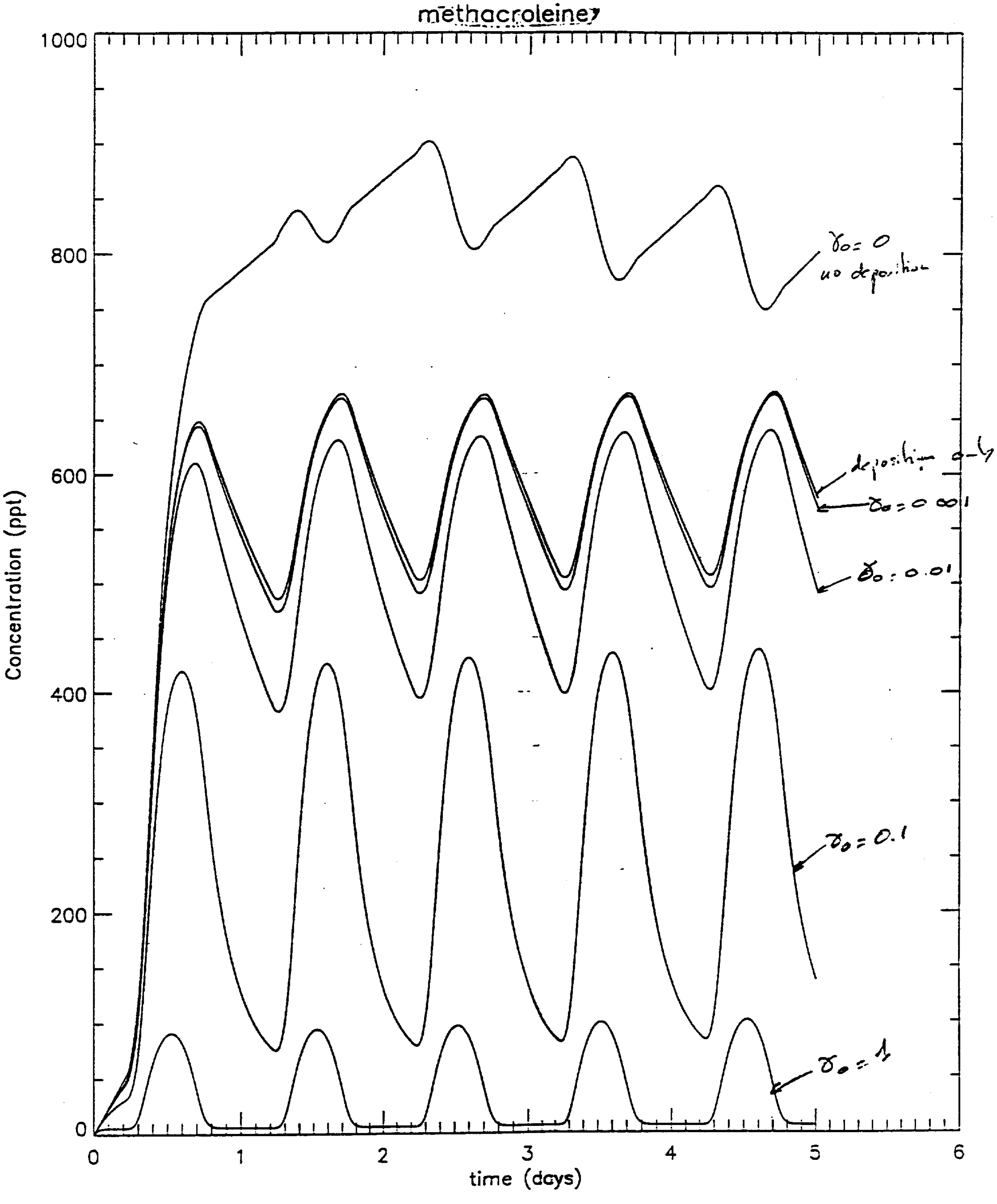

Available area
1.5
1
0.5
0
1/km
surface deposition, 1 km PBL
surface deposition, 2 km PBL
Aerosol
0
10
20
30
40
Visual Range, km


Lifetime against deposition
Time, s
10^0
10^2
10^4
10^6
0
10
20
30
40
Visual Range, km
γ = e-4
surface
γ = 1

NOx = 500 ppt
O3 = 60 ppb.

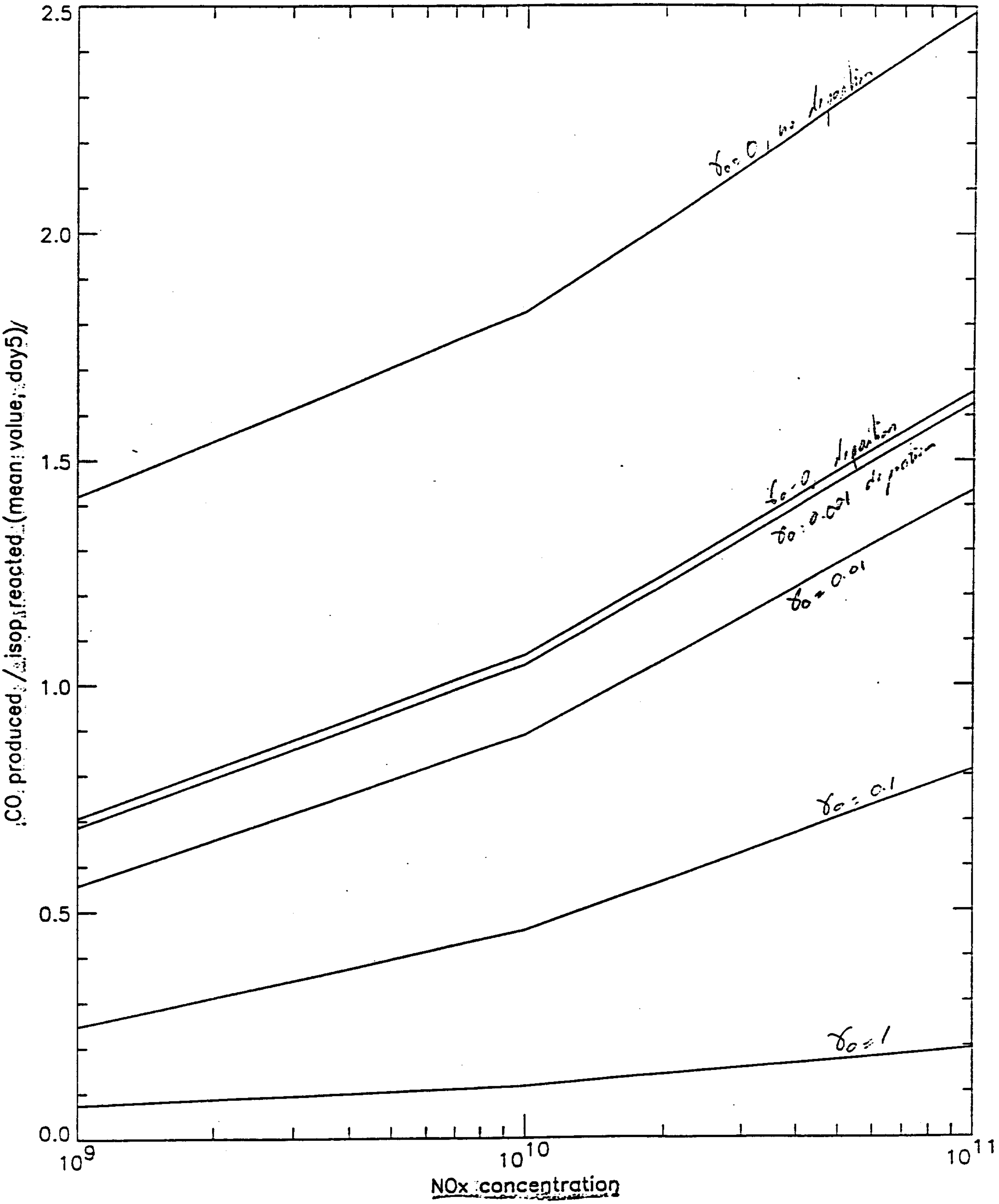


NOx = 500 ppt
isoprene = 1 ppb
O_3 = 60 ppb



mean value, day 5
(taken between 9am – 5pm)

/ O_3 = 50 ppb



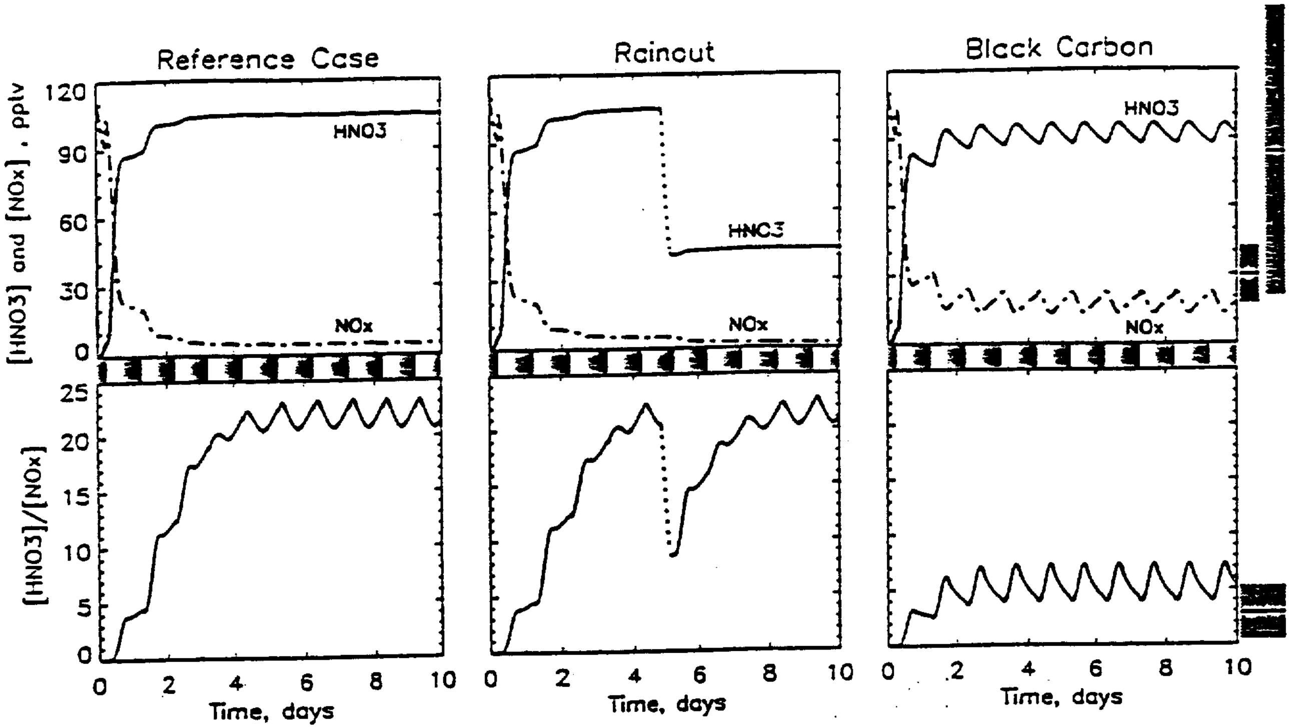


Figure 1. HNO_3 and NO_x concentrations (top panel), and $[HNO_3]/[NO_x]$ ratio (bottom panel) calculated over a 10-day period for MLOPEX 2 summer conditions, for the reference case, with an episodic rainout, and including heterogeneous reactions on black carbon (BC). Encounter with a cloud on the fifth day of the simulation for the rainout case is indicated by a dotted line. Observed values during MLOPEX 2 summer intensive of HNO_3 (83.5±63.3 pptv), NO_x (29.7±12.5 pptv), and $[HNO_3]/[NO_x]$ ratio (2.8±2.4) are also shown on the right side of the plot for comparison. Shaded periods along abscissa refer to nighttime.

GEOPHYSICAL RESEARCH LETTERS, VOL. 23, NO. 19, PAGES 2609-2612, SEPTEMBER 15, 1996

HNO_3/NO_x Ratio in the Remote Troposphere during MLOPEX 2: Evidence for Nitric Acid Reduction on Carbonaceous Aerosols?

D. A. Hauglustaine,[1] B. A. Ridley, S. Solomon, P. G. Hess, and S. Madronich
National Center for Atmospheric Research, Boulder, Colorado

PLANNED AEROSOL STUDIES (tentative)

- Use box model with detail hydrocarbon chemistry (Master Mechanism)
  - identify species likely to be scavanged by aerosols
  - quantify yields of CO, O3
  - identify critical measurables

- Use regional model to assess impacts:
  - 1st order losses to simulate scavenging by aerosols
  - run model with and without aerosols, for Southeastern US
    - compare production of ozone, CO
    - compare with observations: ozone and CO over wide areas
    - compare with observations: local measurements of oxygenated organics and ratios (e.g., MACR/MVK)

REGIONAL MODEL

Design philosophy

consistency with driving met. model

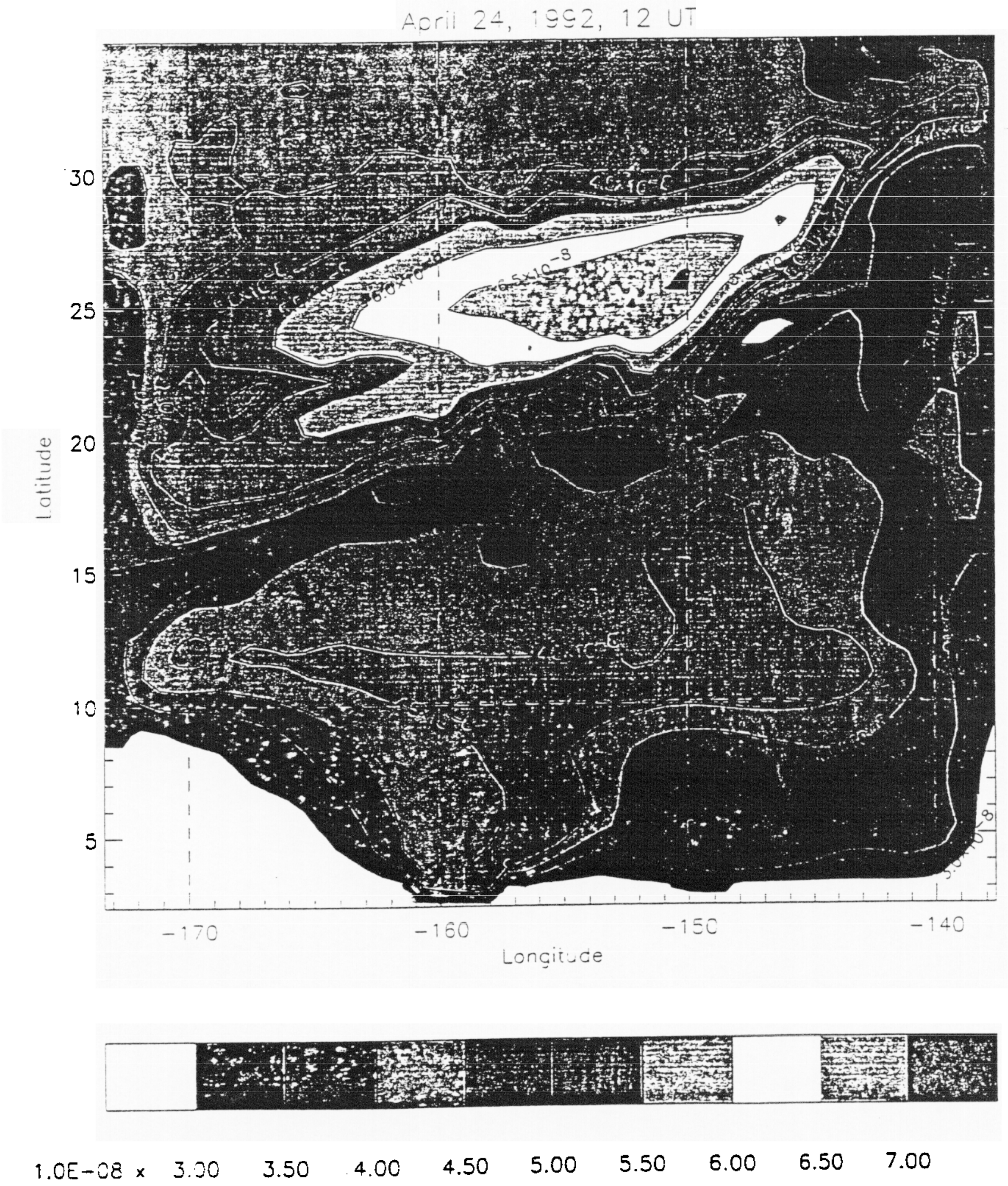
flexibility (location, var. grids, chemistry)

Current configuration

- average fields from MM5 (3 hrs.)
- deep convection (MM5, entrainment/detrainment, downdrafts, modified Arakawa-Schubert param.)
- shallow convection (MM5, entrainment/detrainment
- boundary layer (Holtschlag, CCM2/3)
- dry deposition (Wesley)
- wet deposition (Giorgi and Chameides with MM5 microphysics)
- global emissions (from MOZART)
- Hawaii emissions (from P. Ginoux)
- advection (Smolarkiewicz or Bott)
- gas phase chemistry (Master Mech., IMAGES, recently updated)
- J values (interpolation table, from TUV model) modified by MM5-derived clouds
- solve with Euler Backward Implicit scheme (tested with Gear)
- Visualization postprocessor

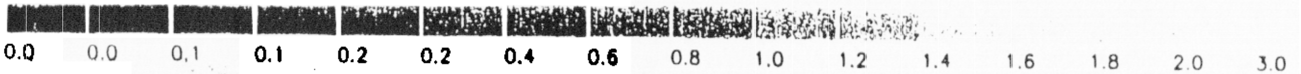
Regional Model

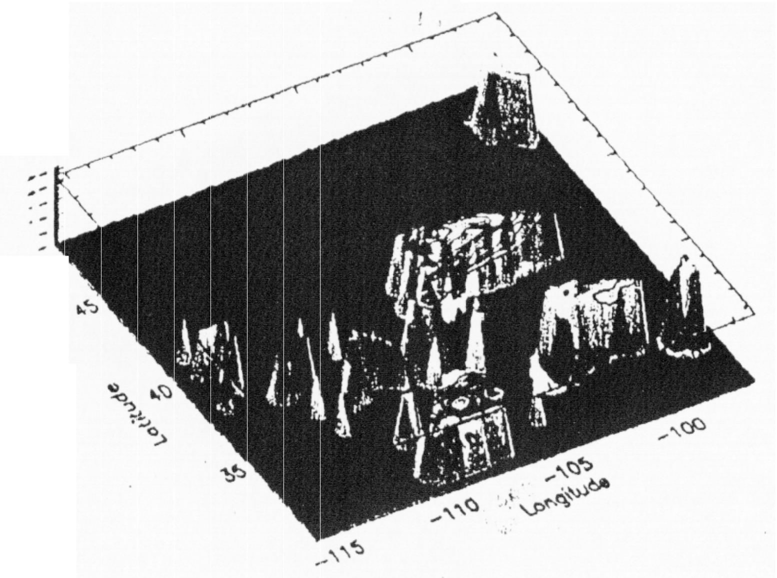
Some Mixing Ratios at the 800 mb Level: Ozone


April 24, 1992, 12 UT

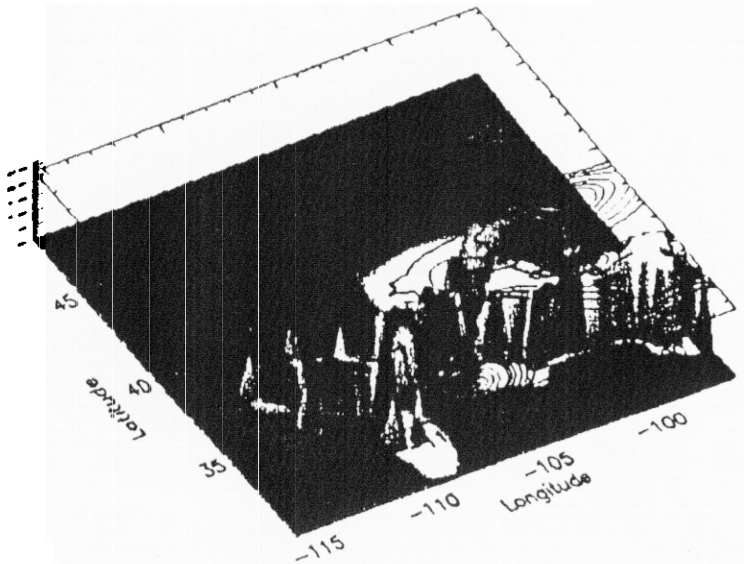
P.Hess, S.Madronich, 1996

1a

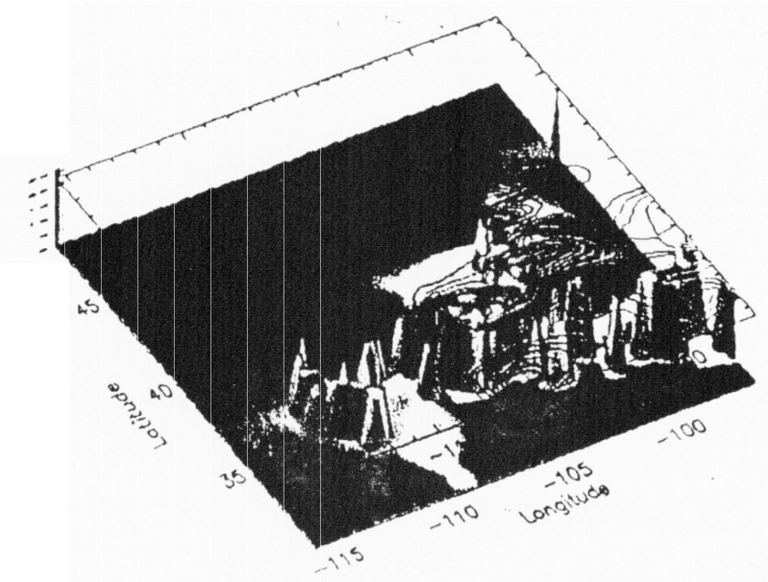




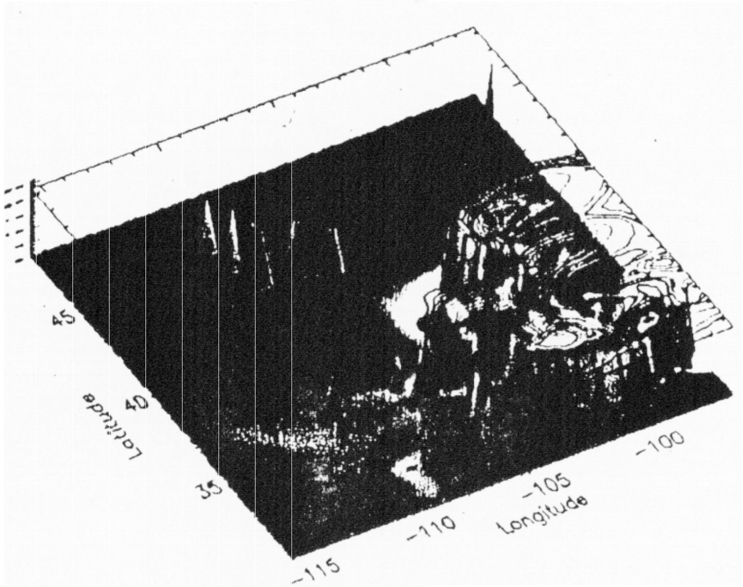
Hour 4



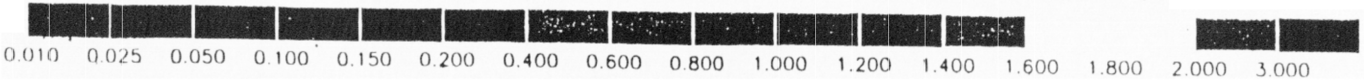
Hour 9

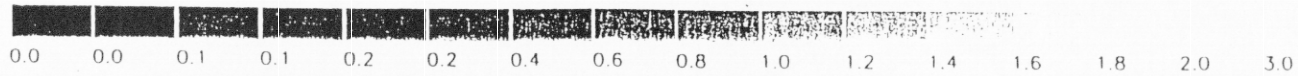


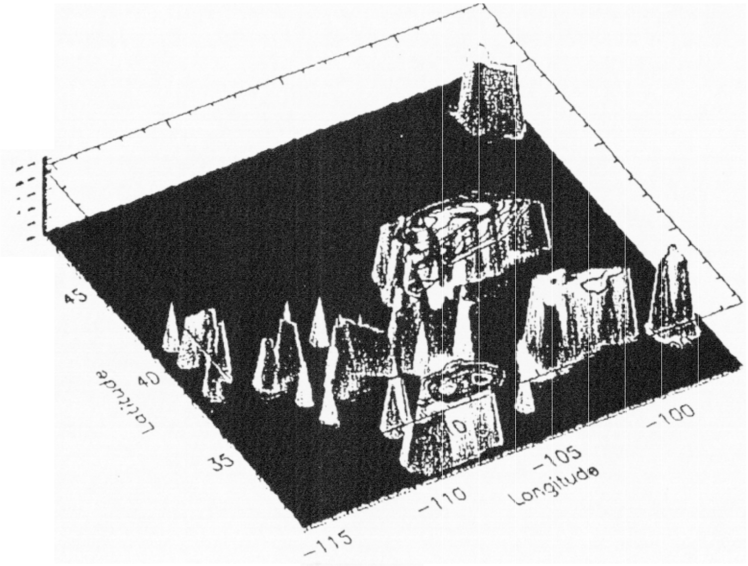
Hour 13



Hour 17







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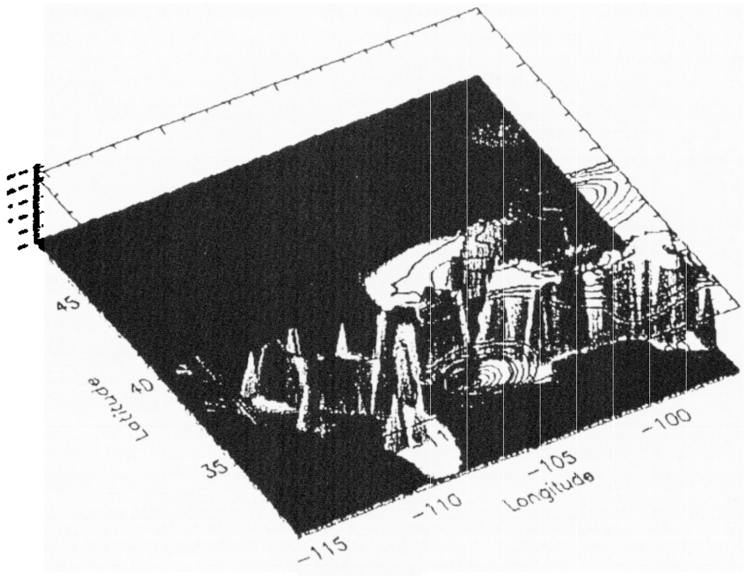
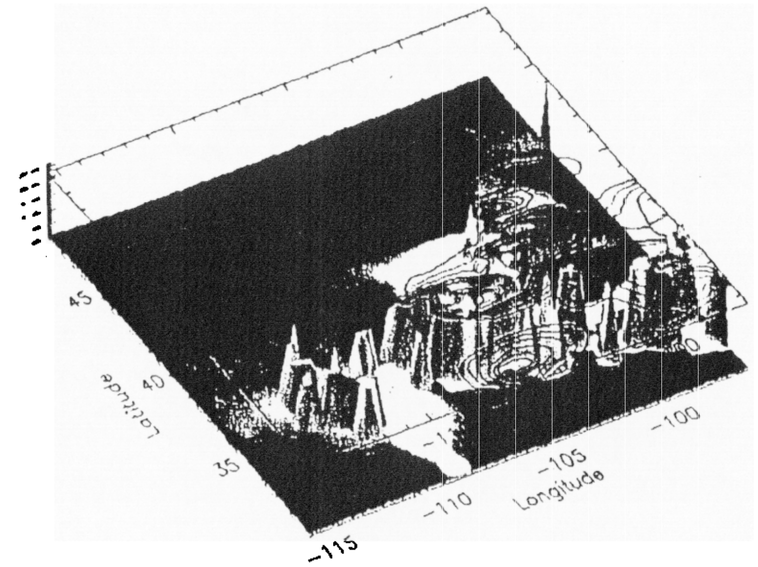
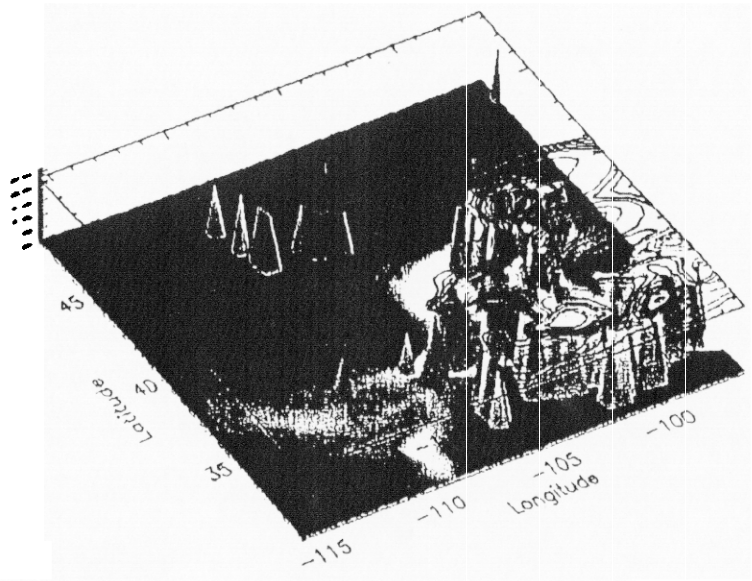


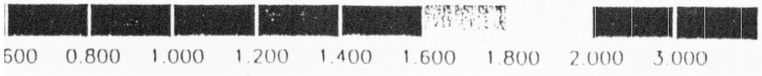
Hour 9

2





Hour 17



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