

# ATMOSPHERIC ASSESSMENT OF AIRCRAFT NITROGEN OXIDES EMISSIONS

by

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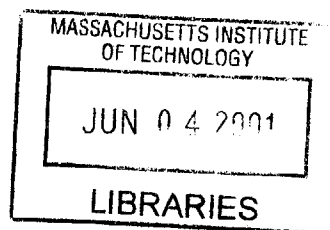
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**NISRINE ADEL AL-KADI**

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## **ABSTRACT**

In recent years, the atmospheric assessment of aircraft nitrogen oxides emissions has become a topic of major interest for both scientists and engineering professionals as well as for local communities and the administrations in many parts of the world. To satisfy the increasing demand for protection against change in ozone concentration and climate forcing, it is necessary to assess the atmospheric effects of current and future world fleets of aircrafts.

This study is focused on the present and future effects of aircraft nitrogen oxide emissions, on the nitrogen oxide and ozone concentration in the atmosphere as well as the corresponding radiative forcing and global climate impact. The emissions of nitrogen oxide from air traffic contribute significantly to the nitrogen oxide concentrations in the upper troposphere and lower stratosphere. Although the direct effect of these emissions of the radiative forcing is negligible, nitrogen oxide plays an important role in the ozone chemistry. This leads to an increase of ozone in the upper part of the troposphere and the lower part of the stratosphere, where the sensitivity of the radiative forcing to changes in ozone is the greatest.

Thesis Supervisor:  
Title:

David H. Marks  
Professor of Civil and Environmental Engineering

**TO MY FAMILY  
ADEL, WAFA AND SALIM  
WITH LOVE**

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# TABLE OF CONTENTS

ABSTRACT	2
LIST OF TABLES	7
LIST OF FIGURES	8
CHAPTER 1: INTRODUCTION	10
CHAPTER 2: AIRCRAFT NO <sub>x</sub> EMISSIONS	12
2.1 JET EXHAUST EMISSIONS	12
2.2 PLUME AND AWAKE PROCESSING OF ENGINE EMISSIONS	12
2.3 ENGINE DESIGN AND NO <sub>x</sub> EMISSIONS	15
2.4 EXHAUST EMISSIONS CALCULATIONS	17
2.5 CHEMICAL CONVERSIONS OF EMISSIONS IN JET PHASE	19
2.6 EVALUATION OF MODEL RESULTS OF NO <sub>x</sub> EMISSIONS	22
CHAPTER 3: PHYSICS AND CHEMISTRY OF THE ATMOSPHERE	26
3.1 STRATOSPHERE/TROPOSPHERE EXCHANGE AND TEMPERATURE STRUCTURE	27
3.2 CHEMISTRY OF THE TROPOSPHERE	28
3.2.1 TROPOSPHERIC OZONE	28
3.2.2 CHEMICAL REACTIONS OF THE TROPOSPHERE	29
3.2.3 OZONE RESPONSE TO NO <sub>x</sub> IN THE UPPER TROPOSPHERE	32
3.3 CHEMISTRY OF THE STRATOSPHERE	34
3.3.1 STRATOSPHERIC OZONE	34
3.3.2 CHEMICAL REACTIONS OF THE STRATOSPHERE	36
3.4 NET EFFECT OF AIRCRAFT NO <sub>x</sub> EMISSIONS ON THE UT AND LS	40
CHAPTER 4 CLIMATE IMPACT OF AIRCRAFT NO <sub>x</sub> EMISSIONS	43
4.1 DEFINITION OF RADIATIVE FORCING	45
4.2 INDIRECT RADIATIVE FORCING OF NO <sub>x</sub>	48

4.3 MODEL RESULTS OF RADIATIVE FORCING DUE TO NO <sub>x</sub> EMISSIONS	50
CHAPTER 5 CONCLUSION	52
CHAPTER 6 RECOMMENDATIONS	53
REFERENCES	54
APPENDIX A: DETAILED MODEL RESULTS	57

## LIST OF TABLES

TABLE 2.1:	Initial concentrations in the plume and concentrations in the ambient at noon and midnight	14
TABLE 2.2:	Typical emission index levels for engine-operating regimes	17
TABLE 2.3:	Calculated changes in principle traffic areas	23
TABLE 2.4:	Global averaged reaction fluxes for major ozone production and destruction terms	24
TABLE 3.1:	Mean composition of the troposphere and typical trace lifetimes	29
TABLE 3.2:	Approximate trace gas composition of the stratosphere	35
TABLE 3.3:	Estimated trace gas sources	41
TABLE 4.1:	Maximum ozone change in the upper troposphere	48
TABLE 4.2:	Globally averaged tropospheric ozone radiative forcing	49



## LIST OF FIGURE

FIGURE 2.1:	Major potential impacts of aircraft emissions	13
FIGURE 2.2:	Oxides of nitrogen emissions from late model engines	16
FIGURE 2.3:	Daytime inter-conversions of oxidized nitrogen compounds in the troposphere	20
FIGURE 2.4:	Nighttime inter-conversions of oxidized nitrogen compounds in the troposphere	21
FIGURE 2.5:	Maximum percentage increase in ozone concentration in principle traffic areas	25
FIGURE 3.1:	Vertical profile of mean temperature and its use to define the troposphere and the stratosphere at different latitudes	28
FIGURE 3.2:	Model calculated OH concentration and net photochemical O <sub>3</sub> production rate as a function of ambient NO <sub>x</sub>	32
FIGURE 3.3:	Net ozone production as a function of NO <sub>x</sub> in the upper troposphere	34
FIGURE 3.4:	Calculation of the rate of ozone loss in the lower stratosphere	42
FIGURE 4.1:	Schematic of possible mechanisms where by aircraft emissions impact climate	44
FIGURE 4.2:	Bar charts of radiative forcing	46

FIGURE 4.3:	Bar charts of radiative forcing in 2050	47
FIGURE 4.4:	Radiative forcing at the tropopause as a function of altitude	49
FIGURE 4.5:	Estimates of northern mid-latitude total ozone column changes percent from NO <sub>x</sub> emission in the troposphere and stratosphere	51

# CHAPTER 1

## INTRODUCTION

In recent years, the assessment of aircraft emissions on the atmosphere has become a topic of major interest for scientists and engineering professionals as well as for local communities and administrations in many parts of the world. The reasons for this is that aircraft operations result in the emission of gaseous and particle effluents, including carbon dioxide, water, hydrocarbons, carbon monoxide, nitrogen oxides, sulfur, soot, etc, which could potentially affect the ozone layer and contribute to climate changes.

Aviation has experienced rapid expansion as the world economy has grown. Passenger traffic has grown since 1960 at nearly 9% per year. Total aviation emissions have increased, because increased demand for air transport has outpaced the reductions in specific emissions from the continuing improvements in technology and operationally procedures. Today the major fraction of the commercial fleet is provided by jet aircraft, which cruise in the upper troposphere and lower stratosphere (typically 9 – 12 km altitude) at subsonic speed.

The aim of this study is to assess the atmospheric effects of aircraft nitrogen oxides emissions in the upper troposphere and the lower stratosphere. This involves reviewing the current understanding of chemical and dynamical processes in the upper troposphere and the lower stratosphere, and to assess how these processes could be perturbed as a result of current and future aircraft emissions. In addition, perturbations in the atmospheric abundances of ozone and in climate forcing, as predicted by atmospheric models, will be presented. Therefore the goal of this study is to compile and to evaluate scientific information related to the atmospheric impact of subsonic and supersonic aircraft emissions and to review the state of knowledge concerning the various aspects of this problem.

The study is arranged as follows:

Chapter 2 briefly discusses the estimates of air traffic and aircraft emissions. It presents an overview of the fate of emissions from the sources to the regional scale on time scales from milliseconds to a day, and space scales from decimeters to several 10 km. Chapter 3 discusses the key physical and chemical processes occurring in the troposphere and stratosphere. The basic structure of the atmosphere is described along with the chemical processes, which control its composition, and the likely effect of certain pollutants on that composition with particular reference to the regions of the atmosphere impacted by aircraft. Chapter 4 discusses the atmospheric impact of nitrogen oxides emissions on climate forcing and its contribution to radiative forcing. It is then followed by conclusions and recommendations in Chapter 5 and Chapter 6.

## **CHAPTER 2**

### **AIRCRAFT NO<sub>x</sub> EMISSIONS**

Present day jet aircrafts cruise at an altitude range of 9-13 km. This altitude range contains portions of the upper troposphere and lower stratosphere (UT and LS respectively). The UT and LS regions are characterized by different dynamics and photochemistry; therefore one needs to consider exhaust placements into these two regions when evaluating the impact of NO<sub>x</sub> on the atmosphere.

#### **2.1 JET EXHAUST EMISSIONS**

The two most abundant products of jet fuel combustion are CO<sub>2</sub> and H<sub>2</sub>O, however they have significant natural background levels in the UT and the LS (Schumann, 1994), therefore they are not of a great concern. NO<sub>x</sub> constitutes the next most abundant engine emission, the emission indices for NO<sub>x</sub> is 5 to 25 g of NO<sub>2</sub> per kg of fuel burned. NO<sub>x</sub> is the most important and the most studied with respect to ozone photochemistry, since its aircraft emission rates are sufficient to affect background levels in the UT and LS (WMO-UNEP, 1985, 1995).

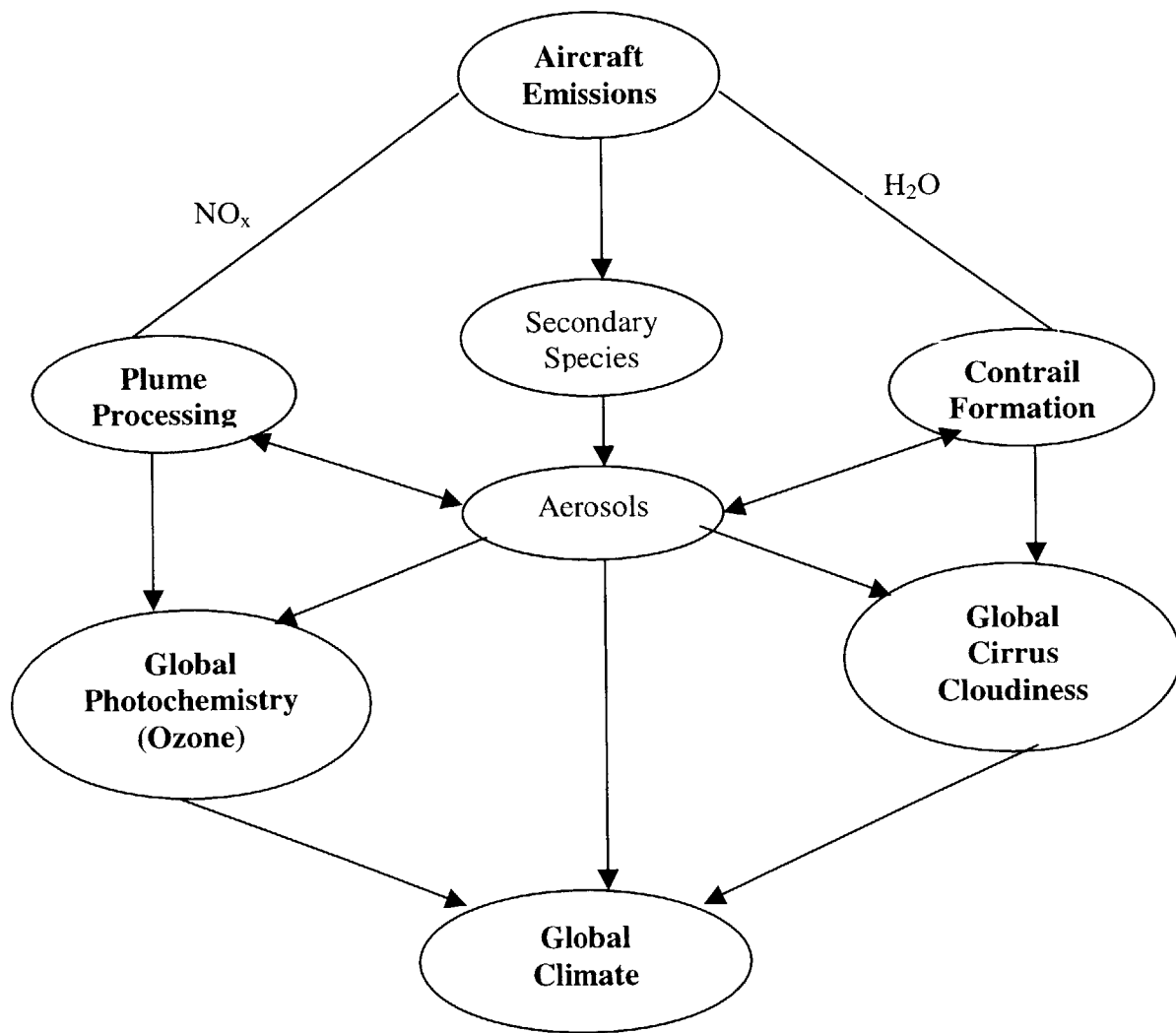
Although the jet exhaust spends a relatively short time in the immediate vicinity behind the aircraft, a number of important processes occur during that time that influence exhaust gas, therefore influencing ozone formation or depletion potential of the exhaust (see Figure 2.1).

#### **2.2 PLUME AND WAKE PROCESSING OF ENGINE EMISSIONS**

The near field jet aircraft exhaust wake is divided into three components commonly termed: jet, vortex and plume dispersion, with three different time scales, 0-10s, 10-100s, 100s-10hours respectively. The jet and vortex are both initiated at the exit plane of the engine and end due to atmospheric shear forces at a distance of approximately 10-20 km behind the aircraft (Schumann, 1994). During the vortex regime there is a strong

suppression of plume mixing and dispersion. The vortex systems are composed of cylindrical core regions that are not well mixed radially and contain only small amounts of ambient air. In the vortex region high concentrations of exhaust species interact with each other and with small amount of ambient gases and particles over a range of temperature that is different than that of the background atmosphere.

**Figure 2.1:** Major potential impacts of aircraft emissions



The plume dispersion regime begins after disintegration of the wake of vortex and extends to an area where the concentration of ( $\text{NO}_x$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$ ) are of the same order of magnitude as the corresponding ambient background levels (see Table 2.1). The plume will mix with the background atmosphere according to a simple dilution law that can be approximated with a Gaussian plume model that includes estimated and measured atmospheric shear and diffusion parameters (Konopka, 1995; Schumann et al., 1995). In the plume dispersion stage, aircraft gases and particle concentration are still higher than the background levels, but they interact with large volumes of ambient species under temperature and pressure conditions of the background atmosphere. In addition to this, chemistry process model calculations indicate that a significant fraction of emitted  $\text{NO}_x$  is converted to the reactive nitrogen form  $\text{NO}_y$  species in the plume dispersion model (Karol et al., 1997).

**Table 2.1:** Initial concentrations in the plume and concentrations in the ambient air at noon and midnight. Numbers not reported are below 1ppt

Initial Concentration	Plume	Background (Noon/midnight)
NO (ppb)	730	0.034
NO <sub>2</sub> (ppb)	98	0.012/0.046
HNO <sub>3</sub> (ppb)	3.1	0.32/0.33
OH (ppt)		0.40
HO <sub>2</sub> (ppt)		3.60
O <sub>3</sub> (ppb)	85.2	85.4/85.6
PAN (ppb)	0.25	0.25/0.26
HCHO (ppb)	1.18	0.056/0.060
CO (ppbm)	2.56	113/113
C <sub>2</sub> H <sub>4</sub> (ppt)	2.37	1.43/0.82, 19 <sup>a</sup>
C <sub>2</sub> H <sub>6</sub> (ppb)	2.10	2.04/2.03
C <sub>3</sub> H <sub>6</sub> (ppb)	0.48	0.002 <sup>a</sup>
NC <sub>4</sub> H <sub>10</sub> (ppb)	0.8	0.028 <sup>a</sup>
o-xylene (ppb)	0.12	0.002 <sup>a</sup>
C <sub>3</sub> H <sub>8</sub> (ppt)		6.3 <sup>a</sup>

<sup>a</sup> The diurnal monthly mean concentrations of short-lived hydrocarbons are given, since the concentrations were reduced during the modeled spin-up time.

Most interaction between ambient ozone and ozone-controlling gases and aircraft exhaust occur in the days and weeks following emission. During that time, aircraft gases and particles participate in the natural chemical cycles that control ambient ozone levels.

### **2.3 ENGINE DESIGN AND NO<sub>x</sub> EMISSIONS**

In the 1960s and 1970s a transition occurred for aircraft engines from being turbojet engines to high bypass ratio turbofan engines. This resulted in improved fuel efficiency, lower noise levels, reduced emissions of CO and HC due to the improved combustion engine efficiencies, but it also created an increase in NO<sub>x</sub> emission due to the higher engine internal temperature and pressure.

The emission of NO<sub>x</sub> is dependent on the following:

- 1) Engine cycle design
- 2) Combustor technology
- 3) Fuel composition

Therefore, the potential for reducing or altering the balance of NO<sub>x</sub> emission is through technology design and or change in operational practice.

Modern, high performance gas turbine “jet” engine are used today to power aircrafts. They are described as a continuous flow heat engines operating at constant pressure. These engines use air as the working fluid to generate the thrust required to propel an aircraft through the atmosphere (Albritton et al, 1997). Fuel aviation, which is mainly kerosene is sprayed at high pressure into the combustion chamber, it mixes with hot high-pressured air that is supplied by the compressor and is ignited (Kuo, 1986).

Formation of NO<sub>x</sub> during combustion occurs through four different routes, namely:

- 1) Thermal NO route
- 2) Prompt NO route
- 3) N<sub>2</sub>O route

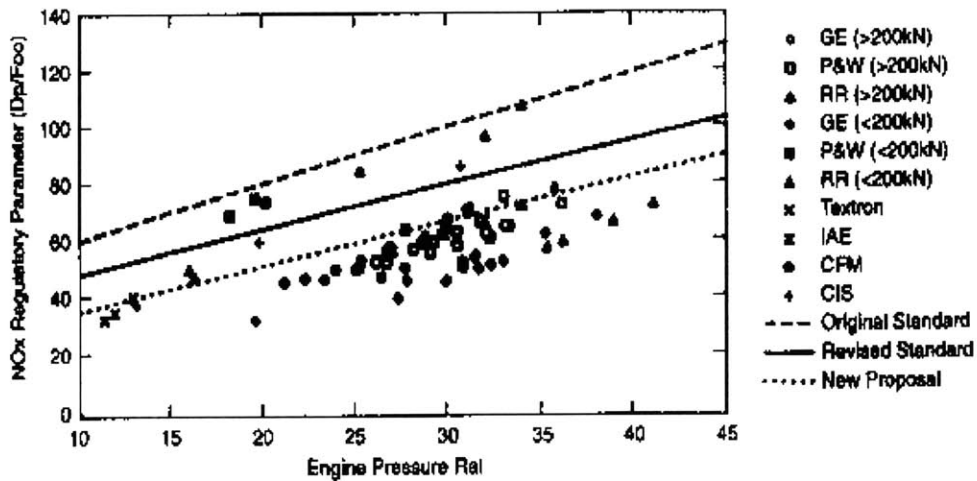


#### 4) Fuel bound nitrogen route

Depending on the combustion conditions, one of the routes can dominate over the other routes. For example under fuel rich conditions, prompt NO is favored in rich flames, whereas in lean premixed combustion in turbines,  $N_2O$  route is the major source of NO (Bowman, 1992).

Nitrogen oxides and other aircraft emitted gases and particles have been regulated on the basis of the landing and take-off (LTO) cycle of an aircraft up to 915m at and around airports (see Table 2.2). The LTO cycle can be divided into four parts: take-off, climbout, approach, and taxi/idle (ICAO, 1981,1993). The regulatory parameter for an emitted species ( $D_p/F_{00}$ ), is defined as the mass of species emitted over LTO cycle divided by the rated power output of engine, and it has units of  $gKN^{-1}$ (see Figure 2.2). It should be noted that the LTO part of flight emissions comprises only a small portions of these emissions.

**Figure 2.2:** Oxides of nitrogen emissions from late model engines



**Table 2.2:** Typical emission index levels for engine-operating regimes. Units are grams pollutant per kilogram of fuel burnt ( $\text{gKg}^{-1}$ )

Operating Conditions				
Species	Idle	Take-off	Cruise	Comments
CO <sub>2</sub>	3160	3160	3160	
H <sub>2</sub> O	1230	1230	1230	
CO	25(10-65)	<1	1-3.5	
HC (as methane)	4(0-12)	<0.5	0.2-1.3	
NO <sub>x</sub> (as NO <sub>2</sub> )	4.5(3-6)	32(20-65)	7.0-11.9	(Short haul)
	4.5(3-6)	27(10-53)	11.1-15.4	(Long haul)
SO <sub>x</sub> (as SO <sub>2</sub> )	1.0	1.0	1.0	

Note: Idle and take-off data are derived from ICAO Engine exhaust emissions databank (ICAO, 1995b). Cruise data are taken from the global 3-D inventories of ANCAT/EC (Gardner, 1997b) and NASA (Baughcum et al., 1996); NO<sub>x</sub> data are averages of data from the two inventories; CO and HC are from the NASA work.

NO<sub>x</sub> emissions from aircraft are important from the point of view of atmospheric chemistry and the potential impacts on ozone and climate. However, engine/aircraft performance, fuel efficiency, technical reliability and durability are of high priority to airlines and manufacturers. Technology advances are sought of as means of improving emissions performance (ICAO, 1995a). The continuing trend to higher temperature and pressure in the advanced engine cycles lead to improved SFC and reduced CO<sub>2</sub> and H<sub>2</sub>O vapor emissions, but without any further technological improvements it would result in higher NO<sub>x</sub> emission levels. Some limitations of NO<sub>x</sub> have been achieved by optimization of fuel-air mixing and distribution within the combustor. Improved combustors are still being developed for existing engine types such as JT8D-200 and DF6-80 series and for new engine models such as Trent, PW4084, BR700 (ICAO, 1997).

## 2.4 EXHAUST EMISSIONS CALCULATIONS

In order to quantify the chemical and climate impact of aircraft NO<sub>x</sub> emission on a global scale, it is important to understand the dispersion and chemical transformations that take place in aircraft plumes before it is homogeneously mixed with surrounding air.

As the exhaust gas and particles move out from the combustor they experience conversions.

The concentration and temperature of the exhaust gases depends on the following two things:

- 1) Amount of fuel mass burned in the engine.
- 2) Amount of the air mass mixed with the exhaust gases.

The details of the mixing process requires three dimensional and time dependent exhaust plume field, due to the complexity of such a process bulk mean values are estimated instead, by using a dilution factor  $N$ , which is defined as the mass of exhaust gasses in plume per mass of fuel burned.

Bulk mean properties in plume differ from ambient values by temperature difference:

$$\Delta T = Q(1 - \eta) / C_p N \quad (2.4.1)$$

The mass concentration and volume mixing ration of gaseous species  $I$ :

$$\begin{aligned} \Delta C_i &= EI_i / N \\ \Delta \eta_i &= EI_i M_{air} / M_i N \end{aligned} \quad (2.4.2)$$

The volume specific concentration of particles such as condensation nuclei (CN):

$$\Delta CN = EI_{CN} \rho / N \quad (2.4.3)$$

The jet velocity relative to the frame of the aircraft:

$$\Delta v = F / m_f N \quad (2.4.4)$$

Area of the plume cross-section of exhaust plume:

$$A = m_f N / \rho v \quad (2.4.5)$$

Where:

$Q \equiv$  specific heat of combustion  $\approx 43 \text{ MJ kg}^{-1}$  for kerosene

$C_p \equiv$  specific heat capacity of plume gases at constant pressure  $\approx 1004 \text{ J kg}^{-1} \text{ K}^{-1}$

$F \equiv$  engine thrust in N

$m_f \equiv$  fuel flow rate in  $\text{Kgs}^{-1}$

$EI_i \equiv$  emission mass of species  $i$

$M_i \equiv$  molar mass of species  $i$

$\rho \equiv$  plume gas density

$\eta = Fv / Qm_f \equiv$  overall propulsion efficiency (between 0.15-0.35)

The identity of individual plumes depends on the deviation of the plume properties from ambient values compared to the natural variability of the specific property in the ambient air. Therefore the plume loses identity quickly in terms of velocity, temperature and humidity, remains measurable longer in terms of concentration increase of CO<sub>2</sub> and is largest in terms of NO<sub>x</sub> and small particle (CN). In terms of NO<sub>x</sub> the concentration increases and remains measurable up to a time scale of the order 5-10 hours.

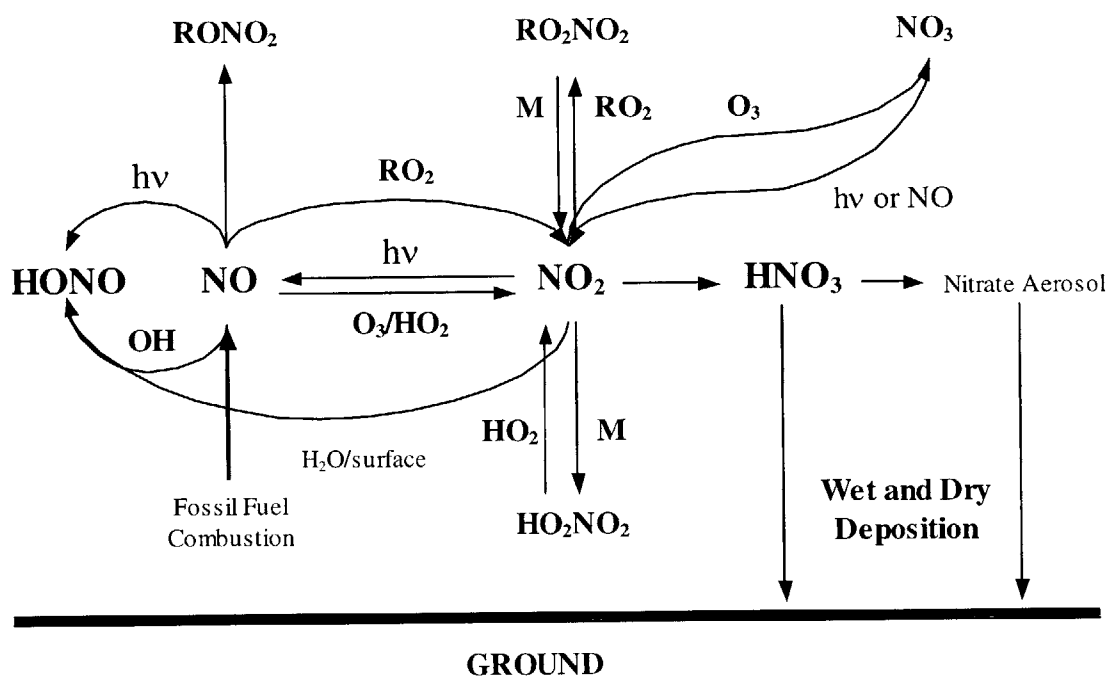
## 2.5 CHEMICAL CONVERSIONS OF EMISSIONS IN THE JET PHASE

Gas phase chemistry emissions include nitrogen oxide component NO<sub>x</sub> composed of NO and NO<sub>2</sub>. At cruise altitude most of the NO<sub>x</sub> is emitted as NO. Ratios of NO<sub>2</sub>/NO of less than 0.05 have been measured for the RB211 engine (Lister et al., 1995). During the early jet phase the air chemistry is unaffected by photolysis (time scale of NO<sub>2</sub> photolysis is of the order of 100s). NO will react with O<sub>3</sub> to produce NO<sub>2</sub> and O<sub>2</sub>. During the nighttime, all the NO gets oxidized this way. During the daytime, photolysis will occur and cause non-zero NO/NO<sub>2</sub> ratio (see Figure 2.3 and 2.4). The reaction of NO with O<sub>3</sub> will result in small reduction of O<sub>3</sub> in young plumes (Ebel et al., 1996). At the engine exit, exhaust contains large concentration of hydroxyl radicals and some other radicals which will tend to oxidize the emitted NO and NO<sub>2</sub> to nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>). This conversion depends on how strongly the OH concentration is at the plane's exit. Photochemical equilibrium is reached after several minutes. During the daytime photolysis of NO<sub>2</sub> causes regeneration of NO. Also photolysis of HNO<sub>2</sub> is a source of OH radicals (Arnold et al., 1998) which together with OH from other sources (Hanisco et al., 1997) causes further conversion of NO<sub>x</sub> to HNO<sub>3</sub>. Also photolysis of HNO<sub>3</sub> limits the conversion of NO<sub>x</sub> to HNO<sub>3</sub>.

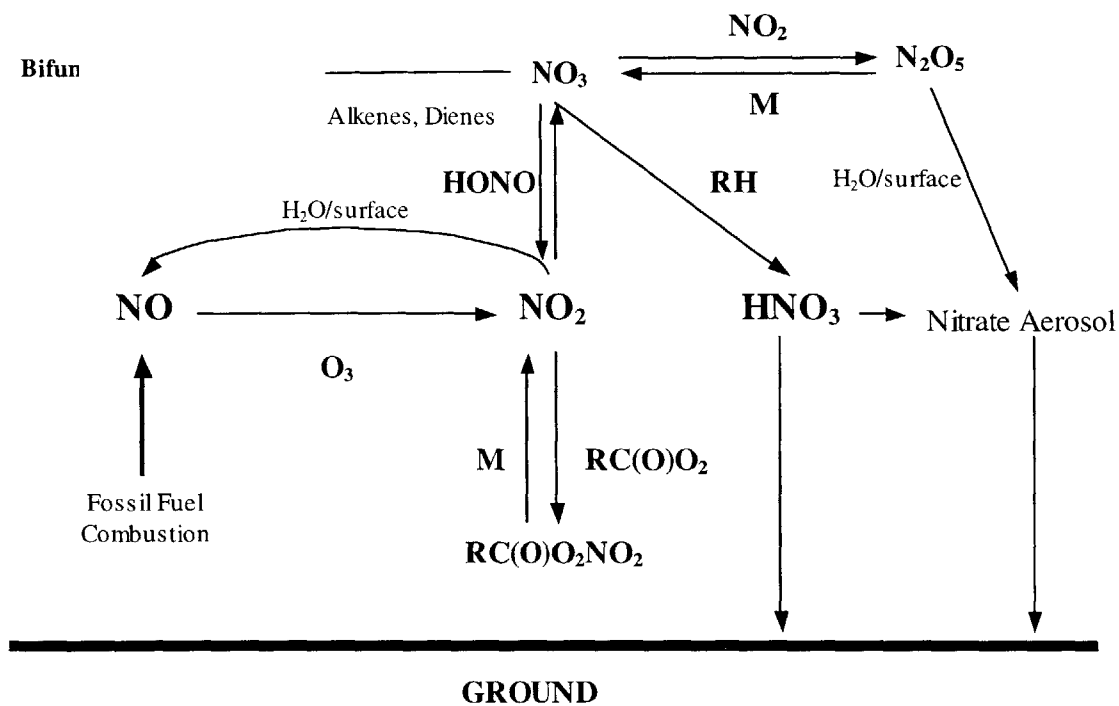
Photochemical change can occur from hours to days. Within several hours, the emitted NO<sub>x</sub> gets converted to HNO<sub>3</sub>, with smaller fraction forming HNO<sub>4</sub>, PAN, organic nitrates

(Mollhoff et al., 1996; Meijer et al., 1996). Recent measurements within a stagnant anticyclone through which air traffic passed for several days showed measurable increase in  $\text{NO}_x$ . This increase in  $\text{NO}_x$  with lifetimes of the order of several days can be attributed to emitted  $\text{NO}_x$  (Schlager et al., 1996).

**Figure 2.3:** Daytime inter-conversions of oxidized nitrogen compounds in the troposphere



**Figure 2.4:** Nighttime inter-conversions of oxidized nitrogen compounds on the troposphere



Over Europe, North America and North Atlantic, air traffic occurs in heavily loaded and rather narrow flight corridors. For example, about 300-500 aircraft pass daily in either of both directions over the North Atlantic (Hoinka et al., 1993) within a corridor of about 1000 km width and 2km altitude (Schumann, 1994). Measurements performed in North Atlantic flight traffic corridor have shown aircraft traces in terms of  $\text{NO}_x$ ,  $\text{CO}_2$ , aerosols,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{HNO}_2$  and  $\text{HNO}_3$ . The largest signals were found in young exhaust plumes of wide body aircraft with maximum value of more than 200 ppbv  $\text{NO}_x$ . Within a flight corridor, the strongest change in background values are expected for  $\text{NO}_x$  with the order of 50-150pptv.

In conclusion, plume processes control the conversion of  $\text{NO}_x$  to  $\text{NO}_y$  during the first day and control particle formation process. The conversion of  $\text{NO}_x$  to  $\text{NO}_y$  reduces the impact of emitted  $\text{NO}_x$  on ozone at global scales.

## **2.6 EVALUATION OF MODEL RESULTS**

The assessment of the impact of  $\text{NO}_x$  emissions on the atmosphere is through the used of models. Large scales models describe these conversions and impacts on air chemistry.

The results of numerous model studies on the impact of aircraft  $\text{NO}_x$  emissions on ozone levels in UT and LS note that the bulk of aircraft  $\text{NO}_x$  emissions from subsonic aviation occurs in an atmospheric region that is sensitive to these emissions. This is because of the low background  $\text{NO}_x$  levels, which are typically of the order of 50 to 200 ppt in the mid-latitude UT and LS. Therefore high  $\text{NO}/\text{NO}_2$  ratios and low  $\text{HO}_x$  concentrations, ozone production (in terms of ozone molecule) per  $\text{NO}_x$  molecule is more efficient in that region of this region than anywhere else in the atmosphere. Because the greenhouse blanketing produced by a given atmospheric ozone increment is directly proportional to the temperature contrast between radiation absorbed and radiation emitted, radiative forcing efficiency is greatest for ozone changes near the tropopause (Lacis et al., 1990), though its climate sensitivity may have different response (Hansen et al., 1997).

Based on numerous model results compiled by Richard Derwent and Randalk Friedl the impact of subsonic aviation on atmospheric composition in the principal traffic areas at 9-13 km altitude, 30-60°N latitude is summarized as follow (See Table 2.3, 2.4 and Figure 2.5):

- Significant local increases in NO<sub>x</sub> levels, by up to hundred ppt
- Significant local increase in ozone, by up to 12 ppb, over a region including air traffic corridors and pole wards of them for January and July calculation.
- Ozone increase or 2-14%, at their maximum in July, downstream and extending to the north of principal traffic areas reflecting the long atmospheric lifetime of ozone in UT and LS.
- Ratios of ozone increments to NO<sub>x</sub> increments on the order of 100, reflecting the high efficiency of the ozone production cycle in the UT and LS.
- Globally averaged ozone inventory increases of 3-10 Tg, or 1-3% up to an altitude of about 15 km.
- Increase in tropospheric hydroxyl radical inventories of 0.3-3% globally up to an altitude of about 15km.

**Table 2.3:** Calculated changes in principal traffic areas and 9-13km regions during summer for five selected models for 1992 aircraft subsonic fleet NO<sub>x</sub> emissions of 0.5 TgNyr<sup>-1</sup>

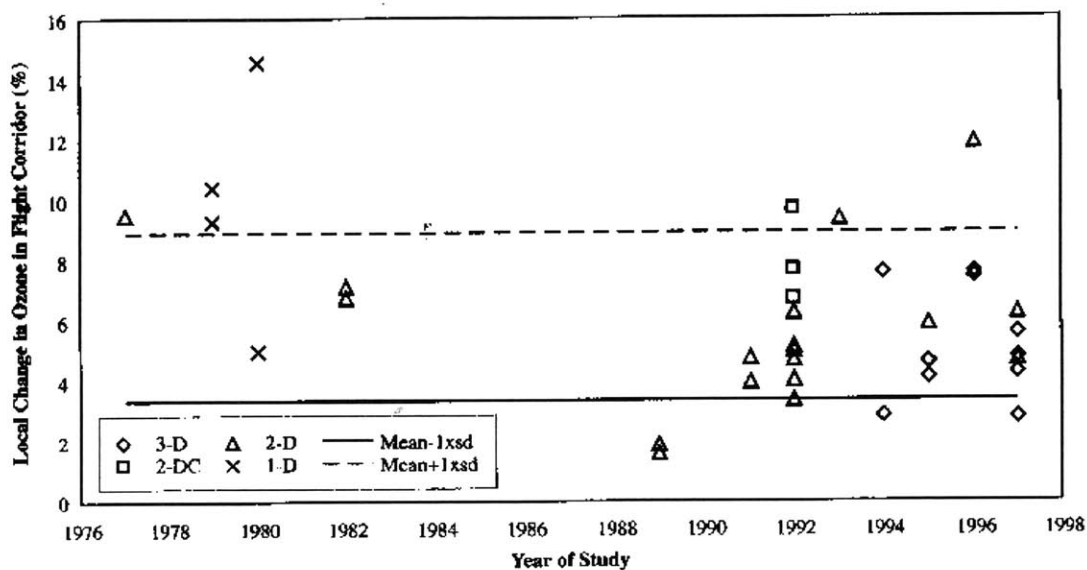
MODEL	Local Ozone Increase During July	
	ppb	%
BISA/IMAGES	4.4	4.3
HARVARD	6.0	4.4
Uio	5.5	3.5
UKMO	12.7	7.6
TM3	10.0	
Range of Previous 48 Studies	3-12	3-9



**Table 2.4:** Globally averaged reaction fluxes for the major ozone production and destruction terms, in  $10^3$  molecules  $\text{cm}^{-3}\text{s}^{-1}$  for January and July (IANOT3DLM table 2)

	January			July		
	Back	$\Delta$	%	Back	$\Delta$	%
<b>Ozone Production</b>						
HO <sub>2</sub> + NO	160.2	4.04	+2.52	225.7	4.59	+2.03
CH <sub>3</sub> O <sub>2</sub> + NO	30.7	0.81	+2.65	39.8	1.29	+3.23
NO + RO <sub>2</sub> IP <sub>1</sub>	9.3	0.00	-0.05	19.8	-0.01	-0.07
NO + RO <sub>2</sub> IP <sub>2</sub>	9.1	0.00	-0.05	18.9	-0.01	-0.04
NO + CH <sub>3</sub> COO <sub>2</sub>	6.3	0.07	+1.12	10.4	-0.02	-0.21
Stratospheric O <sub>3</sub>	16.1	0.00	0.00	9.7	0.00	0.00
Other minor terms	12.9	0.13	+0.98	17.3	0.20	+1.13
<b>Total</b>	<b>244.6</b>	<b>5.04</b>	<b>+2.06</b>	<b>341.4</b>	<b>6.03</b>	<b>+1.76</b>
<b>Ozone Destruction</b>						
HO <sub>2</sub> + O <sub>3</sub>	69.9	1.18	+1.68	129.6	1.86	+1.44
H <sub>2</sub> O + O ( <sup>1</sup> D)	79.1	1.22	+1.54	82.0	1.51	+1.84
OH + O <sub>3</sub>	33.0	1.28	+3.89	51.5	2.73	+5.31
O <sub>3</sub> dry deposition	51.0	1.31	+2.56	52.0	0.59	+1.13
Other minor terms	14.2	0.38	+2.68	36.9	0.87	+2.35
<b>Totals:</b>	<b>247.2</b>	<b>5.36</b>	<b>+2.17</b>	<b>351.9</b>	<b>7.56</b>	<b>+2.15</b>

**Figure 2.5:** Maximum percentage of increase in ozone concentrations in principle traffic areas, in the 9- to 13- km altitude range, 30 – 60° N latitude range, during summer, normalized by assumed global aircraft NO<sub>x</sub> emission to 0.5 TgNyr<sup>-1</sup> and plotted against the year the calculation was performed. Each point represents a particular model study, with the lines showing the one standard deviation (1x sd) range or results



## **CHAPTER 3**

### **PHYSICS AND CHEMISTRY OF THE ATMOSPHERE**

Concerns about NO and NO<sub>2</sub> emissions from present generation subsonic and supersonic aircraft operation in the upper troposphere (UT) and lower stratosphere (LS) were raised more than 20 years ago by Hidalgo and Crutzen (1997) because these emissions could change ozone levels locally by several percent. In 1995 WMO and UNEP concluded that assessments of ozone changes related to aviation remained uncertain and depended critically on NO<sub>x</sub> chemistry and its representation in complex models.

Nitrogen oxides NO<sub>x</sub> (NO and NO<sub>2</sub>) are present throughout the atmosphere. They are very influential in the chemistry of troposphere and the stratosphere, and they are very important in ozone production and destruction processes. This section presents an overview of the atmospheric chemistry in the upper troposphere and lower stratosphere where aircraft emissions occur.

In all regions, the chemistry of the atmosphere is complex; aircraft NO<sub>x</sub> emissions are best viewed as perturbing a web of chemical reactions with a resultant impact on ozone concentrations that differs with location, season... In the upper troposphere and lower stratosphere, aircraft NO<sub>x</sub> emissions tend to cause increased ozone amounts, so increased ozone and its greenhouse effects are the main issues of NO<sub>x</sub> emissions from subsonic aircrafts. The pathways of other atmospheric constituents are also affected. Principal among these effects for NO<sub>x</sub> emissions is the reduction in the atmospheric lifetime and concentration of methane, another greenhouse gas (Ellis et al., 1999).

Aircraft emissions are injected mainly into the free troposphere and the lower stratosphere. These two regions are of a major concern for climate impact and surface environment, because the ozone column resides mainly in the lower stratosphere and any changes no matter how small in the ozone abundance occurs as a result of NO<sub>x</sub> injection, which impacts the surface UV flux.

### 3.1 STRATOSPHERE/TROPOSPHERE EXCHANGE AND TEMPERATURE STRUCTURE

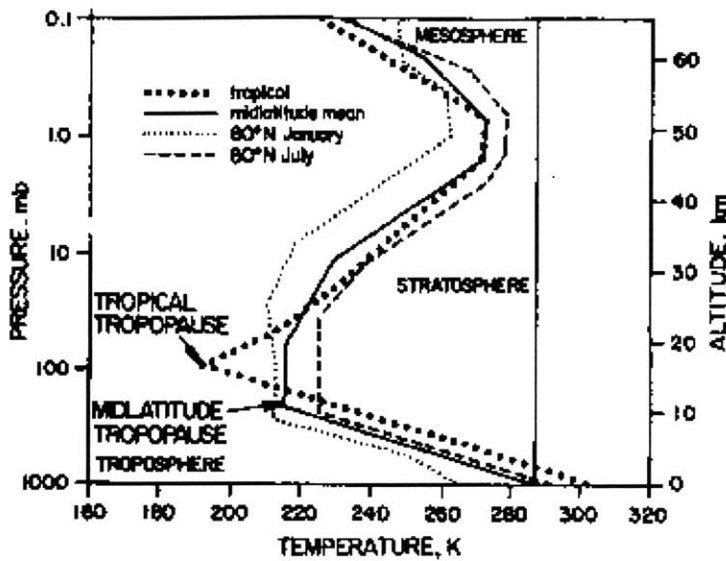
To assess the fate of  $\text{NO}_x$  emission from aircrafts a good understanding of the stratosphere-troposphere exchange is needed. The upper troposphere and lower stratosphere lies between 8-25km altitudes, and the boundary between the troposphere and the stratosphere is between 9-12km at mid-latitudes and depending on the seasons (see Figure 3.1). In the stratosphere, large-scale transport takes place through Brewer-Dobson circulation, induced by momentum deposition by planetary gravity waves. This exchange involves a wide spectrum of scales ranging from large-scale ascent and descent via synoptic scales toward transport by waves, convection, and turbulence (Brewer, 1949; Holton et al., 1995; McIntyre, 1995). In the tropics, upward transport occurs mostly through deep convection, through small-scale vertical mixing by gravity waves (Minschwaner et al., 1996). In the mid-latitude, the exchange between the troposphere and lowermost stratosphere flows in both directions, with a somewhat larger downward component (Siegmund et al., 1996). Around the polar vortices, the exchange in the stratosphere occurs along isentropic surfaces, from the polar vortex toward mid-latitude, by filaments torn off from the vortex boundary (Pierce et al., 1994). The net transport from the troposphere to the stratosphere occurs mainly at low altitudes with net downward transport dominating at high altitude.

The thermal structure of the atmosphere can be described by the following balance:

*(heating by absorption of solar radiation  $\Leftrightarrow$  cooling by terrestrial emission in infra-red)*

The stratosphere is heated from above by absorption of ozone by solar ultra-violet radiation. Convection in the stratosphere is suppressed, causing the chemicals to reside there for a longer time than they would if they were in the troposphere. Opposite of the stratosphere is the troposphere. It is heated from below as a result of convective transport and thermal radiation, which is emitted from the Earth's surface. Convection in the troposphere results from the warm air that is in contact with the ground that underlies the colder air above it.

**Figure 3.1:** The vertical profile of mean temperature and the use to define the troposphere and the stratosphere at different latitudes (Sorg, 1988)



## 3.2 CHEMISTRY OF THE TROPOSPHERE

### 3.2.1 TROPOSPHERIC OZONE

Sources of ozone in the troposphere and the photochemical reactions taking place for the production and destruction of ozone are more numerous than in the stratosphere. In situ photochemistry is the dominant source of tropospheric ozone (see Table 3.1); downward flux of stratospheric ozone represents a significant source in the UT and in winter over high altitudes. Removal of tropospheric ozone occurs predominantly by photochemistry, with some contributions from surface deposition (Karol et al., 1999).

**Table 3.1:** Mean Composition of the troposphere and typical trace gas lifetimes

Species	Formula	Volume mixing Ratio	Lifetime
Nitrogen	N <sub>2</sub>	0.781	1.5 x 10 <sup>7</sup> yr
Oxygen	O <sub>2</sub>	0.209	4000 yr
Water Vapor	H <sub>2</sub> O (surface)	0.01	Days
	H <sub>2</sub> O (tropopause)	10 ppmv	Weeks
Argon	Ar	9.3 x 10 <sup>-3</sup>	Accumulation
Carbon Dioxide	CO <sub>2</sub>	360 ppmv	50-200 yr
Methane	CH <sub>4</sub>	1.73 ppbv	9 yr
Nitrous oxide	N <sub>2</sub> O	313 ppbv	130 yr
Ozone	O <sub>3</sub> (surface)	5-50 ppbv	Weeks
	O <sub>3</sub> (tropopause)	100 ppbv	Months
Carbon monoxide	CO (surface)	50-200 ppbv	2 months
	CO (tropopause)	0.01-1 ppbv	0.005 yr
Nitrogen oxides (NO <sub>x</sub> = NO + NO <sub>2</sub> )	NO <sub>x</sub> (surface)	0.01-1 ppbv	Days
	NO <sub>x</sub> (tropopause)	0.05-0.5 ppbv	Weeks
Sulfur dioxide	SO <sub>2</sub> (Surface)	0.01-1 ppbv	Days
	SO <sub>2</sub> (tropopause)	10-50 pptv	Weeks

### 3.2.2 CHEMICAL REACTIONS OF THE TROPOSPHERE

The nature of the atmosphere is an oxidizing one due to the abundance of O<sub>2</sub>, which results from photosynthetic activity. The O<sub>2</sub> found in the atmosphere is relatively inert and the oxidation capacity of the atmosphere results from ozone formation. The atmospheric lifetime of many trace gases are determined by hydroxyl radicals, which are formed by the photolysis of O<sub>3</sub> by ultraviolet radiation (UV) in the presence of H<sub>2</sub>O according to the following reaction:



About three quarters of all OH reacts with CO and CH<sub>4</sub>, destruction of CO and HC's by OH initiates radical reaction sequences in which O<sub>3</sub> is formed and OH is replenished in the presence of NO<sub>x</sub>.

The main reaction pathways in the troposphere are initiated by the following reactions:



Photolysis of  $\text{NO}_2$  by visible light releases  $\text{NO}$  and results in the formation of  $\text{O}_3$ , to yield  $\text{OH}$ , where  $\text{M}$  represents  $\text{N}_2$  or  $\text{O}_2$ .



$\text{CH}_3\text{O}$  is the reaction intermediate and it reacts with formaldehyde ( $\text{CH}_2\text{O}$ ), which in turn photo dissociates by UV and visible light according to the following equation:

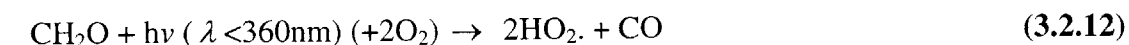


Ozone in the stratosphere is destroyed by catalytic cycles involving homogeneous gas phase reactions of active free radical species ( $\text{HO}_x$ ,  $\text{NO}_x$ ,  $\text{ClO}_x$ ,  $\text{BrO}_x = \text{X}$ ):



$\text{X}$  controls the abundance and the distribution of  $\text{O}_3$  in the stratosphere depending on the rate coefficients and the local abundance of the radicals. The balance between production and destruction of  $\text{O}_3$  is established rapidly on a time scale of less than one day in the upper stratosphere. At lower altitudes production and loss processes slow down so that at altitude below approximately 25 km the local concentration of  $\text{O}_3$  is determined primarily by transport.

The reaction intermediate  $\text{CH}_3\text{O}$  reacts to form formaldehyde ( $\text{CH}_2\text{O}$ ), which in turn will either photo dissociates or react with  $\text{OH}$  to yield  $\text{HO}_2$  :





The hydro-peroxy radical ( $\text{HO}_2$ ) reacts with  $\text{NO}$  to yield  $\text{NO}_2$ .  $\text{NO}_2$  will form  $\text{O}_3$ , which will generate  $\text{OH}$ :

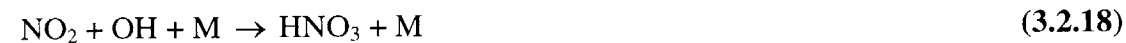


The final reaction product from the oxidation of hydrocarbons (HC's) and  $\text{CO}$  in the atmosphere is  $\text{CO}_2$ :

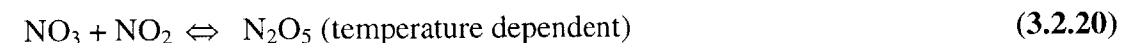


The product,  $\text{HO}_2$ , will convert  $\text{NO}$  to  $\text{NO}_2$  therefore contributing to the formation of  $\text{O}_3$  and the regeneration of  $\text{OH}$ .

The dominant  $\text{NO}_x$  destruction reaction is with  $\text{OH}$  and results in the formation of nitric acid ( $\text{HNO}_3$ ):



Another  $\text{NO}_x$  removal mechanism is heterogeneous destruction on wet surfaces (cloud droplets and aerosols) (Brasseur et al., 1998). This mechanism is initiated by the formation of nitrate radicals:

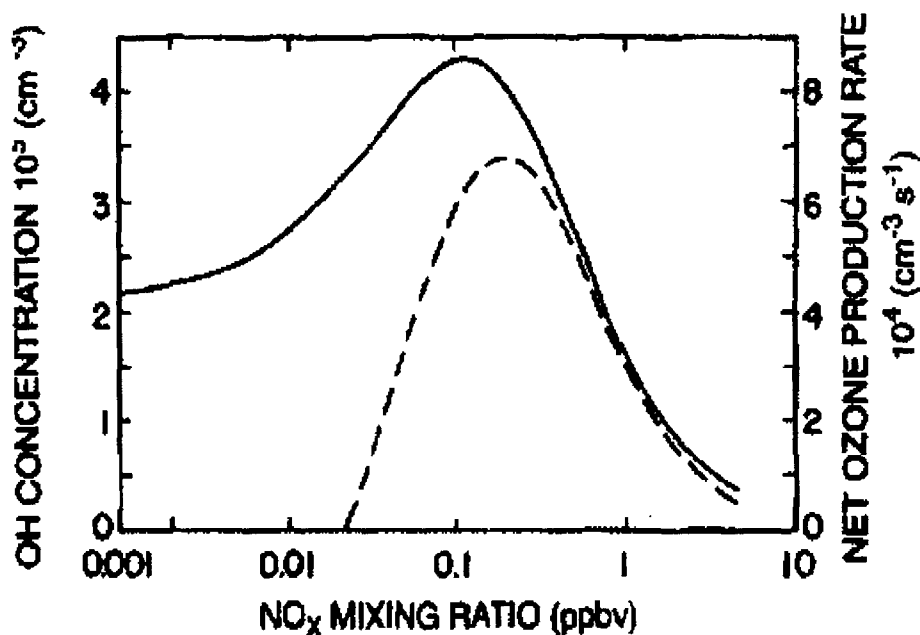


The  $\text{HNO}_3$  formation in the troposphere is considered to be a sink for  $\text{NO}_x$  and  $\text{OH}$  because both the wet and the dry depositions are very efficient  $\text{HNO}_3$  removal processes. However the physical lifetime increases strongly with altitude so that its chemical lifetime gains importance. Therefore in the tropopause region the lifetime of  $\text{HNO}_3$  is mainly determined by photolysis (for example several weeks in mid-latitude summer). In



addition to this *in situ* NO<sub>x</sub> sources such as lightening and aircraft emissions, HNO<sub>3</sub> destruction becomes a dominant NO<sub>x</sub> source, acting as a “reservoir” species (see Figure 3.2)

**Figure 3.2:** Model calculated OH concentration (solid curve) and net photochemical O<sub>3</sub> production rate [P(O<sub>3</sub>)] (dashed curve) as a function of ambient NO<sub>x</sub> (Ehhalt and Rohrer, 1995). Conditions represent the lower mid-latitude troposphere during spring. OH and P(O<sub>3</sub>) increase at NO<sub>x</sub> mixing ratios up to 0.1 – 0.2 ppbv, whereas they decrease at further addition of NO<sub>x</sub>

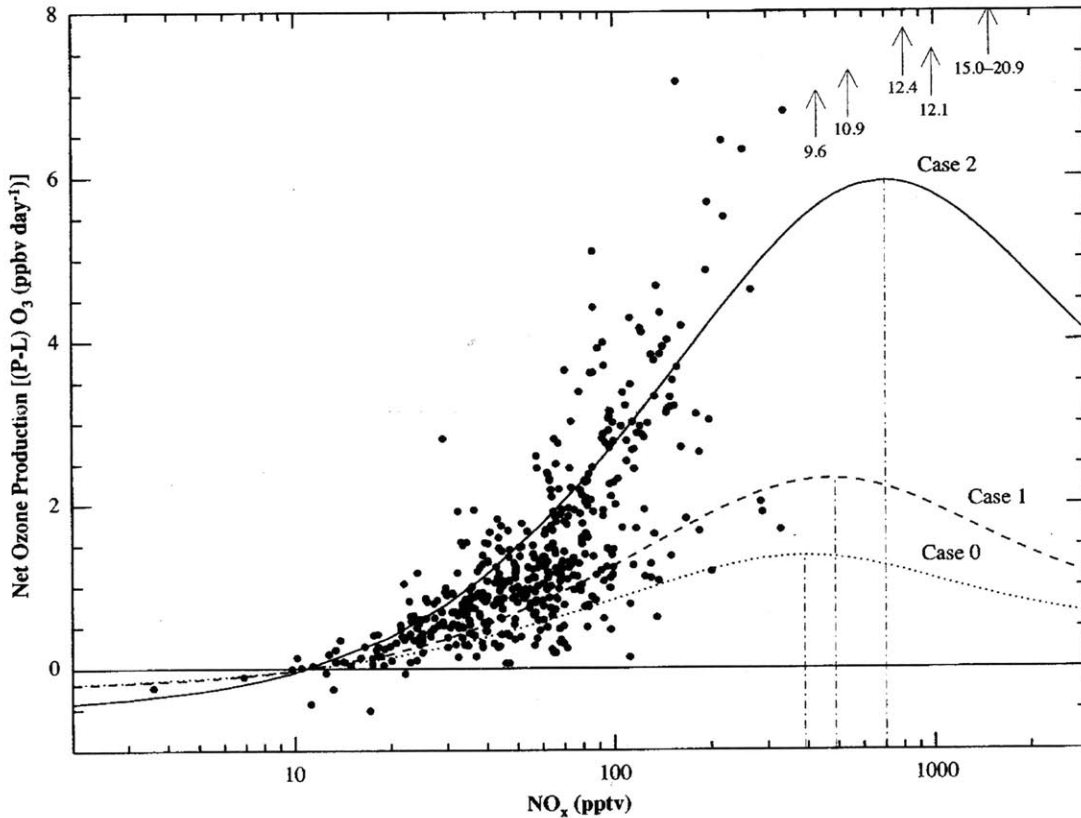


### 3.2.3 OZONE RESPONSE TO NO<sub>x</sub> IN THE UPPER TROPOSPHERE

The availability of NO<sub>x</sub> is a controlling factor in photochemical O<sub>3</sub> formation and the concentration of OH. At low ambient NO<sub>x</sub> mixing ratios emissions of NO<sub>x</sub> can enhance O<sub>3</sub> production. Both OH and O<sub>3</sub> are enhanced through NO<sub>x</sub> emissions at ambient levels below 0.1-0.2ppbv. This efficiency is reduced when NO<sub>x</sub> increases. At NO<sub>x</sub>

concentrations larger than 500 pptv, the net rate of ozone production is expected to decrease with increasing  $\text{NO}_x$ . Depending on the background concentration of  $\text{NO}_x$ , additions of  $\text{NO}_x$  from aviation can increase or decrease the net ozone production rate. Therefore one can say that the background concentration of  $\text{NO}_x$  determines both the magnitude and the sign of the perturbation. Field measurements of  $\text{NO}_x$  in the middle and upper troposphere typically have found  $\text{NO}_x$  to be 50-200 pptv (*Emmons et al., 1997*). Therefore at these concentrations, the rate of net ozone production increases almost linearly with  $\text{NO}_x$  (see Figure 3.3). Therefore it is important to accurately determine the amount of  $\text{NO}_x$  and the  $\text{NO}_x$  reservoir species near the tropopause to quantify photochemical processes and assess the  $\text{O}_3$  and OH perturbations caused by aircraft emission of  $\text{NO}_x$ .

**Figure 3.3:** Net ozone production (24-hr average) as a function of  $\text{NO}_x$  in the upper troposphere (Jaegle et al., 1998). Case 0 illustrates the production rate expected if the only primary source of  $\text{HO}_x$  is the reaction of  $\text{O}^1\text{D}$  with  $\text{H}_2\text{O}$  and  $\text{CH}_4$ . Case 1 is the rate calculated by assuming acetone is present at 510 ppbv, consistent with recent airborne measurements (Singh et al., 1995; Arnold et al., 1997). Case 2 assumes that a convective source of peroxide and formaldehyde provides additional  $\text{HO}_x$  production. These non-traditional  $\text{HO}_x$  sources dramatically increase the ozone production rate in the dry (100 ppmv  $\text{H}_2\text{O}$ ) upper troposphere



### 3.3 CHEMISTRY OF THE STRATOSPHERE

#### 3.3.1 STRATOSPHERIC OZONE

Approximately 80% of atmospheric ozone resides in the stratosphere, where it is produced via in situ photochemistry occurring predominantly in the tropical middle stratosphere. Stratospheric circulation patterns transport ozone from the tropical stratosphere pole ward and then downward from mid-stratosphere.

Ozone formation and destruction rates increase with height and change with latitude in the stratosphere. Consequently ozone “lifetime” decreases with height from about a year in the lower stratosphere to minutes in the upper stratosphere. At the uppermost altitudes, ozone lifetime is short, that its abundance is in local photochemical equilibrium (WMO-UNEP, 1985). At lower altitudes, ozone is not in photochemical steady state, and ozone transport by air motions of various scales becomes very important (see Table 3.2) (Karol et al., 1999).

The chemistry of the stratosphere, relating to the photochemical production and catalytic destruction of ozone is described by a highly complex and coupled system involving a large number of elementary gas phase reactions. Ozone is present in the Earth’s atmosphere at all altitudes ranging from the surface and up to at least 100km. The majority of O<sub>3</sub> resides in the stratosphere with the maximum concentration of 5x10<sup>12</sup> molecules/ cm<sup>3</sup> found at approximately 25km. This concentration of O<sub>3</sub> is controlled chemically by a number of trace species.

**Table 3.2:** Approximate trace gas composition of the stratosphere

Trace gas	Mixing Ratio (ppb)		
	40 km	25 km	15 km
O <sub>3</sub>	5100	5900	89
N <sub>2</sub> O	21	150	300
NO	10	1.1	0.25
NO <sub>2</sub>	3.7	1.2	0.19
HNO <sub>3</sub>	4.2	6.9	0.94
H <sub>2</sub> O	5000	3500	6000 to 40,000
OH	0.12	9.5 x 10 <sup>-4</sup>	3.5 x 10 <sup>-5</sup>
HO <sub>2</sub>	9.8 x 10 <sup>-2</sup>	6.7 x 10 <sup>-3</sup>	1.7 x 10 <sup>-4</sup>
HCl	1.4	0.81	0.06
ClO	1.0	0.04	
ClONO <sub>2</sub>	3.0 x 10 <sup>-2</sup>	0.83	
CH <sub>4</sub>	300	940	1500
CO	25	20	50
H <sub>2</sub>	600	500	500

### 3.3.2 CHEMICAL REACTIONS OF THE STRATOSPHERE

The governing chemical reaction for O<sub>3</sub> formation in the stratosphere is:



At around 20km the net production of O atoms results mainly from the photo dissociation of O<sub>2</sub> by short wavelength ultraviolet radiation.



At lower altitudes (troposphere) O atoms are formed by the photo dissociation of nitrogen dioxide by long wavelength ultraviolet radiation:



Ozone photo dissociates by both UV and visible light to form:



Ozone in the stratosphere is destroyed by catalytic cycles that involve homogeneous gas-phase reactions of the active free radical species X= HO<sub>x</sub>, NO<sub>x</sub>, ClO<sub>x</sub>, BrO<sub>x</sub>, as described by the following chemical reaction:



The reaction (\*) controls the abundance and distribution of O<sub>3</sub> in stratosphere depending on the rate coefficients and the local abundance of the radicals. The balance between the production and destruction of O<sub>3</sub>, is established rapidly on a time scale of less than one day in the upper stratosphere. At lower altitudes production and loss processes slow down so that at altitudes below 25km the local concentration of O<sub>3</sub> is determined primarily by transport (Brasseur et al., 1998).

### *Sources and Sinks of HO<sub>x</sub>:*

The main reservoir species for HO<sub>x</sub> in the stratosphere is water vapor. Active HO<sub>x</sub> species are released by the reaction of H<sub>2</sub>O with excited atomic oxygen:



The two important O<sub>3</sub> destruction cycles involving HO<sub>x</sub> occur in the upper stratosphere and the O<sub>3</sub> destruction is predominantly caused by:



In the lower stratosphere, oxygen is not abundant and the following reaction occurs:



The removal of HO<sub>x</sub> occurs by the following reaction:



### *Sources and Sinks of NO<sub>x</sub>:*

The main reservoir species for NO<sub>x</sub> in the stratosphere is N<sub>2</sub>O and the reactive species are released by reaction with O (<sup>1</sup>D):



The following catalytic cycle occurs and it is the dominant ozone loss process in the middle stratosphere (≈ 25- 35 km):



At lower altitudes the concentration of oxygen is lower, therefore photo dissociation of  $\text{NO}_2$  nullifies the odd oxygen removal effect since the ground state oxygen atoms are produced according to the following reaction:

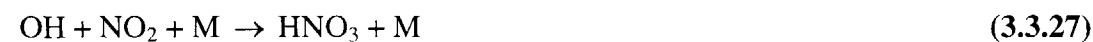


In the lower stratosphere and the troposphere, coupling of NO chemistry with  $\text{HO}_x$  chemistry and CO oxidation, gives rise to the net production of ozone.



The change from net  $\text{O}_3$  production to net  $\text{O}_3$  destruction resulting from  $\text{NO}_x$  chemistry occurs in the lowermost region of the stratosphere. As with the tropopause height, the location of the change over point depends on the altitude and the season (Brasseur et al., 1998). This point is crucial in determining the direct influence of aircraft emissions of  $\text{NO}_x$  on local ozone concentration.

The main reservoir species for NO is nitric acid. Nitric acid is formed in a reaction that couples the  $\text{HO}_x$  and  $\text{NO}_x$  families:



Active nitrogen species are only slowly regenerated from  $\text{HNO}_3$  by photolysis and reaction with OH:



The coupled NO<sub>x</sub>-HO<sub>x</sub> schemes also control the abundance of OH and HO<sub>2</sub> in the lower stratosphere, through conversion of active species to H<sub>2</sub>O. This is counterbalanced through heterogeneous reactions between H<sub>2</sub>O and NO<sub>x</sub>, ClO<sub>x</sub> and BrO<sub>x</sub> species, which lead to the photolytic production of HO<sub>x</sub> (Brasseur et al., 1998).

The major source of stratospheric chlorine is photo dissociation of organic chlorine compounds such as methyl chloride, other chlorinated hydrocarbons and chlorofluorocarbons:



The ozone destruction cycle involves Cl and ClO radicals:

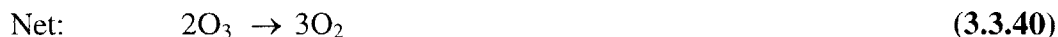


This effect is modified in the presence of NO<sub>x</sub>:



NO<sub>x</sub> offsets the odd oxygen loss. Therefore the extent of ozone destruction at a particular altitude by ClO<sub>x</sub> depends on the amount of NO<sub>x</sub> present.

In recent years it is apparent that ozone loss has occurred in the lower stratosphere and in the mid-latitudes of both hemispheres. The main gas-phase reactions leading to ozone loss in the mid-latitude lower stratosphere involve the HO<sub>x</sub> species:





Attempts to explain quantitatively the trends in lower stratospheric ozone in recent years are through the use of models. But these models, which usually include the above heterogeneous chemistry, have not been successful. Ozone loss appears to have been greater than predicted. The region of greatest uncertainty coincides with that where there is growing extent of aviation activity, which is predicted to increase in the future. The central issue of aircraft emission can potentially influence the level of  $\text{NO}_x$  and atmospheric particles.

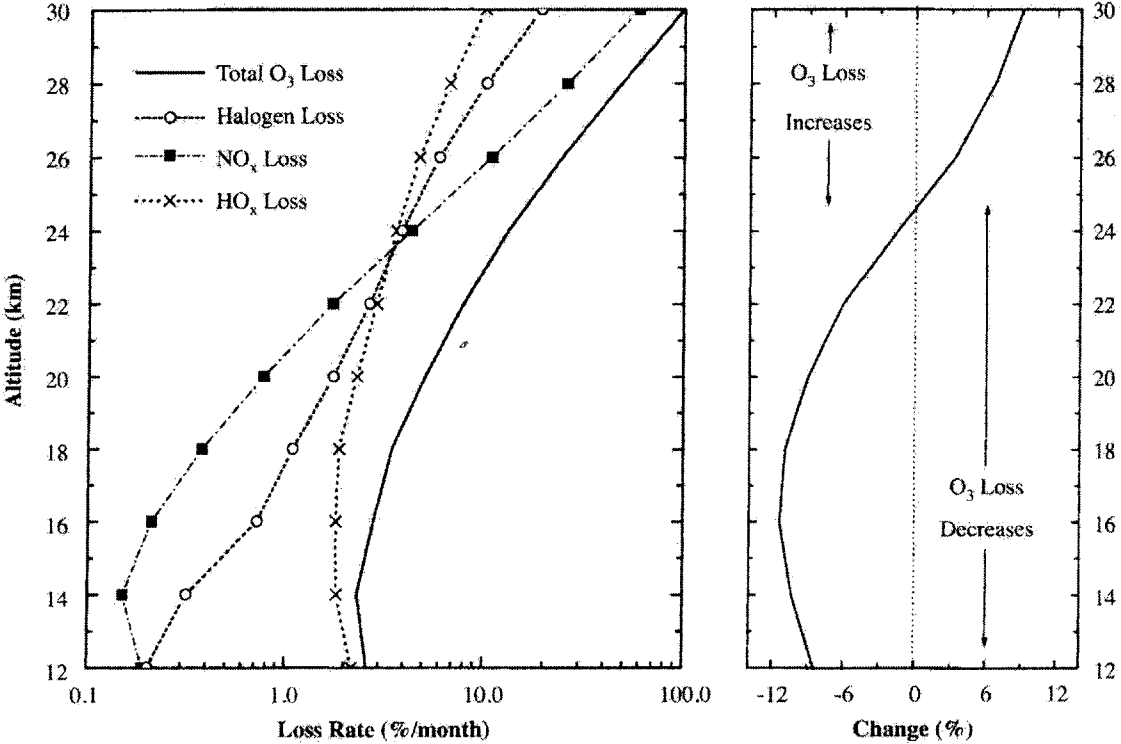
### **3.4 NET EFFECTS OF AIRCRAFT $\text{NO}_x$ EMISSIONS ON THE UPPER TROPOSPHERE AND LOWER STRATOSPHERE**

If the direct impact of aircraft on the chemistry of the UT is an increase in concentration of  $\text{NO}_x$ , one can conclude that the ozone concentration in this region will be higher than they would be in the absence of aviation. This increase occurs because NO speeds the catalytic oxidation rate of CO and reduces the destruction rate of ozone by  $\text{HO}_x$  and halogens (primarily in the stratosphere). The quantitative change in ozone from present aircraft operation is very sensitive to the meteorology of this region of the atmosphere; longer residence times will lead to larger  $\text{NO}_x$  increases and therefore higher ozone (see Table 3.3 and Figure 3.4).

**Table 3.3:** Estimated trace gas sources (IPCC, 1994; WMO, 1995; Lee et al., 1997)

Source	CO <sub>2</sub> (Pgyr <sup>-1</sup> ) (Tgyr <sup>-1</sup> )	CH <sub>4</sub> (Tgyr <sup>-1</sup> ) (TgCyr <sup>-1</sup> )	CO (TgCyr <sup>-1</sup> )	NHMHC (TgNyr <sup>-1</sup> )	NO <sub>x</sub>
Energy use	5.5(5-6)	100(70-120)	500(300-900)	70(60-100)	22(20-24)
Aircraft					0.6(0.4-0.9)
Biomass burning	1.6(0.6-2.6)	40(20-80)	600(400-700)	40(30-90)	
Vegetation					
Soils					7(5-12)
Lightening					5(2-20)
Enteric fermentation		85(65-100)			
Rice paddies		60(20-100)			
Animal waste		30(20-40)			
Landfills		40(20-70)			
NH <sub>3</sub> oxidation					0.9(0-1.6)
N <sub>2</sub> O destruction					0.6(0.4-1)
Domestic sewage		25(20-30)			
Wetlands		115(55-150)			
Oceans		10(5-50)	50(20-200)	50(20-150)	
Freshwaters		5(1-10)			
Termites		20(10-50)			
Total	7.1(6-8.2)	530(450-620)	1250(780-1960)	660(340-1140)	44(30-73)

**Figure 3.4:** In the stratosphere,  $\text{NO}_x$  both catalytically destroys ozone and acts to interfere with the destruction of ozone by reaction of  $\text{HO}_x$  and halogens. Shown is a calculation of the rate of ozone loss in the lower stratosphere for springtime mid-latitude conditions during March. The loss from each family is illustrated. Ozone loss in the lowermost stratosphere is quite slow (a few percent per month). The right panel shows the effect on the removal rate of ozone when 20% more reactive nitrogen is added to the stratosphere uniformly (calculations provided by R. Salawitch using 1D-trajectory model)



## **CHAPTER 4**

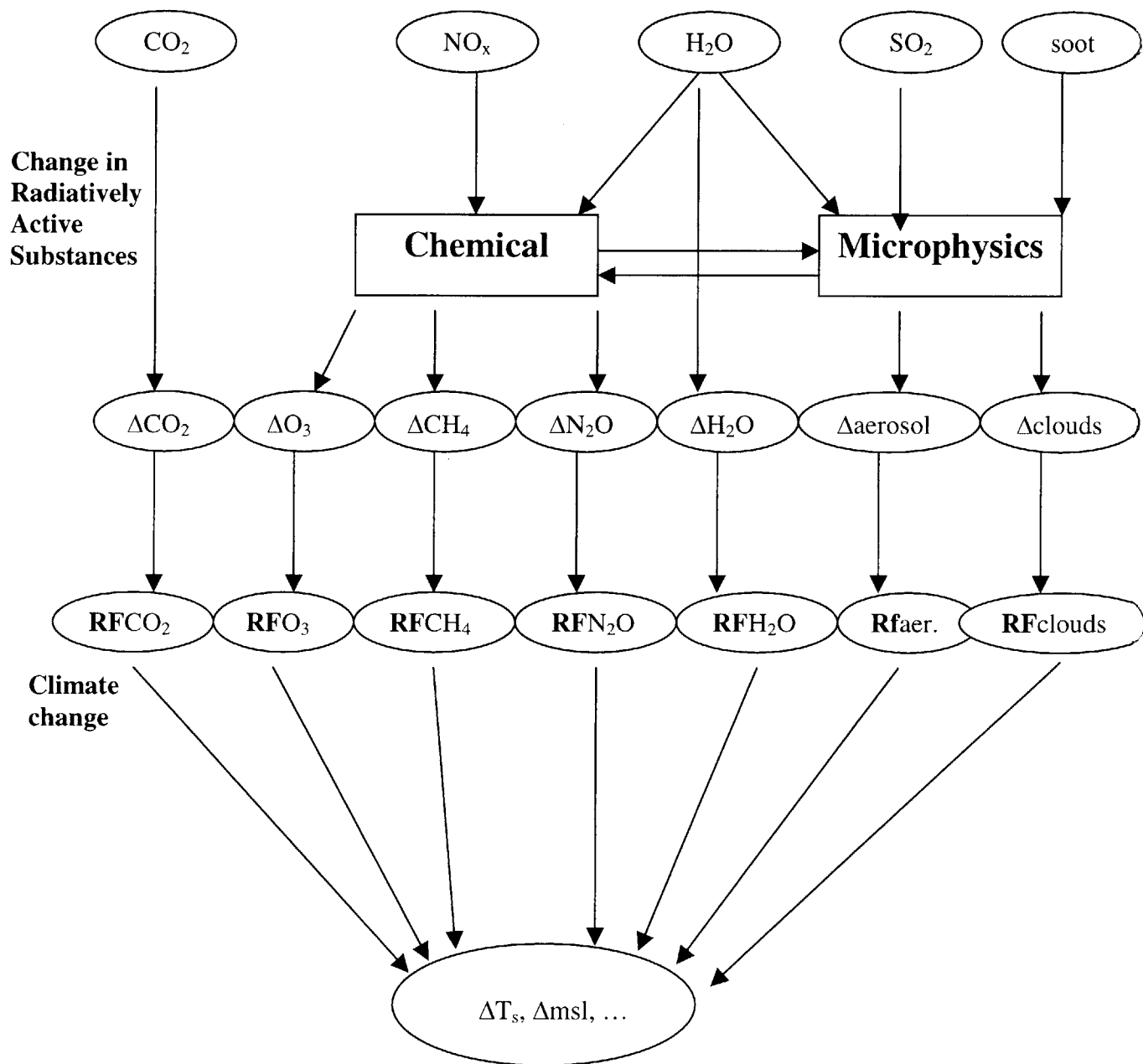
### **CLIMATE IMPACT OF AIRCRAFT NO<sub>x</sub> EMISSIONS**

The two global environmental issues related to aviation are climate change and increase in UV-radiation at the Earth's surface. A change in climate according to the UNFCCC definition is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and which is in addition to natural climate variability observed over comparable time period (see Figure 4.1).

The earth absorbs radiation from the sun, mainly at the surface. The energy absorbed is redistributed by atmospheric and oceanic circulation and is radiated to space at large (terrestrial or infrared) wavelengths. On average, the incoming solar energy is balanced by outgoing terrestrial radiation. Any factor that alters radiation received from sun or lost to space or the redistribution of energy within the atmosphere and between the atmosphere, land and ocean can affect the climate. A change in radiative energy available to the global Earth/atmosphere system is defined as radiative forcing. Hence, radiative forcing (RF) is the global, annual, average of radiative imbalance ( $\text{Wm}^{-2}$ ) in net heating of the Earth's lower atmosphere as a result of human activities since the beginning of the industrial era almost two centuries ago.

The climate impacts of the gases and particles emitted and formed as a result of aviation are difficult to quantify. They can be compared to each other and to climate effects from other sectors by using the concept of radiative forcing. Radiative forcing is a measure of the importance of a potential climate change mechanism. It expresses the perturbation or change to the energy balance of the Earth-atmosphere system in watts per square meter ( $\text{Wm}^{-2}$ ).

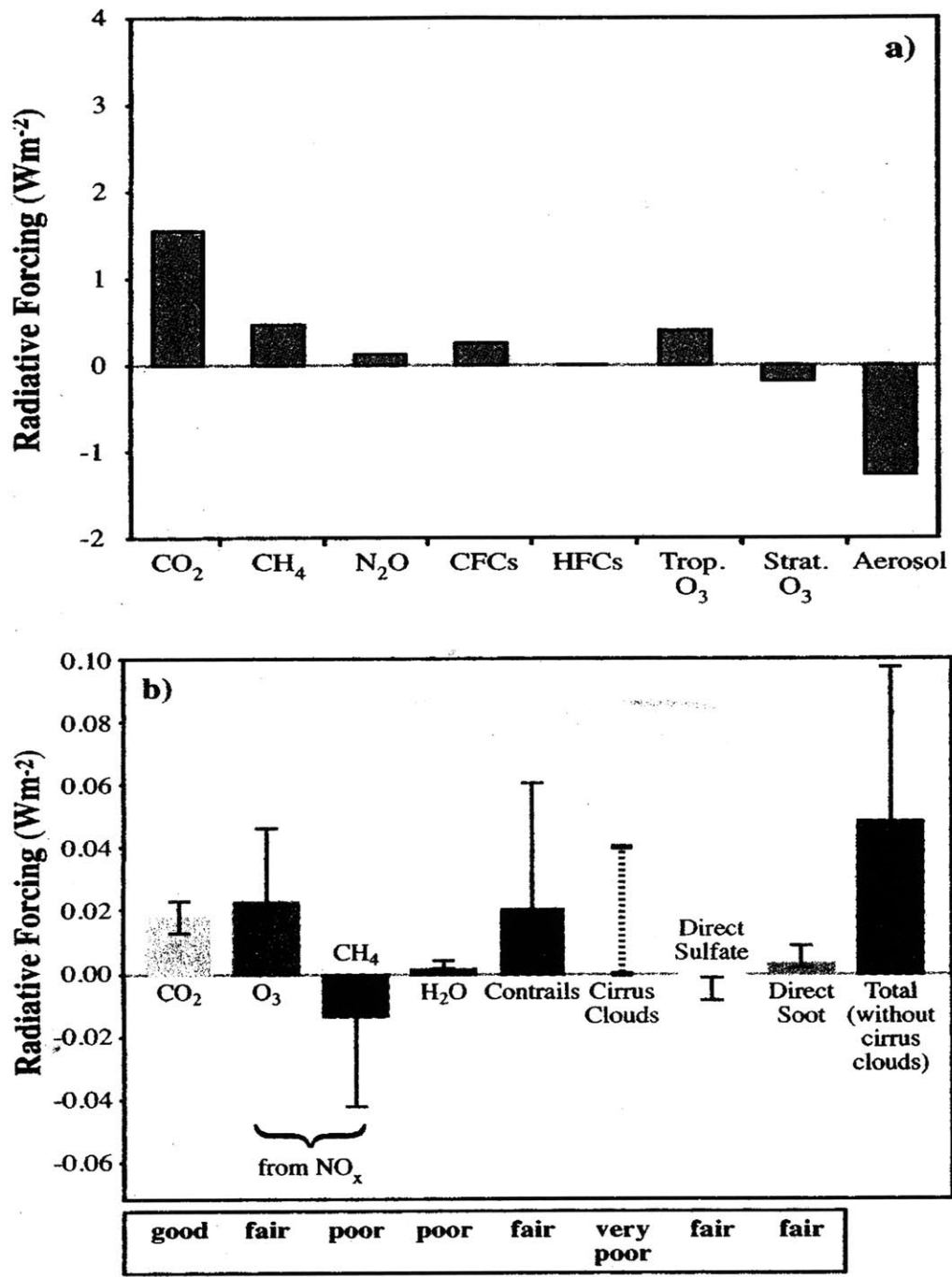
**Figure 4.1:** Schematic of possible mechanisms whereby aircraft emissions impact climate. Climate impact is represented by changes in global mean surface temperature ( $\Delta T_s$ ) and global mean sea level rise ( $\Delta msl$ )



## 4.1 DEFINITION OF RADIATIVE FORCING

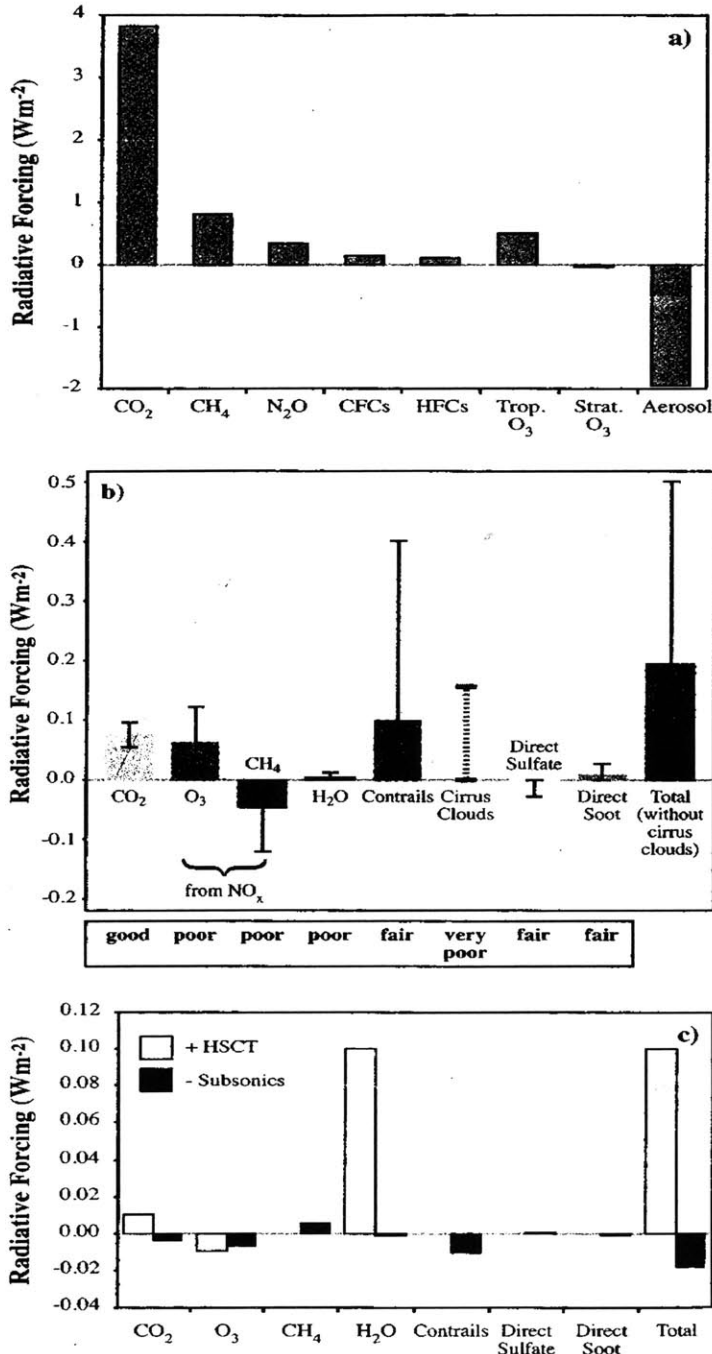
A change in average net radiation at the tropopause, due to changes in the fluxes of either long wave or short wave, or both, has been defined as a radiative forcing of climate (Houghton et al., 1990, 1994). A radiative forcing disturbs the energy balance of the troposphere/stratosphere system, but over time a new balance is established as climate responds to the radiative forcing. A positive radiative forcing means that more energy is trapped in the troposphere/stratosphere climate system. A negative radiative forcing will have a cooling effect. Radiative forcing gives a first order estimate of the climate change potential of the mechanism under consideration. A radiative forcing of the climate initiates a climate response, but there are significant uncertainties related to the magnitude of such responses since they are determined by several complex feedback processes (Fuglestedt et al., 1999).

Aircraft emissions are expected to modify the Earth's radiative budget and climate as a result of several processes (see Figure 4.2 and 4.3): emission of radiatively active substances such as CO<sub>2</sub> and H<sub>2</sub>O; emission of chemical species that produce or destroy radiatively active substances such as NO<sub>x</sub>, which will modify the O<sub>3</sub> concentration, or SO<sub>2</sub>, which will oxidize sulfate aerosols; and emission of substances for example H<sub>2</sub>O and soot which will trigger the generation of additional clouds for example contrails.



**Figure 4.2:** Bar charts of radiative forcing from (a) all perturbation in 1990 (from IPCC, 1996) and (b) aviation effects in 1992.

**Figure 4.3:** Bar charts of radiative forcing in 2050 (a) from all perturbations (from IPCC, 1996), (b) from subsonic aviation, and (c) from additional effect due to supersonic air traffic





## 4.2 INDIRECT RADIATIVE FORCING OF NO<sub>x</sub>

NO<sub>x</sub> affects the climate indirectly by affecting the concentrations of other climate gases through complex chemical processes in the atmosphere. Through the production of tropospheric O<sub>3</sub>, NO<sub>x</sub> emissions lead to positive radiative forcing of the climate. But by affecting the concentration of OH radicals, NO<sub>x</sub> reduces the levels of CH<sub>4</sub> thereby giving negative radiative forcing and therefore cooling (See Figure 4.4, Table 4.1,4.2).

Fishman et al. first pointed out the climate significance of tropospheric ozone changes in 1979. He demonstrated that ozone was an important greenhouse gas. Radiative forcing due to tropospheric ozone is most sensitive to ozone concentrations at a height of about 12km (*Lacis et al., 1990*), where aircraft emissions are at a maximum and where ozone production is most efficient.

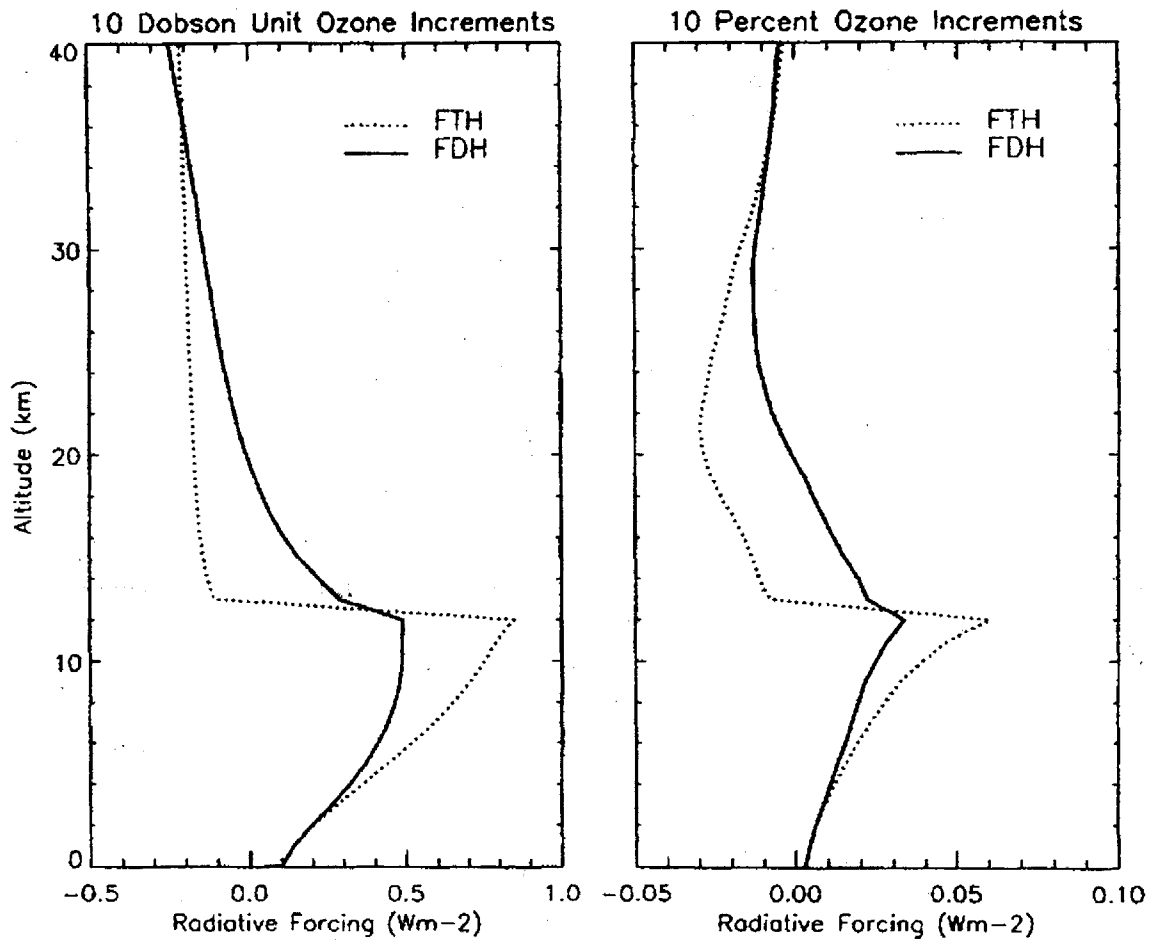
**Table 4.1:** Maximum ozone change in the upper troposphere at mid-latitude associated with present aircraft emissions and corresponding annual radiative forcing calculated with different models

Reference	Ozone Change (%)	Radiative Forcing (Wm <sup>-2</sup> )
Johnson et al. 1992	15	0.047
Hauglustaine et al. 1994a	7	0.05
Fortuin et al. 1995	10-15	0.023
Brasseur et al. 1996	4	0.015
Stevenson et al.	9	0.05

**Table 4.2:** Globally averaged tropospheric ozone radiative forcing associated with various future scenarios of subsonic aircraft emission increase calculated by different models

Reference	Change in NO <sub>x</sub> emission (%)	Radiative Forcing (Wm <sup>-2</sup> )
Mohnen et al. 1993	100	0.04-0.07
Derwent 1994	10	0.006
Fuglestvedt et al. 1996	70	0.02
Brasseur et al. 1996	85	0.011

**Figure 4.4:** Radiative forcing at the tropopause as a function of the altitude where the ozone perturbation is applied (mid-latitude summer conditions). In (a), a 10 Dobson unit (where 1 DU =  $2.69 \times 10^{16}$  molcm<sup>-2</sup> in the vertical column) increment is successively added over a 1 km thick layer and in (b) a 10% increment over a 1 km thick layer is considered.



### 4.3 MODEL RESULTS OF RADIATIVE FORCING DUE TO NO<sub>x</sub> EMISSIONS

Ozone is a complex radiatively active gas, absorbing both incoming short-wave solar radiation and outgoing long-wave infrared radiation. Lacis et al. (1990) calculated the radiative sensitivity of global surface temperature changes in the vertical ozone distribution, using a one-dimensional radiative-convective model. He showed that the radiative forcing was positive for increase in ozone below about 30km, with the greatest sensitivity at the tropopause. This is because the radiative forcing is proportional to the difference in the temperature of the radiation absorbed by the ozone (i.e. the radiation emitted from the Earth's surface), and the radiation emitted by the ozone (which depends upon the temperature of the molecule). The greatest difference between surface and atmospheric temperature is found at the tropopause, the approximate height of maximum aircraft emissions, and maximum ozone production.

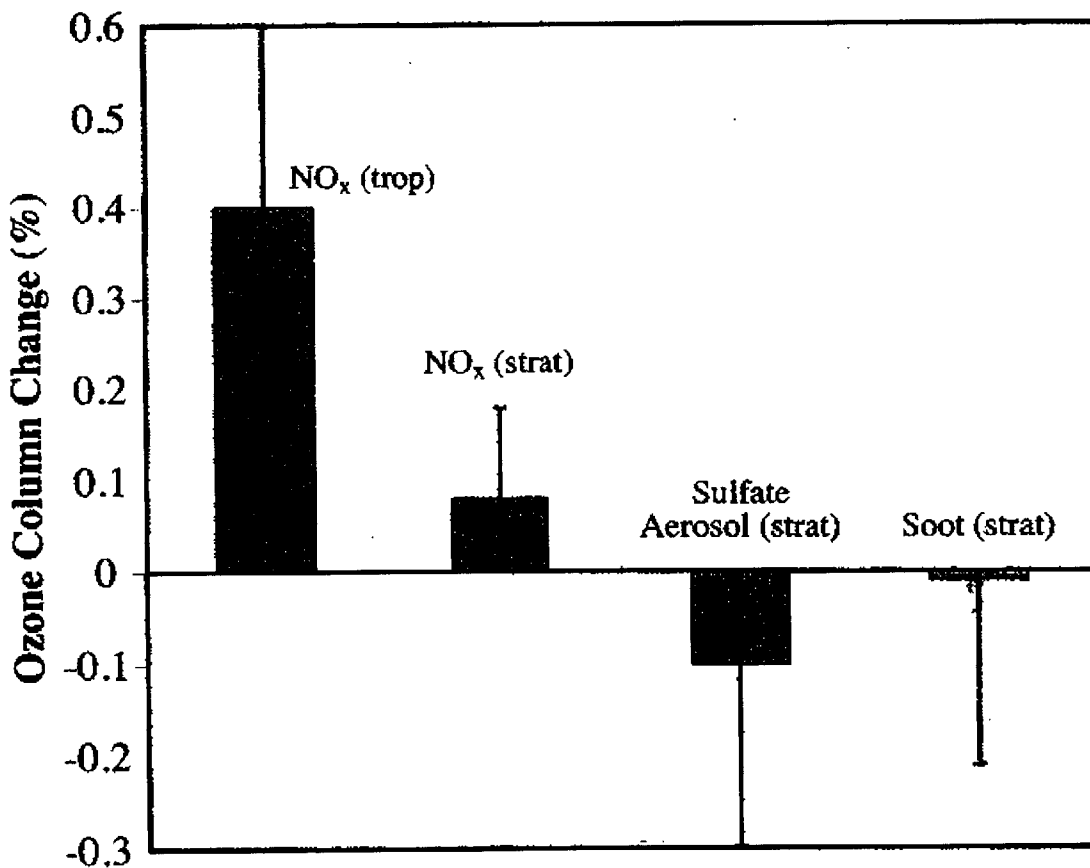
Ozone changes predicted by STOCHEM due to aircraft NO<sub>x</sub> emissions cause a global annual mean radiative forcing of 0.05 Wm<sup>-2</sup>, concentrated in the Northern hemisphere. The calculated forcing peaks at about 0.2 Wm<sup>-2</sup> over Eurasia in April, and 0.12-0.15 Wm<sup>-2</sup> over the North Pole in June (see Figure 4.5).

A three-dimensional Lagrangian tropospheric chemistry-transport model has been developed and used to investigate the role of NO<sub>x</sub> emissions from aircraft on tropospheric oxidant concentrations and to study the changes produced in the ozone production and loss. The model resolves diurnal variations in chemistry, and includes 50 trace gases. The model simulations show that aircraft NO<sub>x</sub> emissions exert significant influence on tropospheric chemistry and local changes to NO<sub>x</sub> concentrations at 250hPa being greater than 50 ppt over Europe, North America and the Atlantic, equivalent total about

NO<sub>x</sub> has a short atmospheric residence time and remains concentrated near flight routes, mainly in the northern mid-latitudes. The lifetime of NO<sub>x</sub> varies from hours to days, giving large spatial variations in the levels of NO<sub>x</sub> (*Fuglestad et al., 1999*).

Ozone is a potent greenhouse gas whose concentration is highly variable and controlled by atmospheric chemistry and dynamics. Aircraft emissions of  $\text{NO}_x$  accelerate local photochemical production of  $\text{O}_3$  in the troposphere; modeling studies suggest that these emissions are responsible today for average  $\text{O}_3$  enhancement of 2-5 ppbv in the middle troposphere at northern mid-latitudes, where aircrafts fly. The ozone increase will generally be proportional to the amount of  $\text{NO}_x$  emitted (Grewe et al., 1999), but evolving atmospheric composition, including increased in surface sources of combustion-related  $\text{NO}_x$ , will affect the aircraft impact.

**Figure 4.5:** Estimate of northern mid-latitude total ozone column change (%) from  $\text{NO}_x$  emission in the troposphere and stratosphere and aerosol emissions in the stratosphere from present subsonic aviation



## CHAPTER 5

### CONCLUSION

The gradual development over the past decades of a large fleet of commercial aircraft has introduced the potential for environmental perturbations at the global scale. With increasing air traffic, aircraft operations have already produced and will produce in the future significant changes in the abundance of upper-tropospheric/ lower-stratospheric ozone as well as in the radiative forcing of the climate system.

This study presented an overview of the chemistry occurring in the upper troposphere and lower stratosphere. It has shown that  $\text{NO}_x$  emissions from present subsonic and supersonic aircraft lead to increase  $\text{NO}_x$  and ozone concentrations at cruise altitudes, especially in air traffic corridors between and over Northern Hemisphere continents and at altitudes of 9–13 km. This is verified by model calculations, which show that ozone increases from aircraft  $\text{NO}_x$  have been on the order of 8 ppb, equivalent to 6% of the ozone density in the principle traffic areas. This study has also shown that  $\text{NO}_x$  emissions from aircrafts affect the climate indirectly by affecting the concentration of other climate gases through complex chemical processes in the atmosphere. Through the production of tropospheric  $\text{O}_3$ ,  $\text{NO}_x$  emissions lead to positive radiative forcing of the climate. But by affecting the concentrations of OH radicals,  $\text{NO}_x$  reduces the levels of  $\text{CH}_4$  therefore giving negative radiative forcing and cooling.

## **CHAPTER 6**

### **RECOMMENDATIONS**

Large uncertainties still remain and must be addressed in the future for quantifying the atmospheric impact of present and future fleet of aircraft. More reliable predictions of future change in the lower stratosphere and upper troposphere will only be possible if fundamental processes occurring in the atmosphere are better understood.

Since it remains difficult to establish experimentally the response of the atmosphere to chemical emissions by the current fleet of aircraft, observational approaches based on careful analyses of case studies with detailed knowledge of meteorological situations should be used along with models. Models are needed for the understanding of these atmospheric measurements and are so far the only tools available to make predictions of future perturbations. Since the global chemical transport models of the atmosphere and climate models are still in their early development, further evaluations and improvements of these models are required.

## REFERENCES

- Albritton, D. L., Brune, W.H., Douglas, R. C., Prather, M. J., Ravishankara, A. R., Rood, R. B., Stolarski, R. S., Watson, R. T. and Wuebbles, D. J. (1993) The atmospheric effects of stratospheric aircraft. Interim Assessment Report of the NASA High Speed Research Program, NASA Reference Publication 1333.
- Albritton, D., Amanatidis, G., Angeletti, G., Crayston, J., Lister, D., McFarland, M., Miller, J., Ravishankara, A., Sabogal, N., Sundararaman, N. and Wesoky, H. (1997) Global atmospheric effects of aviation. Proceedings of the Symposium, Virginia Beach, Virginia, 15- 19 April 1996, NASA CP-3351
- ANCAT (1995) A global inventory of aircraft NO<sub>x</sub> emissions- a first version (1994) prepared for the AERONOX research project. In The Impact of NO<sub>x</sub> Emissions from Aircraft Upon the Atmosphere at Flight Altitudes 8-15 km (AERONOX), ed U. Schumann, pp. 129-194
- Anderson, M. R., Miake-Lye, R. C., Brown, R. C. and Colb, C. E. (1996) Calculations of exhaust plume structure and emission on the ER 2 aircraft in the stratosphere. *Journal of Geophysical Research* 101, 4025-4032.
- Baughcum, S. L., Chan, D. M., Happenny, S. M., Henderson, S. C., Hertel, P. S., Higman, T., Maggiora, D. R. and Oncina, C. A. (1993) Emissions scenarios development: scheduled 1990 and projected 2015 subsonic, March 2 and March 4 aircraft. The Atmospheric Effects of Stratospheric Aircraft: A Third Program Report. NSAS References Publication 1313, pp. 89- 131.
- Beirer, K. and Schreier, F. (1994) Modeling of aircraft exhaust emissions and infrared-spectra for measurements of nitrogen oxides. *Annales Geophysicae* 12, 920-943.
- Bernsten, T. and Isaksen, I. S. A. (1997) A global 3-D chemical transport model to the troposphere: 1. Model description and CO and ozone results. *Journal of Geophysical Research* (in press).
- Borrman (1992) Control of combustion-generated nitrogen oxides emissions: technology driven by regulation. 24<sup>th</sup> Symposium (international) Combustion, The Combustion Institute, Pittsburgh.
- Brasseur, G., Muller, J. F., and Granier, C. (1996) Atmospheric impact of NO<sub>x</sub> emissions by subsonic aircraft: a three-dimensional model study. *Journal of Geophysical Research* 101, 1423-1428.
- Chalita, S., Hauglustaine, D. A., Le Treut, H. and Muller J. F., (1996). Radiative forcing due to increased tropospheric ozone concentrations. *Atmospheric Environment* 30, 1641-1646.

- Crutzen, P. J., Lelieveld, J. and Bruhl, C. (1994) Oxidation processes in the atmosphere and the role of human activities: observations and model results, In Environmental Oxidants, eds J. O. Nriagu and M. S. Simmons, pp. 63-93, Wiley, New York
- Crutzen P. J. (1971) Ozone production rates in an oxygen, hydrogen, nitrogen-oxide atmosphere. *Journal of Geophysical Research* 76, 1173-1177.
- Danilin, M., Grewe, V., Kohler, I., Sausen, R., Bruhl, C., Gorss, J. U., and Steil, B. (1998) Impact of aircraft NO<sub>x</sub> emissions on tropospheric and stratospheric ozone. Part II: 3-D model results. *Atmospheric Environment* 32, in press.
- Derwent, R. G. (1982) Two dimensional model studies of the impact of aircraft exhaust emissions on tropospheric ozone. *Atmospheric Environment* 16, 1997-2007
- Fuglestvedt, J. S., Isaksen, I. S. A. and Wang, W. C. (1996) Estimates of indirect global warming potentials for CH<sub>4</sub>, CO and NO<sub>x</sub>. *Climate Change* 34, 405-437.
- Gardner, R. M., Adams, J. K., Cook, T., Falk, R. S., Fleuti, E., Forsch, W., Larson, L. C., Lecht, M., Lee, D. S., Leech, M., Lister, D. H., Masses, B., Morris, K., Newton, P. J., ten Have, H., Schmitt, A., Vandenburg, C. (1995) A global inventory of aircraft NO<sub>x</sub> emissions in The Impact of NO<sub>x</sub> Emissions from Aircraft upon the Atmosphere at Flight Altitudes 8- 15 km, ed U. Schumann, pp. 129-194.
- ICAO (1981) Annex 16, Vol. II, Environmental Protection: Aircraft Engine Emissions, 1<sup>st</sup> Edn, Montreal.
- ICAO (1995a) CAEP/ Working Group 3 Meeting, Bonn, Germany 1995: Combined Report of the Certification and Technology Subgroups, Working Paper 2, Montreal.
- ICAO (1995b) Aircraft engine exhaust emissions databank (i) 1<sup>st</sup> Edn, Doc 9646-AN/943,1995 and (ii) Addendum 1; CAEP/3- IP/13, Montreal.
- IPCC (1992) Radiative forcing of climate, in climate change 1992. The Supplementary Report to the IPCC Scientific Assessment, Cambridge University Press.
- Isaksen, I. S. A (ed) (1988) Tropospheric Ozone. Regional and Global Scale Interaction, NATO ASI Series. Reidel, Dordrecht.
- Kasibhatla, P. S. (1993) NO<sub>y</sub> from subsonic aircraft emissions: A global 3-dimensional study. *Geophysical Research Letters* 21, 1707-1710.

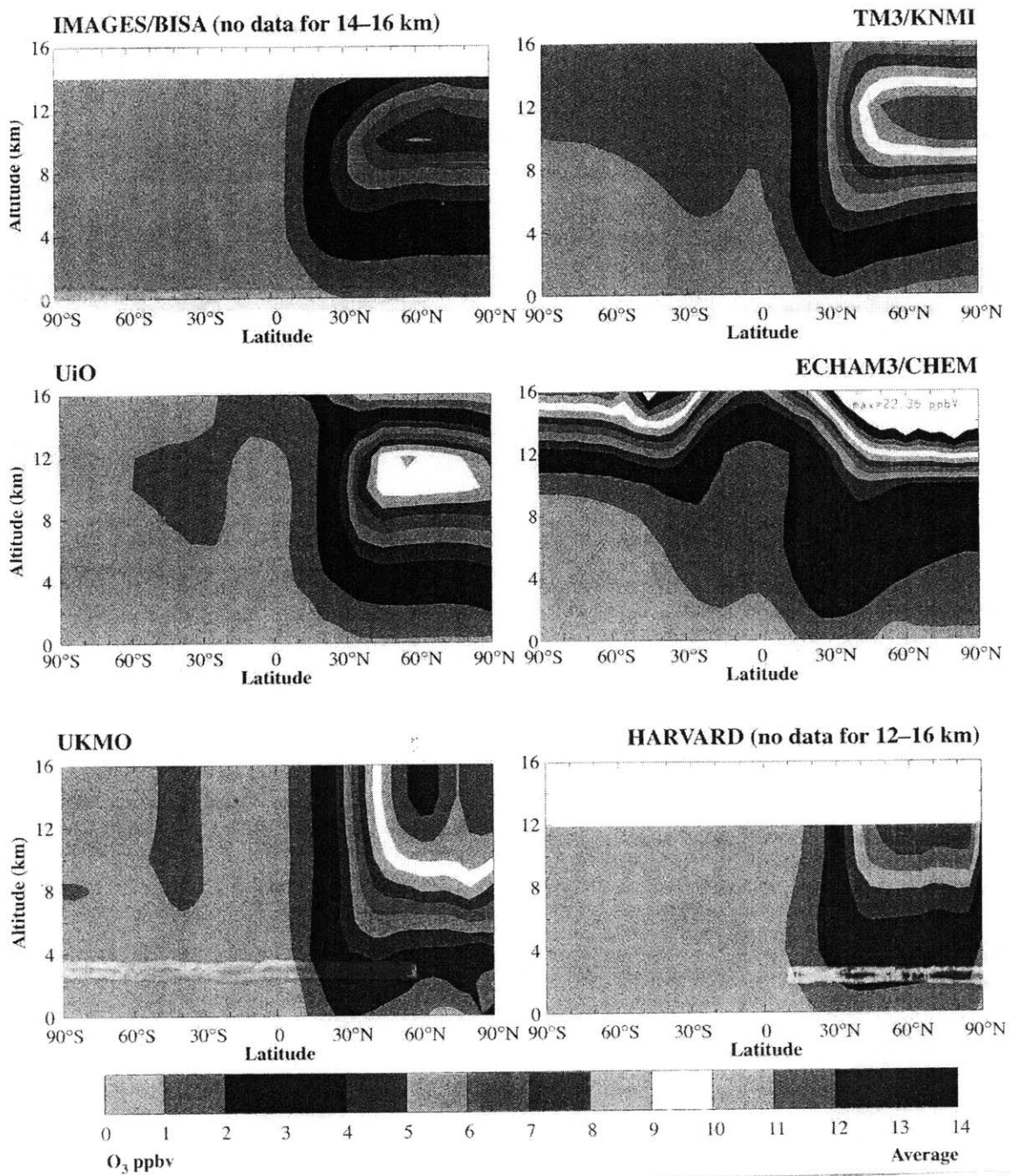


Muller, J. F. and Brasseur, G. (1995) IMAGES: A three-dimensional chemical transport model of the global troposphere. *Journal of Geophysical Research* 100, 16,445-16,490.

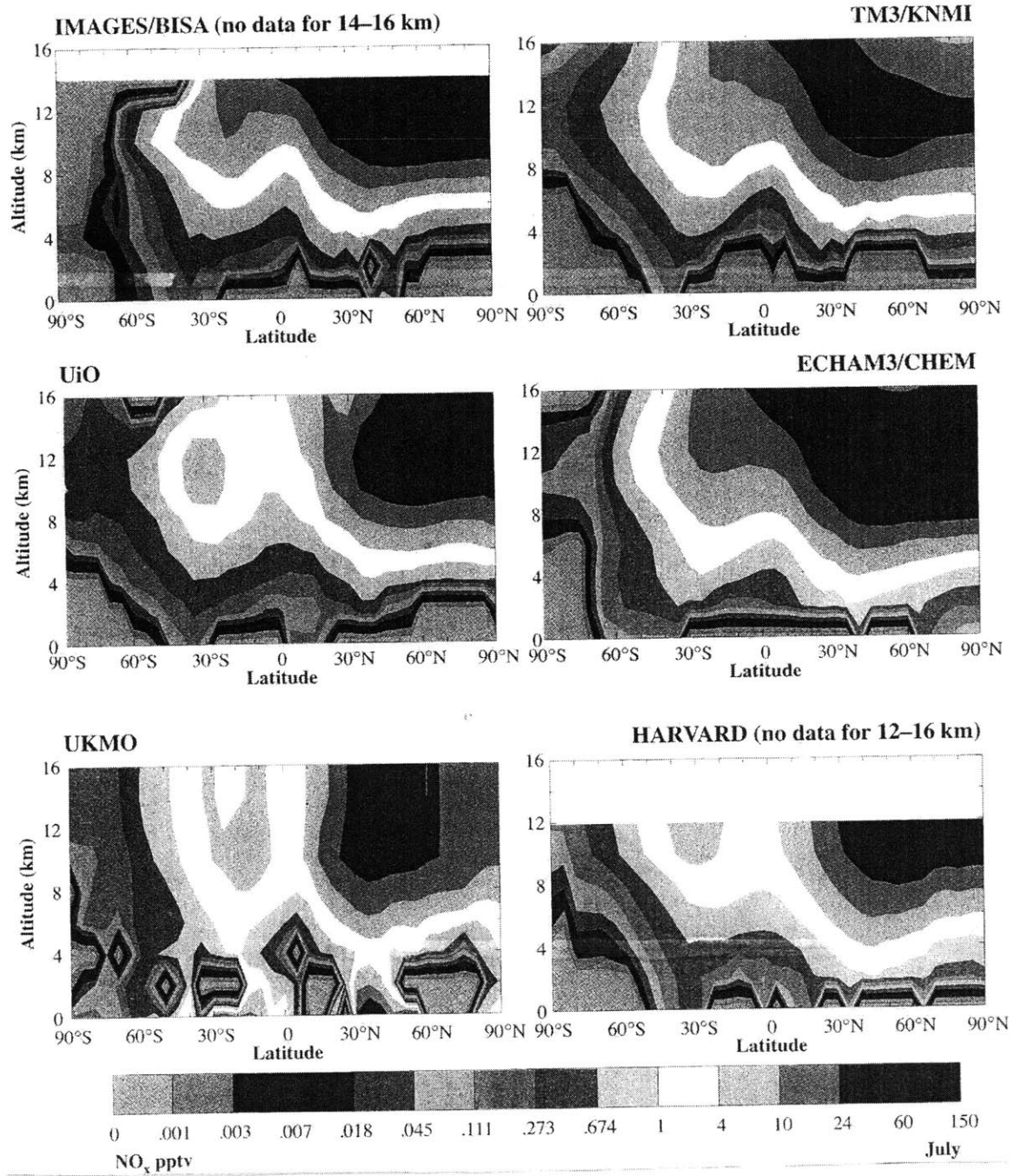
NASA (1995) Scientific assessment of the atmospheric effects of stratospheric aircraft. NASA Reference Publication 1381, November 1995.

**APPENDIX A:  
DETAILED MODEL RESULTS**

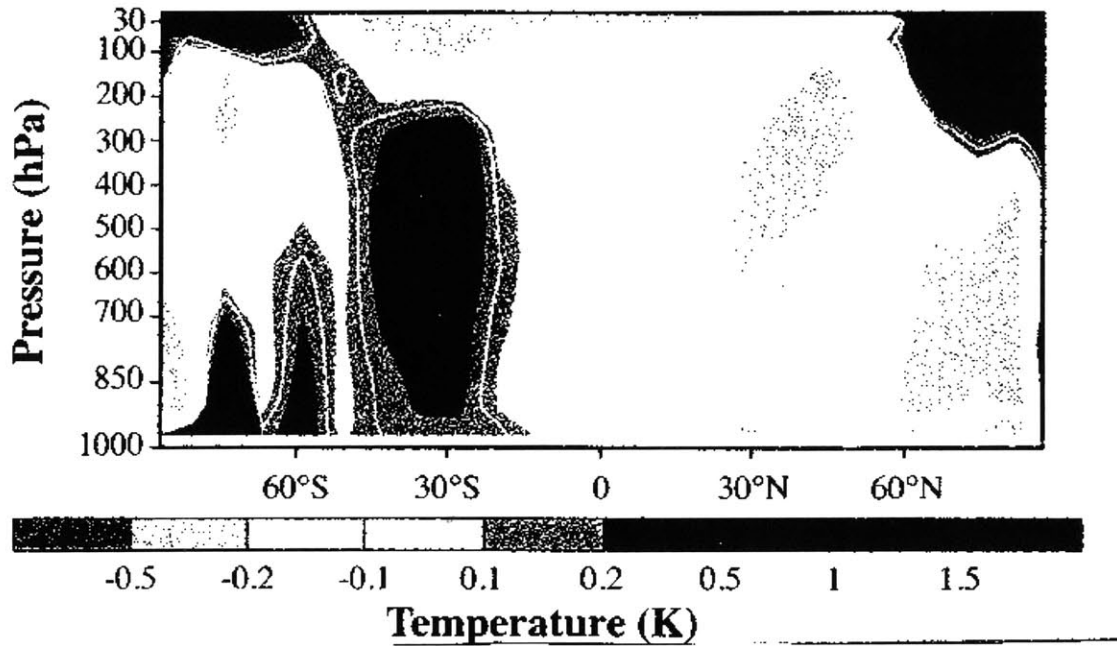
**Figure A-1:** Annual (2015) and zonal average increase of ozone volume mixing ratios [ppbv] from aircraft emissions calculated by six 3-D models



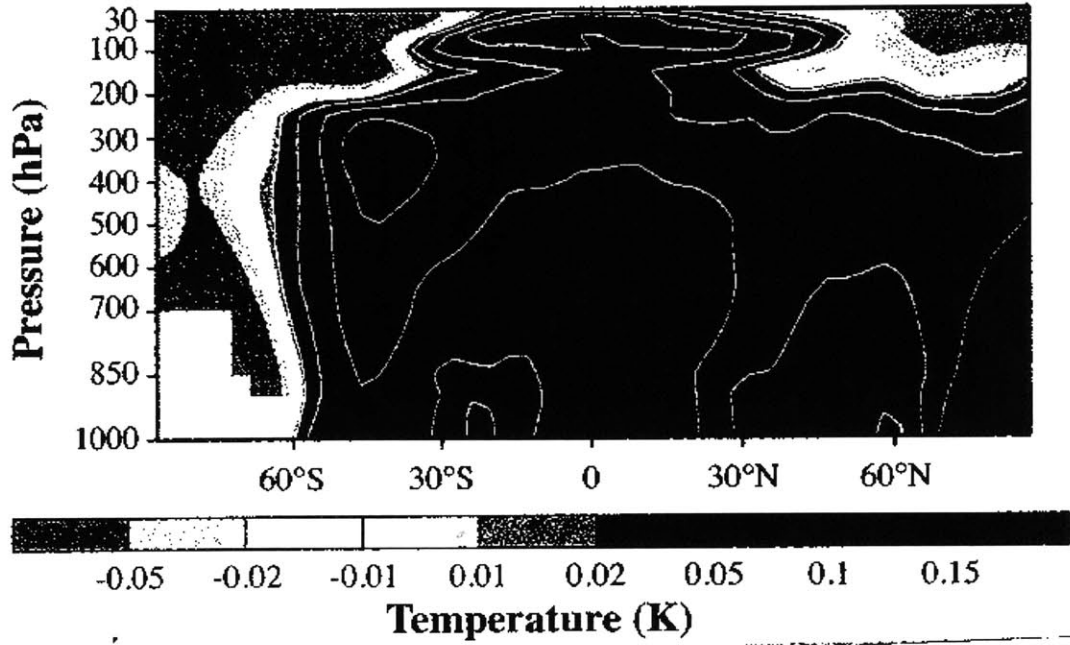
**Figure A-2:** July zonal average increase in NO<sub>x</sub> [pptv] from aircraft



**Figure A-3:** Equilibrium change of annual, zonal mean temperature (K) caused by ozone perturbation due to  $\text{NO}_x$  emissions of a projected sub- and supersonic aircraft fleet for the year 2015, as simulated with the GISS model (*Rind and Lonergan, 1995*)



**Figure A-4:** Equilibrium change of annual, zonal mean temperature (K) caused by ozone perturbation due to NO<sub>x</sub> emission of 1991-92 air traffic (CLR-2), as simulated with the ECHAM4/MLO model (*Ponater et al., 1998*)



**Figure A-5:** Equilibrium change of annual, zonal mean temperature (K) resulting from the anthropogenic increase of well-mixed greenhouse gases from 1990 to 2015, as simulated with the ECHAM4/MLO model (*Ponater et al., 1998*)

