# **Ozone and Related Gases in the Lower Atmosphere**

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Dedicated to

my Parents, Grandparents

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# CHAPTER 1

# Introduction

Many of the global environmental changes forced by human activities are mediated through the chemistry of the atmosphere. Important changes include the global spread of air pollution, increases in the concentrations of tropospheric oxidants (including  $O_3$ ), stratospheric O<sub>3</sub> depletion, and global warming. Since the agricultural and industrial revolutions, the delicate balance between physical, chemical, and biological processes in the Earth system is being perturbed as a result, for example, of the quasi-exponential growth in the world population. The use of increasing amounts of fossil fuel and the related emissions of carbon compounds to the atmosphere, and the intensification of agricultural practices including the large use of fertilizers are major man made activities. The observed increase in the atmospheric abundance of CO results mainly from fossil fuel burning, although biomass burning is an important secondary source. Atmospheric concentrations are additionally influenced by exchanges of carbon with the ocean and the continental biosphere. Observed increases in the abundance of tropospheric O<sub>3</sub>, which contribute to deteriorating air quality, result from complex photochemical processes involving industrial and biological emissions of nitrogen oxides, hydrocarbons, and certain other organic compounds. Ozone is a strong absorber of solar ultraviolet radiation in the stratosphere while it contributes to greenhouse forcing in the troposphere. The rapid increase in the atmospheric abundance of industrially manufactured chlorofluoro-carbons (CFCs) has produced the observed depletion in stratospheric O<sub>3</sub> and formation of "ozone hole" over Antarctica. Common trace gases found in polluted air include CO, O<sub>3</sub>, nitrogen oxides (NO<sub>x</sub>=NO+NO<sub>2</sub>), SO<sub>2</sub> and hydrocarbons. Inventories and documentation of the mixing ratios of these gases are needed to make policy decisions and to determine their impacts on environment, climate, health and agriculture.

Gases other than N<sub>2</sub>, O<sub>2</sub>, Ar, and H<sub>2</sub>O are present in the atmosphere at extremely low concentrations and are called trace gases. Despite their low concentrations, these

gases can be of critical importance for the greenhouse effect, the  $O_3$  layer, smog, and other environmental issues. Ozone is not directly emitted but it is photochemically produced from the other emitted pollutants in the troposphere. Sources, sinks and budgets of some  $O_3$  related trace gases are discussed in the following sections.

## **1.1** Ozone in the troposphere

Tropospheric O<sub>3</sub> is only a trace gas that plays a controlling role in the oxidation capacity of the atmosphere. Ozone and its photochemical derivative, OH, are the major oxidants for most of the reduced trace gases. Without  $O_3$ , reduced gases such as CO, hydrocarbons, and most of the sulfur and reactive nitrogen compounds would accumulate to the levels substantially above those in the present atmosphere. Environmentally, high level of  $O_3$  at the surface are a major pollutant because of their detrimental effects on human health and plants. Elevated and potentially harmful levels of O<sub>3</sub> have been observed extensively in industrialized as well as developing countries. Tropospheric O<sub>3</sub> also plays an important role in global warming because of its strong absorption band, centered at 9.6  $\mu$ m, particularly in the upper troposphere where the temperature is low [Fishman et al., 1979; Wang et al., 1986]. Tropospheric O<sub>3</sub> levels have increased since pre-industrial times (1860), particularly in the Northern Hemisphere (NH) [Oltmans et al., 1998]. It is estimated that  $O_3$  has contributed 0.2-0.6 Wm<sup>-2</sup> to the radiative forcing since 1860. compared to 1.5 Wm<sup>-2</sup> from the CO<sub>2</sub> [IPCC, 1996]. Considering the entire troposphere, there are two major sources of O<sub>3</sub>: in situ photochemical production and transport from the stratosphere. Two major loss processes roughly balance these processes: destruction at the Earth's surface and in situ photochemical loss.

#### **1.1.1** Photochemical production of O<sub>3</sub>

The photochemistry of  $O_3$  formation is, in principle, rather well understood. Ozone formation is initiated by OH attack on hydrocarbons and CO, which leads to peroxy radicals (HO<sub>2</sub>, RO<sub>2</sub>) formation. These react with nitric oxide to produce nitrogen dioxide, which photolyses yielding O-atoms which in turn, combine with molecular oxygen leading to the production of O<sub>3</sub>. The photochemistry of tropospheric O<sub>3</sub> formation in simplified form [*Liu. et al.*, 1987] is given below.

$NMHCs + OH + O_2 \rightarrow RO_2 + H_2O$	( <i>R</i> 1.1)
$RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB$	( <i>R</i> 1.2)
$HO_2 + NO \rightarrow NO_2 + OH$	( <i>R</i> 1.3)
$2(NO_2 + hv + O_2 \rightarrow NO + O_3)$	( <i>R</i> 1.4)

*net* :  $NMHCs + 4O_2 \rightarrow 2O_3 + CARB + H_2O$ 

NMHCs is the abbreviation for nonmethane hydrocarbon species and CARB stands for carbonyl compounds. Similar  $O_3$  productive cycles take place for CO and CH<sub>4</sub> also, but  $O_3$  yield is much higher for NMHCs. On an average CO, CH<sub>4</sub>, and NMHCs produce 1, 3.5, and 10-14  $O_3$  molecules, respectively by photochemical production.

#### **1.1.2** Transport of O<sub>3</sub> from the stratosphere

High concentrations of O<sub>3</sub> are found in the Earth's stratosphere, but strong stratification suppresses efficient exchange of this ozone-rich air with the underlying troposphere. Upward transport of tropospheric trace constituents occurs mainly through equatorial deep convective systems. In contrast, significant downward transport of ozone-rich stratospheric air is thought to take place only outside the tropics by exchange processes in upper-level fronts associated with strong distortions of the tropopause. Ozone from the stratosphere is transported down across the tropopause by the so-called tropopause folding events [Danielson, 1968] in which tongues of stratospheric air intrude into the tropopause, usually at extra-tropical latitudes. Estimates of the amount of O<sub>3</sub> transported from the stratosphere to the troposphere on an annual basis rely on measurements of conserved tracers or on general circulation models but are quite uncertain. In the Northern Hemisphere (NH), O<sub>3</sub> fluxes seem to maximize in spring, being as much as five times the value in the fall. The NH stratosphere-to-troposphere O<sub>3</sub> flux has been estimated to fall in the range of  $(3-8) \times 10^{10}$  molecules cm<sup>-2</sup>s<sup>-1</sup> [*Crutzen*, 1995]. The Southern Hemispheric (SH) flux may be about half as large. An estimate for the total O<sub>3</sub> production in the stratosphere is about  $5 \times 10^{13}$  molecules cm<sup>-2</sup>s<sup>-1</sup>; only 0.1% of all O<sub>3</sub> produces in the stratosphere leaks down the troposphere [Crutzen, 1995]. The estimated global O<sub>3</sub> loss from the photolysis in the troposphere is  $14 \times 10^{10}$  molecules cm<sup>-2</sup>s<sup>-1</sup>, which exceeds the amount of O<sub>3</sub> from the stratosphere-to-troposphere exchange.

#### **1.1.3** Photochemical loss of O<sub>3</sub>

Tropospheric  $O_3$  was originally believed to be transported from the stratosphere and destroyed at the surface. However, gas phase photochemical production and destruction of  $O_3$  in the troposphere may be more important in controlling the tropospheric abundance. One of the theoretical arguments that supports the photochemical theory is the existence of an  $O_3$  sink:

$O_3 + hv(<320nm) \rightarrow O_2 + O(^1D)$	( <i>R</i> 1.5)
$O(^{1}D) + H_{2}O \rightarrow 2OH$	( <i>R</i> 1.6)
$OH + CO \rightarrow H + CO_2$	( <i>R</i> 1.7)
$H + O_2 + M \rightarrow HO_2 + M$	( <i>R</i> 1.8)
$HO_2 + O_3 \rightarrow OH + 2O_3$	( <i>R</i> 1.9)

 $Net: 2O_3 + CO + H_2O + hv \rightarrow 2O_2 + CO_2 + 2OH$ 

Loss of  $O_3$  from the troposphere takes place by photolysis to  $O(^1D)$  followed by the reaction of  $O(^1D)$  with H<sub>2</sub>O. The rate-limiting step for  $O_3$  loss is given by the following reactions:

$$O(^{1}D) + H_{2}O \rightarrow 2OH....(R1.10)$$

Ozone is also consumed by reactions with HO<sub>2</sub> and OH in remote regions of the troposphere:

$$HO_2 + O_3 \rightarrow OH + 2O_2 \dots (R1.11),$$
  
$$OH + O_3 \rightarrow HO_2 + O_2 \dots (R1.12)$$

Additional loss of  $O_3$  takes place by reaction with organic materials at the Earth's surface (dry deposition).

## 1.1.4 Dry deposition at Earth's surface

Dry deposition refers to removal of gases from the atmosphere to the Earth's surface, by a direct transfer process, and without the involvement of any precipitation. Wet deposition, on the other hand, is a term used for all deposition processes in which the gases or particles are carried to the surface by precipitation process. Dry deposition due to the

transport of trace gases and particles to the Earth's surface. Also it is an important loss process for many other reactive and soluble trace gases. The flux (F) of a gas to the surface is commonly expressed as the product of a deposition velocity  $(u_d)$  and the concentration (C) of the gas in air:

 $F = -u_d C$ .....(1.1)

## **1.1.5** Tropospheric budget of O<sub>3</sub>

Ozone abundance in the troposphere typically vary from less than 10 ppbv over remote tropical oceans up to about 100 ppbv in the upper troposphere, and often exceed 100 ppbv in the downwind of polluted metropolitan regions. This variability, reflecting its rapid chemical turnover, makes it impossible to determine the tropospheric burden from the available surface sites, and we must rely on infrequent and sparsely sited profiles from ozone sondes [*Logan*, 1999]. The total column of  $O_3$  is measured from satellites, and these observations have been used to infer the tropospheric  $O_3$  column after removing the

Atmospheric processes	$Tg O_3 yr^{-1}$
Sources Chemical Production HO <sub>2</sub> +NO CH <sub>3</sub> O <sub>2</sub> +NO RO <sub>2</sub> +NO Transport from stratosphere	3400-5700 3000-4600 70% 20% 10% 400-1100
Sinks Chemical loss $O(^{1}D)+H_{2}O$ $HO_{2}+O_{3}$ $OH+O_{3}$ Others Dry deposition	3400-5700 3000-4200 40% 10% 10% 500-1500

 Table 1.1: Global budget of tropospheric ozone. Adapted from IPCC [1994].

much larger stratospheric column [*Fishman and Brackett*, 1997; *Hudson and Thompson*, 1998]. The current burden of tropospheric  $O_3$  is about 370 Tg, which is equivalent to a globally averaged column density of 34 DU or a mean abundance of about 50 ppbv.

Global models of tropospheric chemistry that integrate HOx-NOx-COhydrocarbon chemical mechanism in a three-dimensional framework have been used to estimate the importance of different sources and sinks in the tropospheric  $O_3$  budget. Table 1.1 gives the range of results from the current generation of models. It is now fairly well established that chemical production and loss within the troposphere largely control the abundance of tropospheric  $O_3$ . Transport from the stratosphere and dry deposition are relatively minor terms.

#### **1.1.6** Effects of O<sub>3</sub> exposure to plants, vegetation and human health

Studies indicate that, for many crop species, the elevated  $O_3$  concentrations result in a substantial reduction in yield. U.S., European, and Japanese studies indicate that crop yields are depressed by repeated, intermittent exposures to  $O_3$  above ~50-70 ppbv over a growing season [*Adams et al.*, 1989; *Unsworth and Geissler*, 1993; *Kobayashi*, 1992]. Yield loss in some crops caused by various levels of ozone exposure is shown in Figure 1.1. A study by Environmental Protection Agency shows the reduction in yield of crops



**Figure 1.1**: Effect of seasonal  $O_3$  concentrations on agricultural crop yields derived from a Weibull Parametric Fit of NCLAN  $O_3$  exposure and yield. Data taken from Adams et al. [1989] and Chameides et al. [1999].

exposed to ozone. At an ozone concentration of 60 ppbv, soybean yields decreases to about 60 percent of normal, while wheat, corn decrease to about 90 percent of normal. Based on the evaluation of over 500 different forms for a crop response index of  $O_3$  air

quality, the findings of several scientists are summarized by *Lee et al.* [1988]. A useful exposure metric is "SUM06", a 3-month sum of all daytime, 1-hour-averaged  $O_3>60$  ppbv. Crop yields were found to be reduced by 10% or more when SUM06 was around 15-25 ppmv-hour [*Heck and Crowling*, 1997]. Linear and Weibull models were used to evaluate the performance of the indices used in the study. The Weibull model [*Rawlings and Cure*, 1984] is of the form.

Yield =  $\alpha \times \exp[-(\text{Exposure index/s})^{\circ}]$ ....(1.2)

Where

 $\alpha$  = Theoretical maximum yield at zero O<sub>3</sub> concentration,

s = The O<sub>3</sub> exposure when the yield is 0.37

c = Dimensionless shape parameter,

Exposure index = one of the exposure index used

**Table 1.2:** Air Quality Index for  $O_3$  (ppbv). Adapted from recent EPA (Environmental Protection Agency) report, USA.

Index Values	Descriptors	Cautionary Statements for Ozone
0 to 50	Good	None.
51 to 100	Moderate	Unusually sensitive people should consider limiting prolonged outdoor exertion
101 to 150	Unhealthy for Sensitive Groups	Active children and adults, and people with respiratory disease, such as asthma, should limit prolonged outdoor exertion
151 to 200	Unhealthy	Active children and adults, and people with respiratory disease, such as asthma, should limit prolonged outdoor exertion; everyone else, especially children, should limit prolonged outdoor exertion.
201 to 300	Very Unhealthy	Active children and adults, and people with respiratory disease, such as asthma, should limit prolonged outdoor exertion; everyone else, especially children, should limit outdoor exertion.

Ozone is harmful to human health because  $O_3$  reacts readily with the membranes of the eye and those lining the lung's air passages. Air quality standards for  $O_3$  in terms of the US EPA's Air Quality Index are shown in Table 1.2. Ozone can produce the following health effects:

1. Eye irritation

- 2. Breathing problems such as shortness of breath or pain during deep breaths
- 3. Lung damage such as increased respiratory illness and decreased lung function
- 4. Coughing, wheezing, chest tightness or pain, dry throat, headache or nausea
- 5. Intensification of asthma symptoms
- 6. Reduced resistance to infection; reduced functioning of immune system
- 7. Tired feeling
- 8. Reduced athletic performance
- 9. Increased cardio-respiratory deaths

## **1.2** Carbon monoxide in the atmosphere

The major sources of CO are both anthropogenic and natural, including fossil fuel combustion, biomass burning and oxidation of CH<sub>4</sub> and non-methane hydrocarbons (NMHCs) [Jaffe et al., 1997]. More than half of atmospheric CO emissions today are caused by human activities, and as a result the Northern Hemisphere contains about twice as much CO as the Southern Hemisphere. The primary sink for CO is its oxidation by the OH radical, and soil uptake is also a small sink. Carbon monoxide has a tropospheric lifetime of around 2 months [Logan et al., 1981; Brasseur et al., 1999]. Carbon monoxide plays a significant role in the atmosphere and also affects air quality. High CO mixing ratio can directly affect human health [Maynard and Waller, 1999] and can cause lower crop yields [Halloway et al., 2000]. Carbon monoxide does not absorb terrestrial infrared radiation strongly enough to be counted as a direct greenhouse gas, but its role in determining tropospheric OH indirectly affects the atmospheric burden of CH<sub>4</sub> [Isaksen and Hov, 1987] and can lead to the formation of O<sub>3</sub>. The oxidation of CO initiates photochemical reactions which result in O3 production on a regional scale [Noveli et al., 1998]. In much of the troposphere, its reaction with OH represents 90-95% sink of CO [Logan et al., 1981], and about 75% of the removal of OH [Thompson, 1992].

Because of its relatively short lifetime and distinct emission patterns, CO has large gradients in the atmosphere. Measurements from a globally distributed network of sampling sites indicate that CO decreased globally by about 2 % yr<sup>-1</sup> from 1991 to 1997 [*Novelli et al.*, 1998] but then increased in 1998. Some recent evaluations of the global CO budget are presented in Table 1.3. The Asian emissions of CO were 279 Tg in 2000, of which 67 Tg , or 24%, comes from open biomass burning. The component is largely due to residential biofuel combustion (96 Tg or 34%) and transportation sources (78 Tg or

28%). Estimated values of CO emissions are 116 Tg and 63.3 Tg for China and India, respectively [*Streets et al.*, 2003].

	Range of estimates (Tg CO yr $^{-1}$ )	
Sources	1800-2700	
Fossil fuel combustion/industry	300-550	
Biomass burning	300-700	
Vegetation	60-160	
Oceans	20-200	
Oxidation of methane	400-1000	
Oxidation of other hydrocarbons	200-600	
Sinks	2100-3000	
Tropospheric oxidation by OH	1400-2600	
Stratosphere	~ 100	
Soil uptake	250-640	

**Table 1.3:** Estimates of the global tropospheric carbon monoxide budget (in Tg(CO)/yr) from different sources. Adapted from Jacob [1999].

## **1.3** Methane in the atmosphere

Methane is the most abundant organic trace gas in the atmosphere. The most important known sources and sinks of atmospheric CH<sub>4</sub> are listed in Table 1.4. Atmospheric CH<sub>4</sub> is a greenhouse gas whose radiative properties and atmospheric chemistry affect both climate and stratospheric O<sub>3</sub>. After water vapor and CO<sub>2</sub>, CH<sub>4</sub> is the most abundant greenhouse gas in the troposphere and on a per molecule basis, CH<sub>4</sub> has a greater climate warming potential than CO<sub>2</sub>. Hansen and Sato [2001] estimated a change in radiative forcing for CH<sub>4</sub> in 2000 and they compared with pre-industrial value, including direct and indirect effects, of 0.7  $Wm^{-2}$ , which is one-half the change in forcing due to CO<sub>2</sub> increase. In the stratosphere, CH<sub>4</sub> acts as a sink for chlorine atoms and is therefore important in stratospheric  $O_3$  chemistry. The atmospheric  $CH_4$  affects hydroxyl radical (OH) abundance on global scale. This can alter degradation rates (lifetimes) of CH<sub>4</sub> and other trace species in the troposphere. Systematic measurements of atmospheric CH<sub>4</sub> show that its global abundance at Earth's surface continues to increase; the average growth rate was 7.9 ppbv yr<sup>-1</sup> from 1984 to 2000. Emissions from manure and enteric fermentation in animals represent the largest sources of CH<sub>4</sub> emissions in Asia at 36.2 Tg (34%), followed by rice cultivation (24.2 Tg, 23%). The distribution of CH<sub>4</sub> emissions among source types varies considerably from country to country.

	Rate, Tg $CH_4$ yr $^{-1}$ ; best estimate and range of uncertainty		
Sources, natural	160 (75-290)		
Wetlands	115 (55-150)		
Termites	20 (10-50)		
Other	25 (10-90)		
Sources, anthropogenic	375 (210-550)		
Natural gas	40 (25-50)		
Livestock (ruminants)	85 (65-100)		
Rice paddies	60 (20-100)		
Other	190 (100-300)		
Sinks	515 (430-600)		
Tropospheric oxidation by OH	445 (360-530)		
Stratosphere	40 (30-50)		
Soils	30 (15-45)		
Accumulation in atmosphere	37 (35-40)		

**Table 1.4:** Estimates of the global methane budget (in  $Tg(CH_4/yr)$  from different sources. Adapted from Jacob [1999].

The only organic compound sufficiently long-lived to be transported to the stratosphere in significant amount is  $CH_4$ . The mixing ratio of  $CH_4$  is quite uniform in the troposphere, with a present-day value of about 1.8 ppmv. Thus air entering the stratosphere from the troposphere contains approximately this amount of  $CH_4$ . The destruction of  $CH_4$  in the stratosphere is via reaction with OH, just as in the troposphere, and via reaction with O (<sup>1</sup>D) and with Cl atoms:

$$O(^{1}D) + CH_{4} \longrightarrow OH + CH_{3}....(R1.13)$$
$$Cl + CH_{4} \longrightarrow HCl + CH_{3}...(R1.14)$$

Because of the strong temperature dependence of the reaction of OH with  $CH_4$  and the low concentrations of  $O(^1D)$  and Cl atoms in the lower stratosphere, chemical destruction of  $CH_4$  in the lower stratosphere is quite slow. Thus its mixing ratio can be used a tracer for dynamical processes (its chemical lifetime is longer than the time-scale for the dynamical processes).

## **1.4** Nonmethane hydrocarbons in the atmosphere

NMHCs have several roles in atmospheric chemistry which include: (1) enhancing  $O_3$  production when NOx is also present and forming photochemical smog, (2) decreasing OH radical mixing ratios, (3) contributing to the global atmospheric CO mixing ratio, (4)

being a tracer of atmospheric transport, (5) leading to the production of organic nitrates which can sequester NOx and allow it to be transported throughout the troposphere, (6) producing organic aerosols, and (7) being a link in the global carbon cycle [*Singh and Zimmerman*, 1992; *Fehsenfeld et al.*, 1992]. The amount of O<sub>3</sub> produced by the oxidation of NMHCs depends on the NOx mixing ratio. In low NOx conditions, O<sub>3</sub> mixing ratios may decrease. In polluted air parcels with sufficient NOx, O<sub>3</sub> mixing ratios may increase and form photochemical smog.

	$Emissions (TgC yr^{-1})$
Sources	
Anthropogenic	
Transportation	22
Stationary source fuel combustion	4
Industrial processes including	
natural gas production	17
Biomass burning, forest fires, incineration	45
Organic solvents	15
Anthropogenic subtotal	103
Natural	
Oceanic	
Light hydrocarbons	5-10
$C_9$ - $C_{28}$ <i>n</i> -alkane	1-26
Terrestrial	
Microbial production	6
Emissions from vegetation	
isoprene	500
monoterpenes	125
other	$520^a$
Natural subtotal	$\sim 1170$
Total emissions	~1273

 Table 1.5: Estimates of global NMHC emissions.

<sup>a</sup>Extremely uncertain.

Adapted from Singh and Zimmerman, 1992, and Guenther et al., 1995.

## 1.4.1 Sources of NMHCs

Hydrocarbons have both anthropogenic and natural sources. The anthropogenic sources include fossil fuel combustion, natural gas leakage, evaporation of fuels, industrial processing of wastes and chemicals, automobile exhaust, and biomass burning [*Singh and Zimmerman*, 1992]. Some examples of common anthropogenic hydrocarbons include acetylene, ethane, ethene, propane, propylene, butane, pentane, benzene, and toluene. The

natural sources are the ocean and vegetation emissions. The natural sources of NMHCs are estimated to be an order of magnitude larger than their anthropogenic sources. Furthermore, emissions of natural hydrocarbons depend on temperature; thus global warming could lead to enhanced emission rates [*Fehsenfeld et al.*, 1992; *Brasseur et al.*, 1999]. Sources of these compounds are variable in time and space, and emission estimates remain quite uncertain, but recent estimates of the magnitude of NMHCs sources are listed in Table 1.5. Other potential negative impacts of hydrocarbons are that they may be toxic and carcinogenic, and may cause plant damage and forest decline [*Field et al.*, 1992; *Fehsenfeld et al.*, 1992]. Thus, hydrocarbons have several major roles in determining the chemical composition of the troposphere.

#### **1.4.2 Sinks of NMHCs**

The primary sink of hydrocarbons is oxidation by the OH radical. Wet and dry depositions are less important sinks. The main sink for hydrocarbons with an abstractable hydrogen atom, denoted below as RH, is through oxidative reaction with OH radical:

$$RH + .OH \rightarrow R. + H_2O.....(R1.15)$$

**Table 1.6:** Calculated lifetimes for selected NMHCs compounds with respect to the reaction with OH. Values are calculated for a 12-hr daytime average OH radical concentration of  $2 \times 10^6$  molecule cm<sup>-3</sup>s<sup>-1</sup>. With rate constants at 298 K for reactions of NMHCs with OH [Atkinson, 1994; 1997]

Species	Lifetime	Reaction rate with OH $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup>
Ethane	45 days	0.254
Propane	10 days	1.12
N-butane	4.7 days	2.44
N-pentane	2.9 days	4.0
Acetylene	14 days	0.82
Ethene	1.4 days	8.52
Propene	5.3 hours	26.3
I-butane	4.7 days	2.34
I-pentane	3.1 days	3.9

Because rate of the above reaction differs significantly among the various NMHCs, their tropospheric lifetimes vary widely. Hydrocarbons have lifetimes of minutes to months [*Singh and Zimmerman*, 1992]. Life times of some light NMHCs are presented in Table

1.6. Comparing model results calculated with and without NMHCs oxidation chemistry indicates that NMHCs oxidation adds 40-60% to surface CO levels over the continents and slightly less over the oceans. Free tropospheric CO levels increase by 30-60%. The overall yield of CO from the NMHCs mixture considered is calculated to be about 0.4 CO per C atom [*Poisson et al.*, 2000].

### 1.4.3 Budget of NMHCs

Hundreds of NMHCs are released into the atmosphere from a variety of anthropogenic and biogenic sources, with emissions exceeding 1000 TgC yr<sup>-1</sup>. Although anthropogenic

 Table 1.7: Global sources of individual NMHC species. Adapted from Singh and Zimmerman
 [1992], and Guenther et al. [1995].

Hydrocarbon	Emission (TgC yr <sup>-1</sup> )	Major Sources		
Ethane	10-15	Natural gas emissions, biomass burning, oceans, vegetation		
Ethene	20-45	Fuel combustion, biomass, terrestrial ecosystem		
Acetylene	3-6	Fuel combustion, biomass burning		
Propane	15-20	Natural gas, biomass burning, oceans, vegetation emissions		
Propene	7-12	Fuel combustion, biomass burning, oceans		
N-butane	1-2	Fuel combustion, natural gas, biomass burning, oceans		
I-butane	1-2	Fuel combustion, natural gas, biomass burning, oceans		
N-pentane	1-2	Fuel combustion, natural gas, biomass burning		
I-pentane	2-3	Fuel combustion, natural gas, biomass burning		

emissions dominate in urban and industrial areas, natural emissions account for over three-fourth of total NMHCs emissions globally [*Guenther et al.*, 1995]. Emission estimates and sources for specific NMHCs of importance are given in Table 1.7. Virtually all activities related to energy use or transfer result in the release of NMHCs into the atmosphere. In industrialized countries, fossil fuel combustion (including automobiles), natural gas (75% Methane, 25% Ethane, Propane, and Butane) and industrial processing of chemicals and waste are major sources of anthropogenic NMHCS, while in less

developed parts of the world, biomass burning is an important component. Emission of nonmethane volatile organic compound (NMVOCs) in Asia are subject to high degree of uncertainty due to great variety of sources. Anthropogenic emission is estimated to be 52.2 Tg in all of Asia (measured as full molecular weights of the constituent compounds). According to an estimate [*Streets et al.*, 2003] the emissions of NMVOCs are at 17.5 Tg and 10.84 Tg from China and India, respectively. Model evaluation of annual mean surface distributions of some important NMHCs species are shown in Figure 1.2 [*von Kuhlmann et al.*, 2003b].



**Figure 1.2:** Annual mean surface distribution of  $C_2H_6$ ,  $C_3H_8$ ,  $C_2H_4$  and  $C_3H_6$  from the T63 simulation. Adapted from von Kuhlmann et al. [2003b].

#### 1.4.4 Reactivity with respect to O<sub>3</sub> formation

The product of a VOC's (volatile organic compound) concentration and its OH rate constant will determine in approximate manner its relative role as an  $O_3$  precursor. A species with a large concentration may not necessarily be an important  $O_3$  precursor if it is unreactive; conversely, a compound with a small concentration can be important if it is extremely reactive. An air mass can have a large total VOC concentration but low  $O_3$  producing capacity if the VOC's present is relatively unreactive. NMHCs almost doubles



**Figure 1.3:** Observed NOx and OH-reactivity-adjusted VOC (expressed as propene) in various regions of the troposphere. Isopleths shown are midday rates of  $O_3$  production (ppbv  $h^{-1}$ ) calculated using box model. Adapted from Chameides et al. [1992].

the net photochemical production of  $O_3$  in the troposphere and leads to 20-80% higher  $O_3$  concentrations in NOx-rich boundary layer, with highest increases over and downwind of the industrial and biomass burning regions [*Poisson et al.*, 2000]. To account for the combined effect of OH reactivity and concentration, one adopts an OH-reactivity-based method [*National Research Council*, 1991]. In this method a propene-equivalent concentration, Prop Equiv(j), for each VOC species j is given by

*Conc(j)* is the concentration of species *j* expressed in ppbC,  $k_{OH(j)}$  is the rate constant for the reaction between species *j* and OH, and  $k_{OH(C_3H_6)}$  is the rate constant for the reaction between OH and propene. Figure 1.3 shows ranges of observed NOx and OH-reactivity adjusted VOC (expressed relative to propene) in four different types of atmospheres: urban-suburban, rural typical of eastern United States, remote tropical Brazilian forests, and remote marine boundary layer. This figure indicates a strong relationship between O<sub>3</sub> and NOx, but little with the reactivity-adjusted VOC concentrations in continental areas. For example, while the reactivity-adjusted VOC increases by almost two orders of magnitude from the remote marine region to the tropical forest sites due to biological organic emissions.



**Figure 1.4:** *Maximum incremental reactivities of some organics (grams of*  $O_3$  *produced per gram of VOC). Adapted from Barbara J. Finlayson-Pitts [2000].* 

To measure the ozone-forming capability of individual organic, a number of hydrocarbon "reactivity scales" have been developed over the years [*Carter*, 1994]. A useful definition of reactivity is that of *incremental reactivity* (IR), defined as the amount of O<sub>3</sub> formed per unit VOC added or subtracted from the VOC mixture in a given air mass [*Carter and Atkinson*, 1989; *Brown and Seinfeld*, 1994 a, b].

IR=
$$\Delta$$
[O3] /  $\Delta$ [VOC].....(1.4)

At the limit  $\triangle$ [VOC] tends to zero. An important feature is that the IR of VOC varies with VOC/NOx ratio of the air mass into which it is introduced. The IR values peak at ratio of ~6 and drop off significantly at higher values. The peak IR value of a VOC is known as its *Maximum Incremental Reactivity* (MIR). The MIR of some VOCs are shown schematically in Figure 1.4.

## **1.5** Reactive nitrogen compounds (NO<sub>x</sub>) in the atmosphere

Nitric oxide (NO) and nitrogen dioxide are two active nitrogen constituents in the atmosphere. The sources of NOx (=NO+NO2) include fossil fuel combustion, biomass burning, aircraft emissions, soils, lightning, and transport from the stratosphere. The primary surface emission is NO, but because of rapid inter-conversion the two species are often grouped together as NOx. NOx has a lifetime of hours to a week. [*Singh*, 1987; *Brasseur et al.*, 1999]. Chemical interactions of odd nitrogen constituents with other trace species are important in oxidation process throughout the Earth's atmosphere. The amount

**Table 1.8:** Estimates of the global tropospheric NOx budget (in TgN yr<sup>-1</sup>) from different sources. Adapted from Jacob [1999].

	Source, Tg N yr <sup>- 1</sup>		
Fossil fuel combustion	21		
Biomass burning	12		
Soils	6		
Lightning	3		
NH <sub>3</sub> oxidation	3		
Aircraft	0.5		
Transport from stratosphere	0.1		

of NOx in the troposphere is important because it influences the mixing ratios of  $O_3$  and OH. Furthermore, NOx and NMHCs are responsible for the formation of photochemical smog [*Chameides et al.*, 1988; *Brasseur et al.*, 1999]. In the absence of these odd nitrogen species tropospheric oxidation processes involving CH<sub>4</sub>, other hydrocarbons, or CO would not lead to significant  $O_3$  production. Since the sources of  $O_3$  in the troposphere are

from photochemical production and transport from the stratosphere, possible trends in troposphere in  $O_3$  are closely coupled to the distribution of odd nitrogen and its transport across atmospheric boundaries. Significant global emissions of NOx from various sources are summarized in Table 1.8. Total NOx emissions in Asia were around 26.8 Tg in 2000. The transport sector has the highest share of Asian NOx emissions (37%), followed by power generation (27%) and industry (18%). An inventory of gaseous emission from various Asian countries and total emission from America and Europe continents are given in Table 1.9.

Country	$SO_2$	NO <sub>x</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	NMVOC
China	20,385	11,347	3,817	115,749	38,356	17,432
Japan	801	2198	1,203	6806	1143	1920
Korea	829	1322	411	2824	1433	1161
Indonesia	884	1317	587	23,105	6443	6903
Philippines	713	326	152	4102	2563	1398
Thailand	961	1086	351	10,815	3567	3052
Bangladesh	140	220	123	4827	3608	819
India	5536	4591	1,886	63,340	32,851	10,844
Pakistan	1416	539	221	7076	5415	1344
Asia Total	34,316	26,768	9,868	278,564	106,821	52,150
America	16,498	25,038	5,840	94,033	61,450	17,907
Europe	33,337	15,603	4,642	85,424	34,195	20,750

**Table 1.9:** Summary of emissions of each species in Asian, America and Europe during 2000. Data are in Gg (Tg for  $CO_2$  only). Adapted from Streets et al., 2003 for Asia while data for America (USA) are taken from recent EPA report.

## **1.6** Atmospheric processes and their roles

## 1.6.1 Boundary layer and meteorology

Concentrations of pollutants in the ambient air are not only determined by their rates of emissions but also by the nature and efficiencies of physical and chemical "sinks" e.g. chemical transformation as well as wet and dry deposition to Earth's surface. To a large extent, these competing processes are affected not only by direct dispersion and transport

but also by meteorological factors such as temperature, sunlight intensity, and the presence of inversion as well as clouds and fogs. The boundary layer is lowest part of the atmosphere, closest to the Earth's surface. *Stull* [1988] defines the boundary layer as "that part of the troposphere that is directly influenced by the presence of the Earth's surface, and responds to surface forcing with a time scale of about an hour or less." Typical boundary layer height range ~100 to 3000 m in altitude. The rest of the overlying troposphere is called the free troposphere. Figure 1.5 summarizes the role of inversions and the boundary layer in terms of the typical changes in mixing of the atmosphere close



**Figure 1.5:** Schematic of mixing processes in atmosphere close to the earth's surface as a function of time of day. Adapted from Stull [1988].

to the Earth's surface at various times of the day [*Stull*, 1988]. At midday, there is generally a reasonably well mixed convective layer lying above the surface layer into which the direct emissions are injected. As the Sun goes down, radiative cooling results in the formation of a stable nocturnal boundary layer, corresponding to a radiation inversion. Above this is a residual layer that contains the species that were well mixed in the boundary layer during the day but that do not mix rapidly during the night with either the nocturnal boundary layer below or free troposphere above. At sunrise, heating of the Earth's surface results in mixing of the contents of the nocturnal boundary layer and residual layer above it. Clearly, such meteorological changes can have significant impacts on the spatial distribution of pollutants emitted at the earth's surface, leading to chemistry that varies both spatially and diurnally.

#### **1.6.2** Photochemistry

Atmospheric processing is the combined effects of photochemical reactions and mixing in an air mass [Smyth et al., 1996]. Trace gas mixing ratios in the troposphere are largely regulated by photochemistry. The mixing ratio of a trace gas at a given point in time and location reflects emission sources, dynamical mixing, photochemical processing, and removal processes that have influenced an air mass as it is transported through the troposphere. Therefore, the study of these processes will provide a photochemical history of an air mass [Parrish et al., 1992]. Important photochemically produced species that can be used to determine the extent of photochemical processing that has occurred in an air mass include O<sub>3</sub>, NOx, NO, HNO<sub>3</sub> and peroxyacetyl nitrate (PAN). Organic nitrate formation during NMHCs oxidation, and their transport and decomposition affect the global distribution of NOx and thereby  $O_3$  production. The impact of short-lived NMHCs extends over the entire troposphere due to the formation of long-lived intermediates like CO, and other compounds [Poisson et al., 2000]. The transport of air mass has important implication for photochemistry. For instance, when air masses that contain fresh emissions undergo rapid transport, they can arrive at remote regions and still have great potential for photochemistry because the trace gases would not have been significantly altered during the fast transport [Gregory et al., 1997]. Furthermore, photochemical reactions are important because of their influence on the hemispheric background mixing ratio of trace gases. The trace gas mixing ratio in an air mass can be diluted by mixing with the background air which can result in raising the background mixing ratio [Smyth et al., 1996].

#### 1.6.3 Transport

The process whereby air motions carry physical or chemical properties from one region of the atmosphere to another are collectively referred to as transport. Transport enables different chemical species, with different local sources, to interact. Through transport processes, human activities have global consequences, changing the chemical balance in remote regions of the atmosphere. Meteorologists have nomenclature for different scales of motion depending on the process of interest. The largest is global or planetary scale, which includes average description of variations on the scale of continents. The synoptic scale refers to dynamical system with a scale of about 1000 km that make up most of the daily weather variations. Mesoscale refers to phenomenon from ten to hundreds of kilometers, such as individual fronts or lines of thunderstorms. Small-scale processes range from the scale of an individual cloud or plume to molecular level. Small-scale and mesoscale motions are most important in the planetary boundary layer (PBL) and the troposphere. Atmospheric gases can be transported through the atmosphere by several processes, such as convection, advection, and frontal circulation.

#### 1.6.3.1 Advection

Another transport process is advection, which is horizontal transport due to wind. It can also result in the transport of emissions over great distances. In addition, pollution can be lifted from the boundary layer to the upper troposphere in the warm air ahead of cold fronts. Frontal activity has been found to be a major mechanism for exporting Asian pollution to the western Pacific [*Bey et al.*, 2001] and for transporting pollution off eastern North America [*Milne et al.*, 2000]. When characterizing air masses, the lifetimes of the trace gases need to be considered. Trace gases have longer lifetimes in the upper troposphere because the temperatures are colder and there is no surface deposition loss, which means it is more likely for long-range transport of pollutants to occur [*Donnell et al.*, 2001]. Pollutants with short lifetimes will not be transported as far because their mixing ratios will be depleted during transport due to photochemical and other removal processes. Therefore, long-lived species are more likely to exhibit higher mixing ratios in an air mass [*Gregory et al.*, 1996].

Intercontinental transport of air pollution is important in the study of photochemistry and pollution transport. Transport times between continents are typically 5-10 days [*Wild and Akimoto*, 2001]. Several studies have documented the transport of outflow between continents. Asian outflow is influenced by intercontinental transport. Anthropogenic pollution originating from Europe, Africa and the Middle East has been found to potentially contribute to high altitude Asian outflow [*Talbot et al.*, 1997; *Bey et al.*, 2001].

#### 1.6.3.2 Convection

Convection is fairly rapid vertical mixing resulting from heating at the surface that causes air to rise to higher altitudes and for air to subside downward to replace the air that rose. CHAPTER 1

It can occur in tens of minutes to hours. Often, the vertical updraft occurs in clouds and the downdraft in the surrounding area of the cloud. It is particularly important for the upward motion of air in the tropical regions. Convection vertically redistributes trace gases, and can result in gases with surface sources and/or short lifetimes to be transported to the upper troposphere (UT) [*Brasseur et al.*, 1999]. Once in the UT, gases can be transported thousands of kilometers. Convection is an integral process in pollution transport and in atmospheric processing. For instance, one study found that following the convective transport of  $O_3$  precursors, specifically NOx, to the UT greater than 30% more  $O_3$  could be produced in the tropospheric column [*Pickering et al.*, 1992]. Therefore, it is also important to study the vertical distributions of trace gases in an air mass. Moist convection is characterized by rapid updrafts (driven by latent heat release from condensing water) with sustained velocities of up to several meters per second over regions of the order of a kilometer in diameter. In the upper troposphere (particularly the



**Figure 1.6:** Convective turnover rates in the tropical troposphere. The gray shaded outline provides a schematic representation of the structure of the convective cloud. The arrows represent entrainment fluxes (lower two arrows) and detrainment fluxes (top three arrows). The average convective mass fluxes (in g  $m^{-2} s^{-1}$ ) and the implied turnover time constant (inverse of turnover rate; in days) of the reservoirs are given for each model (in red for the GISS II model and in blue for the Oslo model). Figure adapted from IPCC [2001].

tropics), where moist convective adjustment holds, trace gases are strongly influenced by rapid upward transport within convective clouds and slow descent outside convectively active regions, and nearly all air parcels have had recent contact with the tropical boundary layer (Figure 1.6). Convective clouds are often associated with the formation of precipitation and anvil cirrus clouds. This leads to efficient scavenging of soluble gases by precipitation where convection is active.

The study of moist convective processes and transport have long used equivalent potential temperature (EPT) as a tracer, because it is conserved in the condensation and evaporation of water [*Emanuel*, 1994]. EPT is defined as follows:

The temperature of a parcel of air after all moisture and latent heat is condensed out of an air parcel then descended adiabatically to the 1000 mb level.

$$\theta_e = \left(T + \frac{q^*L}{Cp}\right)^* \left(\frac{p_o}{p}\right)^{\frac{R}{Cp}}....(1.5)$$

Where:

- *T Temperature*
- q Specific humidity
- $p_o, p$  pressure
- L Latent heat
- R Univ. gas constant
- Cp Specific heat capacity

The primary source of EPT is at the surface. The surface sensible and latent heat fluxes, driven by solar heating, can be considered EPT source to the atmosphere [*Betts*, 1992], and the primary sink is radiative cooling of the troposphere. Consequently, the tropical atmosphere is characterized by a decrease of EPT with height. The tropical atmosphere is always close thermally to moist neutrality [*Betts et al.*, 1998]. Therefore, the vertical transports by moist convection are the primary mechanism for the vertical mixing of the atmosphere. Many researchers have used EPT as a tracer to track the downdraft air [*Betts*, 1973, 1976; *Betts and Silva Dias*, 1979].

## 1.7 Usage of NMHCs measurements

NMHCs have also been used as tracers of atmospheric motions and chemistry. Following are some key conclusions that have resulted from the studies of NMHCs:

- Since, some NMHCs react with chlorine atoms at a rate 100-1000 times faster than OH (e.g. C<sub>2</sub>H<sub>6</sub>), these have been used to infer the presence of Cl atoms in the marine boundary layer.
- NMHCs concentration ratios (e.g. C<sub>4</sub>H<sub>10</sub>/C<sub>2</sub>H<sub>2</sub>) have been used as indicators of OH radicals in urban/rural atmosphere. Other ratios such as that of C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> provide qualitative measures of the age of an air mass.
- 3. Seasonal cycles of NMHCs provide convenient means validating the chemistry and dynamics of global photochemical models.

### **1.7.1** Tracer of atmospheric transport

Hydrocarbons have several applications in the study of the composition of an air mass. They can be used to study the history of the photochemical, transport, and removal processes that the trace gases in an air mass have undergone [Parrish et al., 1992]. Due to their various lifetimes, ratios of selected hydrocarbon mixing ratios are an indicator of the photochemical age, and they can show the extent of photochemical processing the hydrocarbons in an air mass have gone through since they were emitted into the atmosphere. Ages determined from hydrocarbon ratios are dependent upon both photochemistry and transport [McKeen and Liu, 1993]. Hydrocarbons can indicate the age of an air mass most effectively when they have similar sources but different lifetimes [Parrish et al., 1992; Smyth et al., 1996]. For example, a common ratio that is used is the C<sub>2</sub>H<sub>2</sub> to CO ratio. Acetylene has a much shorter lifetime (two weeks) than CO (two months). Therefore, as an air mass ages, the C<sub>2</sub>H<sub>2</sub> mixing ratio decreases faster, lowering the ratio C<sub>2</sub>H<sub>2</sub>/CO rapidly. A lower ratio indicates a photochemically aged air mass that has undergone extensive atmospheric processing (i.e., oxidation and dilution), and a higher ratio means that the air mass is younger and has been influenced by fresh emissions [McKeen and Liu, 1993; Smyth et al., 1996]. In addition, another valuable use of hydrocarbons is as tracer of anthropogenic pollution. For instance, CO and C<sub>2</sub>H<sub>2</sub> are both derived from combustion, thus air masses containing these species are known to have a continental source.

#### **1.7.2** Seasonal trends and photochemical removal

As mentioned earlier, the relative mixing ratios of different gases offer important information about their sources and can provide insight into photochemical processing and mixing. In order to examine influences affecting seasonal variations of the NMHCs, an analysis using hydrocarbon ratios has been applied. The analysis is based on the assumption that the ratio of concentration of two species can be used to characterize the age of an air mass from the specific point of time when those two species were simultaneously introduced into that air mass. For long range transport, dilution can not be neglected due to non-negligible concentrations of the longer-lived species which will bias the determination of age, as has been shown by *McKeen and Liu*, [1993]. However, the calculation still offers insight into the NMHCs removal processes. If the dilution effects are neglected then the change in the concentration ratio  $r_{ij}=C_i/C_j$  of two hydrocarbons i and j due to photochemical removal as a function of time in a given air mass can be described as follows:

$$r_{ij} = r_{ij}^{0} \exp(t.(1/\tau_{i} - 1/\tau_{j}))....(1.6)$$
  
with  $r_{ii}^{0} = r_{ij}$  at  $t=0$ 

 $\tau_i$  and  $\tau_j$  are the lifetimes of compounds *i* and *j*, respectively. Since the only known relevant removal mechanism for light alkanes in the troposphere is the reaction with OH radical,  $\tau$  can be calculated from the OH radical concentration and the reaction rate constant *k*.

$$\tau_i = \frac{1}{[k_i.[OH]]}$$
....(1.7)

Equation (1) can be then written as

$$r_{ii} = r_{ii}^{0} \exp(t.[OH].(k_{i} - k_{i}))....(1.8)$$

We can use a second equation describing the concentration ratio of another pair of hydrocarbons  $r_{kj}=Ck/Cj$  to eliminate *t.[OH]* from equation (3) and obtain the following equation describing the dependence of  $r_{ij}$  from  $r_{kj}$ .

A plot of  $\ln r_{ij}$  versus  $\ln r_{kj}$  should give a straight line with the slope of

$$a = \frac{(k_j - k_i)}{(k_j - k_k)}....(1.10)$$

and the intercept,

In order to apply equation (4) to our data we have to assume that local sources of alkane do not contribute significantly to the observed concentrations. If the slope measured from observed values of species comes close to the calculated value (from literature data) then effect of dilution is really negligible and if the deviation of slope values are considerable, dilution do play important role in the distribution of trace species.

### 1.7.3 Age of air parcel

The travel time of pollutant gases from the source is also known as their "age". It is estimated from the measured ratio between two trace compounds with different lifetimes in the atmosphere [*de Gouw et al.*, 2001]. The age an air mass  $\Delta t$  is estimated from

Where  $[A]_t$  and  $[B]_t$  are the measured mixing ratios of the compound A and B and  $[A]_0/[B]_0$  is the ratio between the mixing ratios of the compounds A and B assumed at the source. It is assumed that the removal of compounds A and B is only determined by reaction of A and B with OH radicals with rate coefficient of  $k_A$  and  $k_B$ , respectively. Where [OH] is the 24-hour averaged concentrations of OH radicals.

## **1.7.4 Effects of dilution**

The ratios of the concentrations of the light hydrocarbons have been used to obtain the photochemical age estimates. In this technique it is assumed that the relative abundances of a set of hydrocarbons varies with time, as the more reactive species disappear at a

faster than the less reactive ones. Initial implementations of this technique considered only reactions of hydrocarbons with OH or Cl. Recent works have indicated that hydrocarbon ratios depend also on dilution effects.

Following *Mckeen and Liu* [1993] and *Mckeen et al.* [1996], the change in the concentration of a hydrocarbon X with mixing ratio [X] is approximated as

$$\frac{dX}{dt} = -L(x)[X] - K([X] - [X]^b)....(1.13)$$

Where the L(x) is rate of disappearance due to reaction with OH ( i.e., kx[OH]), K is a mixing coefficient which expresses the overall rate for the dilution of hydrocarbon containing source air with background air and  $[X^b]$  is the background concentration of X.

## **1.8** Objectives and chapter details of the thesis work

This thesis is focused on the study of  $O_3$  and its precursor gases (CH<sub>4</sub>, CO, NMHCs etc.) with an emphasis on NMHCs in different environments. The following objectives are addressed:

- To study the temporal (diurnal and seasonal) distributions of O<sub>3</sub> and some of its precursor gases at Ahmedabad and Mt. Abu.
- To study the transport of O<sub>3</sub> and other trace gases like CO, CH<sub>4</sub> and NMHCs over the Bay of Bengal under two different wind flow regimes, NE flow in the winter while SW during summer season. NMHCs and their ratios were used to estimate the age and sources of the air parcels.
- To study the vertical distributions of O<sub>3</sub> along with simultaneously measured meteorological parameters like relative humidity and temperature over Delhi and Madras using MOZAIC (aircraft measurements) data.

The thesis comprises six chapters including this introductory discussion of the background work done in this field in **Chapter 1**.

**Chapter 2** discusses experimental techniques applied for in-situ measurements of  $O_3$  and analyses of air samples for measurements of various trace gases (CH4, CO and NMHCs). In the beginning operational details and working principle of  $O_3$  analyzer are discussed. Basic elements of gas chromatography and their operational details and measurements methods applied for the measurements of CO, CH4 and NMHCs in the laboratory at PRL are discussed. Basic principles and some technical details involved in

#### CHAPTER 1

the measurements of UV-B and total solar fluxes are summarized. In the final section of this chapter brief discussion of MOZAIC instrumentation for the measurements of  $O_3$  and water vapor (relative humidity) are presented.

**Chapter 3** deals with the measurements made at Ahmedabad (urban site) and Mt. Abu (remote, hilltop). Discussion includes a detailed study of observed diurnal and seasonal variations in various trace species during 2002 with more emphasis to NMHCs species measurements. These measurements of NMHCs are compared with earlier measurements made at other sites in the Northern Hemisphere (NH). Correlation studies in various trace species are discussed to investigate the possible sources of pollutants. NMHCs measurement data are also studied to infer the dominant atmospheric processes, responsible in the observed distributions of various trace gases at Ahmedabad and Mt. Abu.

**Chapter 4** is focused mainly to discuss the distributions and transports of various trace gases ( $O_3$ , CO,  $CH_4$  and NMHCs) measured in the different seasons over the Bay of Bengal. Apart from chemical characterization detailed discussion of various distribution features are also made. Both dynamical (wind fields and back trajectories) and chemical (trace gas ratios) traces are incorporated to discuss the transports of trace gases over the Bay of Bengal. These measurements are also compared with earlier measurements made over the Bay of Bengal, Indian Ocean and Arabian Sea.

**Chapter 5** is based on the analyses of MOZAIC data observed over Madras (Chennai) and Delhi during 1996-2001 period. The data set consists of simultaneous vertical measurements of  $O_3$ , water vapor and meteorological parameters in the troposphere. Annual and inter annual (1996-98) variations in  $O_3$  and water vapor distributions are discussed in detail. Case studies of some selected measurements ( $O_3$ , RH and temperature) are also made to investigate the underlying atmospheric processes in observed distributions. Supporting Rainfall, wind field and back trajectory data also support discussions.

**Chapter 6** presents the summary of important resulted obtained in this work. It also describes the basis provided by this work for future studies
## CHAPTER 2

## Instruments and Experimental Methods

## 2.1 Measurements of ozone in the atmosphere

The amount of ozone in the atmosphere is measured by instruments on the ground and also carried aloft in balloons, aircraft, and satellites. Measurements involve drawing of air into an instrument that contains a system for detecting ozone. Other measurements are based on ozone's unique absorption of light in the atmosphere where sunlight or laser light is carefully measured after passing through a portion of the atmosphere containing ozone. The detection techniques make use of ozone's unique optical and chemical properties.

The main two techniques developed for ozone measurements are chemiluminescent and electrochemical methods. However, the chemiluminescent substance is subject to deterioration when exposed to light and to moisture. Extensive measurements were made in fifties using electrochemical method. This method makes use of the reaction of ozone with potassium iodide (KI) solution, which gives iodine. But electrochemical method, based on oxidation and reduction reactions, also has interferences by SO<sub>2</sub> (a reducing agent) and NO<sub>2</sub> (an oxidizing agent), if the levels of these species are sufficiently high. More importantly, these methods need regular and frequent calibration [Regener, 1960; Komhyr, 1969]. A method well established for measurements of surface ozone, is the UV absorption technique, in which absorption of UV radiation at wavelength of 253.7 nm takes place by ozone molecules. Figure 2.1 depicts a simplified block diagram of ozone analyzer based on UV absorption technique. Measurement of ozone in laboratory using ultraviolet (UV) light was started in 1912 [Fonrobert, 1916]. Since then this method has greatly improved with advancement of technology. In the present study surface measurements were made in different environments using UV absorption based ozone analyzer (Dasibi, USA). Technical details of this instrument are discussed below.



**Figure 2.1:** A simplified layout of the ozone analyzer showing the working principle of the system. Adapted from Dasibi operating and maintenance manual [1990].

#### 2.1.1 Principle of operation

Figure 2.2 represents a schematic diagram of optics and pneumatic subsystem of Dasibi ozone analyzer. A fixed quantity of "zero gas" and the same quantity of "sample gas" are drawn-in alternately to the optics bench in the instrument by utilizing a pump and sampling system. The zero gas (reference) is ambient gas, but with the ozone "scrubbed";



**Figure 2.2:** Schematic diagram of optics and pneumatic subsystem of Dasibi ozone analyzer. Adapted from Dasibi operating and maintenance manual [1990].

the sample gas is the pure, unaltered ambient gas, with the ozone still present. A stable UV light source is placed at one end of the optics bench (absorption cell) and the level of

UV radiation transmitted across the optics bench is measured by a UV detector which is placed at its opposite end. Alternate, consecutive measurements of the absorption of UV radiation during the zero gas (reference) cycle and the sample gas (measurements) cycle are made by the photometer. Appropriate signal processing of each individual measurement pair by the electronic system yields the instantaneous ozone concentration in accordance with the Beer-Lambert law. During the reference cycle, air is drawn into the photometer through a scrubber, which removes all ozone, and the light intensity ( $I_o$ ) is determined. The valve is then switched to allow ambient air to fill the cell. During this measurements cycle the light intensity (I) is determined. The Beer Lambert law is more often expressed in its integrated form, the attenuation of radiation of wavelength ( $\lambda$ ) on passing through a sample thickness (I) and number density (n) is

$$\frac{I(\lambda)}{I_o(\lambda)} = \exp[-\sigma(\lambda)nl]$$

The relationship between these measurements and the ozone concentration as follows.

$$[O_3] = (-\frac{1}{al} \ln \frac{I}{I_o})(\frac{T}{273})(\frac{760}{P}) \times \frac{10^6}{L}$$

Where:

 $[O_3] = O_3$ , concentration, ppm

- a = absorption coefficient of  $O_3$  at 254 nm=308 atm<sup>-1</sup>cm<sup>-1</sup> at 0°C and 760 torr
- l = optical path length, cm
- $T = sample temperature, ^{\circ}K$
- P = sample pressure, torr
- $L = correction factor for O_3 losses$
- $\sigma$  = absorption cross section

Subsystems of an ozone analyzer are described below.

#### 2.1.2 UV photometer

A photometer is a device, which quantitatively determines the amount of light crossing a prescribed area. The UV photometer in ozone analyzer consists of a stable UV light source which is placed at one end of the optics bench, and a suitable UV detector which is placed at the opposite end. The detector provides an electrical output which is directly proportional to the amount of UV radiation striking its sensitized surface. Ozone present

in the sample gas attenuates the intensity of the UV radiation traversing the bench during the measurement cycle in accordance with Beer's law. This attenuated signal is detected and compared with the unattenuated signal from the previous reference cycle. The two signals are processed digitally by the electronics for direct presentation as ozone concentration.

The UV light source is a low pressure, cold cathode mercury vapor lamp with 92 percent of its output concentrated at the 253.7 nm emission line. The absorption spectrum of ozone contains a maximum at the wavelength of 253.7 nm, which is also the main emission line of mercury, as shown in Figure 2.3 Emission at wavelengths shorter than 200 nm is eliminated by a Vycor optical filter around the lamp. The detector is "solar blind" Cesium Telluride vacuum photodiode with a broad pass-band centered near 253.7



**Figure 2.3:** Absorption spectrum of ozone (solid thin line) and main emission lines of mercury at low pressure (continuous vertical lines). Dashed curve shows the response of the UV detector used in ozone analyzer. Adapted from Dasibi operating and maintenance manual [1990].

nm. The total optical selectivity of lamp and detector is such that better than 99.5 percent of the system response is due to 253.7 nm light. The optical bench is a sealed chamber to contain and physically isolate the sample gas. Quartz windows allow the beam of UV radiation to pass through the chamber from the lamp to the detector, both of which are mounted externally. For monitors with long optical paths that must be "folded" to fit in

the instrument, quartz mirrors are mounted in a triangular optical block to bend the UV radiation through 180°.

#### 2.1.3 Sample handling system

The reference cycle is implemented by use of catalytic converter (which selectively converts ozone in the sample gas to oxygen, but does not affect any of the other constituents). During this cycle, the gas selection valve routes ambient gas through the catalytic converter and then directs this gas into the optics bench for measurements by the photometer. During the measurement cycle, the gas selection valve bypasses the catalytic converter and routes the sample gas directly into the optical bench for measurements by the photometer. The ozone scrubber is a two-piece aluminum assembly that contains a replaceable cartridge (copper screens coated with manganese dioxide (MnO<sub>2</sub>)). The response time of the solenoid valve in ozone analyzers is about 10 seconds.

#### 2.1.4 Calibration of ozone

Calibration of the ozone analyzer is done regularly by using in-built ozone generators. The Dasibi analyzer was calibrated at Research Center, Juelich, Germany in 1998. This analyzer was also inter-compared for a day on the Indian Oceanic Research Vessel (ORV) Sagar Kanya along with the simultaneous measurements of ozone made on NOAA's ORV Ronald Brown during INDian Ocean EXperiment (INDOEX) campaign in March, 1999. The comparison showed a good agreement with a correlation coefficient ( $r^2$ ) of better than 0.95. The detection limit of the ozone analyzer is 1 ppbv, the absolute accuracy is above 95% [*Kleinman et al.*, 1994].

#### 2.2 Measurements of hydrocarbons in the atmosphere

Although a rough picture of the source, distribution, and sinks of the hydrocarbons is beginning to emerge, doubts remain as to reliability and reproducibility of the various analytical techniques employed in deriving the hydrocarbon concentrations in the atmosphere. The analysis of the hydrocarbons is complicated by the great number and variety of hydrocarbons species that are present in the atmosphere.

#### **2.2.1** Present methods for NMHCs analysis

The general methods employed for hydrocarbon analysis by the scientific community have been discussed by Singh [1980], Westberg and Zimmerman [1993] and summarized in Apel et al. [1994]. The most common approach is based upon a gas chromatographic separation of the individual hydrocarbons and the detection of each using a flame ionization detector (FID). For chromatographic separation of the compounds we need a proper column stationary phase and temperature program of the oven in which the column resides. Many column materials have been used successfully in recent years and the column chosen by an investigator is dependent upon the analysis required. Commonly used detectors (e.g., Flame Ionization Detector, Mass Spectrometer (MS)) are not sufficiently sensitive to measure ambient hydrocarbons at low concentrations. For these measurements it is necessary to collect a large volume of air sample and then preconcentrate the hydrocarbons present in the known sample volume before injection on to the column. There are several methods available for pre-concentration prior to injection. In one common method the hydrocarbons are cryogenically trapped in a glass bead-filled, stainless steel or nickel loop immersed in liquid oxygen, argon, or nitrogen. Gas chromatograph (GC)-FID peak identifications are typically accomplished by running known standard mixtures (qualitative) and noting the elution (or retention times) of each particular compound of interest. Elution times for each hydrocarbon can be very reproducible if the system is operated under nearly identical conditions for each run. Peak detection is more facile for GC-MS systems as one can use the mass spectrometer for specific detection even if there is co-elution.

Other techniques for ambient hydrocarbon analysis are possible but have not been used widely to date (e.g., photoionization detection of aromatics and isoprene). Column measurements of selected hydrocarbons have been done spectroscopically [*Rinsland et al.*, 1987]. Tunable diode laser systems can also be applied to the detection of selected short-chain hydrocarbon species, but the research has not yet defined the sensitivity and practicality of these methods for most atmospheric hydrocarbons at trace concentrations.

Instrument calibration is a critical component of volatile hydrocarbon analyses. Accurate standard is a prerequisite for quality analyses. Various standard hydrocarbons or mixtures of hydrocarbons are employed by the investigators to calibrate their instruments in order to quantify the mixing ratio of hydrocarbons in an ambient air sample. Some investigators prepare their own standards. Others use secondary standards from a commercial source, while still others purchase gravimetric from a national laboratory. The sensitivity of the FID detector to the molecules of the light NMHCs ( $C_2$ - $C_8$ ) shows a nearly linear response to the molecular weight of the hydrocarbon or number of C atoms/mol although differences between compounds are noted (Figure 2.4). These differences are typically less than 10% for the compounds that have been studied. Many investigators have taken advantage of this and simply report the concentrations of a



**Figure 2.4:** *Relative response of the flame ionization detector (FID) versus compound. Adapted from Apel et al. [1994].* 

myriad of hydrocarbons referenced to a particular standard material (e.g., propane from National Institute of Standard and Technology (NIST)). Other laboratories do not rely on the molecular weight linearity of the FID detector. These laboratories generate a standard for each compound that they wish to analyze, and calibrate their instruments accordingly.

#### 2.2.2 Measurement of NMHCs using GC techniques

A basic chromatograph is represented diagrammatically in Figure 2.5. The term chromatography covers the separation techniques in which the separation of compounds is based upon the partition or distribution of the analytes between two phases in a dynamic system. In gas chromatography (GC) we have a gaseous mobile phase and a



**Figure 2.5:** Schematic representation of a basic gas chromatograph. Adapted from Fowlis [1995].

liquid or solid stationary phase. All the solute molecules spend the same amount of time in the gas phase. The difference in retention times, i.e. how long it takes to elute the compound from the column, depends upon its retention by stationary phase. Thus, the



Figure 2.6: The flame ionization detector (FID). Adapted from Fowlis [1995].

heart of the gas chromatograph is the column in which the separation of the components takes place. Since temperature will influence the volatility of the analytes, the column is placed in a thermostatically controlled oven. Gas chromatography requires a supply of carrier gas of sufficient quality and pressure to achieve the desired separation. Carrier gases, usually nitrogen, helium or hydrogen are normally supplied from compressed gas cylinders. Carrier gas should be inert, dry and free of oxygen to prevent degradation of the column. Depending upon the requirements various detectors can be coupled with gas chromatograph. Flame Ionization Detector (FID) is one of the commonly used detectors for hydrocarbons. The construction of a typical flame ionization detector is shown in Figure 2.6, it consists essentially of a base in which the column eluent is mixed with hydrogen, a polarized jet and a cylindrical electrode arranged concentric with the flame. Air is supplied to the detector to support combustion. The assembly is contained in a stainless steel or aluminum body to which are fitted a flame ignition coil and electrical connections to the collecting electrode, and a polarizing voltage to the detector. Gas chromatographic technique coupled with FID have been used for the analyses of  $C_2-C_5$  NMHCs.

#### 2.2.3 Methods for C<sub>2</sub>-C<sub>5</sub> NMHCs analyses at PRL

The experimental system consists of a Hewlett-Packard 5890 series II gas chromatograph (GC) with a Flame Ionization Detector installed. The column is a 50m×0.32mm i.d.;



**Figure 2.7:** A typical chromatogram, showing separation of various NMHCs. Retention time (in minutes) are also shown.

porous layer open tubular (PLOT) column of KCl/Al<sub>2</sub>O<sub>3</sub> stationary phase. High purity Helium (He) is used as carrier gas with a flow rate of 8 ml/min. Hydrogen and zero-air are flame gases with flow rates of 30 and 300ml/minute respectively. Because of their

trace quantities of NMHCs in air samples, it is almost always necessary to preconcentrate hydrocarbon samples before GC analysis. The air samples of up to 1.5 L are preconcentrated using a cryo-trapping procedure. The air to be analyzed is drawn through a so-called cold trap, consisting of a 1/8"stainless steel loop (packed with 75-100 micron size glass beads) submerged in liquid nitrogen. The NMHCs in the air are thus concentrated efficiently in the loop, it had sufficient capacity and cross section so that water vapor trapped simultaneously would not impede the sample air flow at cryogenic trapping temperatures. Both ends of the stainless-steel tube were plugged with a silanized glass wool. The adsorbed NMHCs were thermally desorbed by submerging the loop into boiling water for the re-volatilization of hydrocarbons, and introduced into the GC column by flushing with helium gas through the loop. Six port, dual-position-actuated valves (Valco Instruments, Inc.) perform the gas line switching necessary for these preconcentration steps. During the analyses, the column oven temperature was ramped from 0 °C to 200 °C in three steps to separate the gases of our interest. Under these conditions, this system can resolve 9 identified NMHCs species. A sample chromatogram produced



**Figure 2.8:** Time variations of various NMHCs analyzed from a working standard, representing the stability of the system (GC-FID). NA stands for normalized area w.r.t. sample volume.

on the analytical system is depicted in Figure 2.7. Identification of NMHCs was made by comparison with reference gas mixtures and by computation of retention indices. To check the stability of the system, regular analyses of a reference mixture (Std#2) have been performed. This system (GC-FID) shows good stability throughout the year for various analyzed NMHCs species (Figure 2.8).

#### 2.2.4 Calibration of NMHCs

A dynamic system was used to dilute a flow of the primary 9-component standard (1 ppmv for each species) to several concentrations from 12 ppbv to 300 pptv, these dilutions were used to calibrate the secondary standard (Std#2). Ultrahigh purity zero-air is used for dilution of calibration standard. The response of the FID detector was linear over the range 300 pptv to 10 ppbv for all NMHCs in the 9-component primary standard mixture. Figure 2.9 shows the linear fit scatter plots of various NMHCs levels and their



Figure 2.9: Multi-point calibration plots and their best linear fits for some NMHCs species.

response (normalized with respect to Std#2) showing very good correlation in all analyzed species. Calibrations of individual NMHCs were performed using a Scott (USA) supplied calibration mixture of NMHCs. Calibrations of these NMHCs were also performed using two different calibration mixtures from the Max Planck Institute for Chemistry (Mainz, Germany). The comparison showed good agreement (within 10% for all NMHCs) with calibration mixture from Scott. The reproducibility in NMHCs analyses ranged between 3 to 10% depending upon the compounds, in general lower molecular weight hydrocarbons showed better reproducibility.

## 2.3 GC techniques for CH<sub>4</sub> and CO analyses

The analyses of  $CH_4$  and CO were performed by another gas chromatograph (Varian Vista, 6000, USA). For the separation of  $CH_4$  and CO, a molecular sieve packed SS column of length 5 m was employed. Since FID does not response to carbon monoxide directly, measurements of CO were by converting it into  $CH_4$ . For this, column elutes were allowed to pass through a methanizer (Ni catalyst heated at  $325^{\circ}C$ ) before reaching the detector (FID). The column temperature was kept constant at  $75^{\circ}C$ . Helium gas was



**Figure 2.10:** A typical chromatogram, showing separation of  $CH_4$  and CO.

used as carrier gas, with a flow rate of 30 ml/minute. Analyses were made online at PRL Ahmedabad as well as from the air samples collected in pre-evacuated glass bottles. Air sample was introduced into a sample loop of ~ 3 ml and subsequently injected into the GC column by eight port switching valve (VICI, USA). When the separated gas sample pass through a methanizer with adequate supply of H<sub>2</sub>, CO is catalytically converted into CH<sub>4</sub> by following reaction.

$$CO + 3H_2 \xrightarrow{Ni,325^{\circ}C} CH_4 + H_2O$$

For CH<sub>4</sub> and CO, we used NIST and Matheson supplied calibration mixtures respectively. The analyses of CH<sub>4</sub> and CO showed better than 1 and 5% reproducibility, respectively. A secondary standard was prepared at PRL (Std#2) which was also analyzed at regular intervals during the sample analysis period. A typical chromatogram of methane and CO analyses is shown in Figure 2.10.

#### **2.4** Measurements of UVB and total solar flux

UVB (280-315 nm) radition is measured using UV-Biometer (Solar Light Co, Model 501 A, USA). The principle of UV radiation measurement used in the 501 A UV-Biometer is the same as that used for the Robertson-Berger meter. The solar light enters the detector through quartz dome and input filter. Then the partially filtered light, containing the UV spectrum, excites the phosphor. The visible light emitted by phosphor is detected by the GaAsP diode. The diode and the phosphor are encapsulated in the metal enclosure, which is thermostated by the Peltier element. The current produced by the GaAsP diode is converted to voltage and amplified.

The total radiation flux is measured by using Pyronometer (Kipp & Zonen, Model CM 6B). The pyranometer CM 6B is provided with a thermal detector. This type of detector responds to the total power absorbed and theoretically it is non-selective as to the spectral distribution of the radiation. This implies that naked thermal detector is also sensitive to long-wave infrared (thermal radiation  $\lambda > 3000$  nm) from the environment. The radiant energy is absorbed by a black painted disk. The heat generated flows through a thermal resistance to the heat sink. The temperature difference across the thermal resistance of the disk is converted into voltage. A desiccator in the body prevents dew on the inner side of the dome, which can cool down considerably, at clear windless nights.

## **2.5 MOZAIC Instrumentation for O<sub>3</sub> and relative humidity** measurements

The Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) program was initiated in 1993 by European scientists, aircraft manufacturers, and airlines to collect experimental data. The ozone analyzer is a dual beam UV absorption instrument (Thermo-Electron Model 49-103), which has a detection limit of 2 ppby. Uncertainties in

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the measurements are estimated to be  $\pm 2$  pbbv, although actual performance is better [*Thouret et al.* 1998]. The response time of the instrument is 4s which translates in to a vertical resolution of 30 m. Full details of calibration procedures and mounting in the aircraft are also given in *Thouret et al.* [1998].

Relative humidity and temperature are measured with a capacitive sensor (Humicap-H) and a platinum resistance sensor (PT100), respectively. The Humicapcapacitor together with the PT100 resistor are mounted at the top of an axisymmetric body, which is especially designed for installation in an appropriate housing. The sensor housing is positioned outside the fuselage, 7 m backward from the aircraft nose on the left side just below the cockpit. Air sampling is made at 7 cm distance from the aircraft skin, well outside the aircraft boundary layer. Inside the housing inlet the sampled airflow is divided into two sub-flows. The main flow traverses straight through the housing. The minor flow makes a right angle turn to a smaller channel, perpendicular to the main channel, passing over the sensor elements before reaching a small outlet, located at the lower back side of the housing. The right angle turn of the secondary airflow protects the sensors against dust, water, and particles. The internal boundary layer air is sucked off through small holes in the sidewalls of the housing, minimizing internal boundary layer effects. This protects the core of the sampled airflow from thermal or humidity influences as might originate from contact of the outer parts of the sampled flow with the walls of the housing. Further details of MOZAIC instrumentation are given in Helten et al., [1998].

## Distributions of Trace Gases at Ahmedabad and Mt. Abu

Understanding of the tropospheric  $O_3$  is very important because, besides being a greenhouse gas, it is a precursor for the highly reactive hydroxyl radical (OH), which determines the chemical composition of the troposphere. Ozone is one of the secondary air pollutants whose high concentration is harmful for human and plants [*Finnan et al.*, 1997]. In the lower troposphere,  $O_3$  is mainly produced by photochemistry involving pollutants, which are released from various industrial and other anthropogenic activities. Photochemical  $O_3$  production takes place by photoxidation of CH<sub>4</sub>, CO and NMHCs (nonmethane hydrocarbons) in the presence of sufficient amount of NOx (NO+NO<sub>2</sub>) as mentioned in chapter 1.

Non-methane hydrocarbons play an important role in the chemistry of the troposphere as precursors of O<sub>3</sub> and peroxyacetylnitrate (PAN). Many model studies have indicated that ground level O<sub>3</sub> concentrations, especially peak levels, in rural and semirural areas are sensitive to change in anthropogenic emissions of NMHCs and nitrogen oxides (NOx) [*Sillman et al.*, 1990; *Jacob et al.*, 1993]. Measurements of organic trace gases, particularly NMHCs, have become increasingly valuable to understand important tropospheric processes, both for transport and chemistry. Especially, long term measurement series at remote locations have been instrumental in improving our knowledge on tropospheric sources and sinks of organic trace gases [*Ehhalt et al.*, 1991; *Rudolph et al.*, 1992; *Montzka et al.*, 1996]. Seasonal variations in NMHCs concentrations are influenced by: (1) photochemical removal (primarily by the hydroxyl (OH) radical), (2) NMHCs source strengths, (3) dilution due to atmospheric mixing of air parcels [*Roberts et al.*, 1985; *Rudolph and Johnen*, 1990; *McKeen et al.*, 1996], and (4) transport from source regions to the sampling site [*Klonecki et al.*, 2003]. Seasonal changes in anthropogenic NMHCs source strengths are thought to be small [*Jobson et al.*,

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1994b; *Poisson et al.*, 2000] because they are largely driven by constant urban fossil fuel combustion and leakage from oil and natural gas production [*Friedrich and Obermeier*, 1999]. For the light NMHCs of interest (ethane, propane, acetylene, iso- and n-butane), urban or industrial sources will have higher emissions from evaporation during summer, particularly for the butanes. The  $C_2$ – $C_4$  NMHCs are not emitted in significant quantities by natural (biogenic) sources [*Guenther et al.*, 2000]. Transport and photochemical removal processes are also strongly seasonal.

There is a lack of study related to the tropospheric chemistry in the tropical region. This is the region of large biogenic and pyrogenic emissions of trace gases, including NMHCs, which react with high OH concentration and thus making it the most active photochemical region of the atmosphere [*Andreae and crutzen*, 1997]. Estimations made using the chemical transport model (NASS/GISS) show that on increasing the anthropogenic emissions (by two and four times), O<sub>3</sub> production efficiency is maximum over the Indian region, followed by Japan and China, which is explained on the basis of increase in OH and peroxy radicals [*Berntsen et al.*, 1996].

One of the problems that arises in the interpretation of volatile organic compounds (VOCs) measurements at remote locations is differentiating between large-scale and local effects. Especially for compounds with short atmospheric residence times and no secondary formation processes, even very small local emission rates can have a substantial impact on the observations. The temporal, and consequently also the spatial scale, that is relevant for the interpretation of VOCs concentrations obviously depend on the atmospheric lifetimes and thus the reactivity of the compounds. The rate constants for the reaction of VOCs with OH-radicals, the most important removal process for nearly all VOCs, cover several orders of magnitude, the corresponding lifetimes range from several months or longer to less than an hour. As a consequence, observations of VOCs at a given location will, depending on the individual VOCs, represent spatial scales ranging from some hundred to several thousand kilometers. This complicates the interpretation of seasonal variations and secular trends, but also presents an opportunity to derive insight into the different temporal and spatial regimes that determine the trace gas levels at the measurement location.

Over the Indian region, only limited measurements of  $O_3$  and some of its precursors (mostly CO, CH<sub>4</sub>, NOx) are available [*Lal et al.*, 2000, *Naja et al.*, 2002]. However, till recent years there have been no systematic simultaneous measurements of

surface  $O_3$  and important precursors NMHCs over this region. Recognizing this, studies of  $O_3$  and NMHCs have been made at Ahmedabad and Mt. Abu.

# 3.1 Distributions of $O_3$ , CO, CH<sub>4</sub>, and C<sub>2</sub>-C<sub>5</sub> NMHCs at Ahmedabad

#### 3.1.1 Description of the site, experiments and general meteorology

The observational site, Physical Research Laboratory (PRL), is situated at the western edge of the Ahmedabad (23 °N, 72.6 °E, 49 m asl) city. It is an urbanized city having numerous industries and a thermal power station. The population of Ahmedabad is above 5 million and currently total number of vehicles is over 4.5 million. Figure 3.1(a) represents the number of vehicles in the last three decades. Due to rapidly increasing number of vehicles, the transport related activities are the major contributor to the very



**Figure 3.1(a):** Number of vehicles during the last three-decades at Ahmedabad. Adapted from IIMA.

high levels of various pollutants. Realizing the important roles in photochemical production of  $O_3$  and their large local emission sources, measurements of  $C_2$ - $C_5$  NMHCs at Ahmedabad were started in September 2001, however only a full year 2002 data have been discussed here. Except few months in 2002, simultaneous analyses of CH<sub>4</sub> and CO were also performed. Measured C<sub>2</sub>-C<sub>5</sub> NMHC species are ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>),

butanes ( $C_4H_{10}$ ), pentanes ( $C_5H_{12}$ ), ethene ( $C_2H_4$ ), propene ( $C_3H_6$ ), and acetylene ( $C_2H_2$ ). To avoid any kind of storage related contamination, air samples for analysis were directly sucked in from the terrace of the main building through an SS (Stainless Steel) tube (1/4-inch diameter OD). Measurements of NMHCs were made continuously for 72 hours with 1-hour interval for all the months of the year 2002. Apart from these nine NMHC species, we also have regular observation data for O<sub>3</sub> and solar radiation fluxes for this site. We are using gas chromatography techniques with flame ionization detector (FID) for the analysis of NMHCs,  $CH_4$ , and CO species. Ultra-Violet absorption based analyzer is used for in-situ measurement of O<sub>3</sub>. Other technical details of these instruments have been discussed in chapter 2.

Due to non-availability of regular wind speed and wind direction measurements at Ahmedabd for the year 2002, previous measurements (1994) have been given in Figure 3.1(b). The mean wind fields based on NCEP (National Center for Environmental



**Figure 3.1(b):** Frequency of occurrence (in hours) of wind direction in four direction sectors during, 1994, observed at Ahmedabad. Adapted from Lal et al. [2000].

Prediction) reanalysis data at 925-mb level for different months of 2002 over part of India have been shown in Figure 3.2. Both plots show the general meteorology, in winter months when northeast wind pattern dominates and in summer when southwest wind pattern dominates over this region. Such changes in wind patterns are observed each year [*Asnani*, 1993; *Lelieveld et al.*, 2001]. The wind pattern changes dramatically from southwesterly to



**Figure 3.2:** Monthly averaged NCEP wind field streamlines at 925 mb pressure level during different months of year 2002. The color bar represents the wind velocity (m/s). Big arrow marks show the directions of general wind fields over Ahmedabad and Mt. Abu.

northeasterly after September, which continues till January-February with some dominance of northerly winds. Wind pattern is northwesterly in early spring (March), which changes gradually to southwesterly in late spring (May) and it dominates during the entire summer period (June-August).

#### 3.1.2 Diurnal variations of C<sub>2</sub>-C<sub>5</sub> NMHCs

Various investigations of NMHCs have been attempted to obtain their characteristic mixing ratios in urban sites [Derwent et al., 1995; Pandit and Rao, 1990; Sharma et al., 2000; Seila et al., 1989]. But the long-term study of light NMHCs in tropical urban regions have been rarely reported. Except for the measurements at Kathmandu [Sharma et al., 2000] and Mumbai [Rao et al., 1997], we have not found any reported measurements of NMHCs in the tropical Asia. Diurnal patterns of all C<sub>2</sub>-C<sub>5</sub> NMHCs measured at Ahmedabad for the year 2002 are shown in Figure 3.3(a-i). The presented data are the mean values during summer and winter seasons along with the annual mean. In particular the winter season variability is more enhanced while subsidized during the summer season. The pattern of variability differs from species to species in C<sub>2</sub>-C<sub>5</sub> NMHCs. For example, in alkanes (ethane, propane, i-butane and n-butane) the values are elevated from evening till early morning particularly in winter season. While in unsaturated compounds like ethene, propene and acetylene two sharp peaks, first between 7-11 hours IST (Indian Standard Time; 5.5 hrs ahead of GMT) and second at 18-24 hours IST can be clearly seen. Evening hour peaks are more pronounced (broader peaks with large amplitudes) compared to morning peaks in these species. Only a single peak between 18-24 hours IST in diurnal pattern of pentanes (i-C<sub>5</sub>H<sub>12</sub> and n-C<sub>5</sub>H<sub>12</sub>) is observed. A minimum between 15-16 hours IST is a characteristic feature in the diurnal distribution of all C<sub>2</sub>-C<sub>5</sub> NMHCs. In summer months, the variability is very small otherwise rest of the year we observe very clear diurnal pattern. The annual mean patterns show pronounced diurnal variability in all  $C_2$ - $C_5$  NMHC species. Unlike Ahmedabd, the diurnal variability in Osaka (Japan) shows large morning peaks apart from completely different diurnal patterns in C<sub>2</sub>-C<sub>5</sub> NMHCs [Morikawa et al., 1998].

The distributions of all the hydrocarbons measured in this study are influenced by local emissions. Ethene, acetylene, and propene are mainly emitted from vehicles [*Scheff and wadden*, 1993]. However, there are large differences in their reactivities, as acetylene is less reactive while ethene and propene are highly reactive species. Being a highly



**Figure 3.3:** Seasonal (winter and summer) and annual mean diurnal variation of various  $C_2$ - $C_5$  NMHCs mixing ratios observed during the year 2002 at Ahmedabad.

urbanized and industrialized city, the local emissions particularly the vehicular exhaust varies greatly around the study region apart from the boundary layer height and OH concentration variability. Two observed peaks in ethene, propene and acetylene coincide with peak traffic hours (8-11 hours IST and 17-22 hours IST) at Ahmedabad. Carbon monoxide also shows similar variation. These species have large emissions from automobiles exhaust due to incomplete burning of fossil fuel. Hence, apart from meteorology and OH reactivity the local emissions play very important role in the diurnal pattern of these compounds. Unlike ethene, propene and acetylene we do not observe two sharp peaks in the diurnal distribution of alkanes. The distinct patterns in alkanes suggest more important role of the boundary layer height variation compared to OH loss and local emissions as they are relatively long lived and have not much emission from the vehicles. Single peak during evening hours in pentanes may be attributed to high local emissions, less OH concentration and compressed boundary layer during these hours. Day to day changes in weather can alter the diurnal distribution patterns of NMHCs, for example in cloudy days during winter months; we do not observe much variation yet the values are high. Thus local emissions act as input for diurnal variations driven by meteorology and OH reactivity for many NMHCs at Ahmedbad.

#### 3.1.3 Diurnal variations of CH<sub>4</sub> and CO

Figures 3.4(a) and 3.4(b) show the mean diurnal variation plots of CH<sub>4</sub> and CO, respectively during the summer and winter seasons. In the summer season, apart from the low levels of CH<sub>4</sub> and CO the diurnal patterns also do not show any significant variability except a small evening peak in CO. But in the winter season not only values are elevated but they also show large diurnal variations. Methane and CO distributions show different features in their diurnal variability from each other. Methane starts increasing during evening hours and continues till early morning after that there is a slow decreasing trend, and attains a lowest value between 14-16 hours IST. In the morning (7-11 hours) and evening (18-24 hours), sharp increases in CO have been observed. The mean values of CH<sub>4</sub> are 1.56±0.12, and 2.4±0.33 ppmv while CO values are 191±98, and 615±277 ppbv during the summer and winter seasons, respectively.

Methane is the most abundant atmospheric hydrocarbon, with a lifetime of roughly 9 years [*Prinn et al.*, 1995]. Apart from large emissions due to natural processes CH<sub>4</sub> is also greatly contributed by anthropogenic activities and these play important role

#### **CHAPTER 3**

in its distributions. As far as urban or polluted regions are concerned, CO has insignificant amount of natural sources while there are large emissions from combustion related processes, its atmospheric lifetime is about 2-3 months. In the urban



**Figure 3.4:** Seasonal (summer and winter seasons) mean diurnal variations of  $CH_4$  and CO mixing ratios observed during the year 2002 at Ahmedabad.

environments, most of the CO comes from motor vehicles, so its concentrations closely follow the pattern of traffic at Ahmedabad. These are, therefore, highest during the morning and evening rush hours. When the traffic is lower CO levels show declining trend, and nighttime levels are much lower. Methane is relatively well mixed in the troposphere due to long lifetime also since the mixing ratio is orders of magnitude higher than CO and NMHCs. There are no sharp features in the diurnal pattern of  $CH_4$ . The diurnal pattern of  $CH_4$  in winter season is very much similar to what we have seen for ethane and propane though large differences in their lifetimes. One of the important reasons for this could be the common sources of emissions, like natural gas leakage, petroleum refineries etc. While the variability in CO is quite similar to that of ethene, propene, acetyelene with two sharp peaks in their distributions. It has been well studied that the combustion related processes are important sources of all these compounds, particularly fossil fuel burning. Lowest values of  $CH_4$ , CO and  $C_2$ - $C_5$  NMHCs during afternoon 14-17 hours could be due to the combined effects of high OH concentration and expanded boundary layer (more dilution).

#### 3.1.4 Seasonal variations of C<sub>2</sub>-C<sub>5</sub> NMHCs

Seasonal variations of NMHCs have been studied by surface and airborne measurements at various sites of the globe [*Rudolph et al.*, 1989; *Jobson et al.*, 1994a; *Young et al.*, 1997; *Klemp et al.*, 1997; *Gnauk and Rolle*, 1998; *Laurila and Hakola*, 1996; *Hov et al.*, 1991; *Roemer et al.*, 1999; *Goldstein et al.*, 1995b]. Seasonal variation with a maximum in winter and minimum in summer is frequently observed for hydrocarbons with longer atmospheric lifetimes (e.g. ethane, propane, acetylene) [*Jobson et al.*, 1994a; *Klemp et al.*, 1997]. Many studies have shown that the observed seasonal variations of NMHCs are consistent with their atmospheric removal by OH radicals [*Rudolph et al.*, 1989; *Laurila and Hakola*, 1996; *Klemp et al.*, 1997]. However, such studies have been limited to North American and European locations only.

Figure 3.5(a-i) shows the seasonal variations in nine  $C_2-C_5$  NMHCs at Ahmedabad for the year 2002. All these species show substantial seasonal variations. Like other reported measurements from various parts of the globe, measurements of light NMHCs at Ahmedabad also shows well-defined winter season high and summer season low values. The statistical data of all NMHCs measurements during different months of year 2002 at Ahmedabad are give in Table 3.1. This data set of monthly mean values of various NMHCs shows large range of variability (apart from the diurnal variability). The ranges of variations are 0.54-9.19, 0.98-5.53, 1.0-12.46, 0.15-2.38, 0.51-4.16, 0.55-6.39, 0.73-6.2, 0.58-3.23 and 0.25-0.97 ppbv in  $C_2H_6$ ,  $C_2H_4$ ,  $C_3H_8$ ,  $C_3H_6$ , i- $C_4H_{10}$ ,  $C_2H_2$ , n- $C_4H_{10}$ , i- $C_5H_{12}$  and n- $C_5H_{12}$  respectively. We have compared our seasonal data at Ahmedabad with other reported data from Osaka, an urban region in Japan [*Morikawa et al.*, 1998]. It can be observed very clearly that strength of variability (maximum to minimum ratio) at Ahmedabad is higher compared to Osaka, though the shape of variability is quite similar (phase of the seasonal variation). Not only in urban region but also in remote region of the troposphere the seasonal variations are similar with winter season high and summer season low values of light NMHCs. Comparison of this study and data from many other regions of the world revealed that the concentrations of



**Figure 3.5:** Comparison of annual variation of surface NMHCs mixing ratios (ppbv) measured at Ahmedabad and Osaka (Japan). Osaka data are adapted from Morikawa et al. [1998].

Months	Statistics	C.H.	С.Н.	CaHa	C.H.	i-C.H.	С.Н.	n-C.H.	i-C-H-	n-C-H-a
2002	Statistics	C2116	C2114	C3118	C3116	1-041110	$C_2\Pi_2$	<b>n-C</b> 41110	1-0.51112	<b>II-C511</b> 12
Jan.	Mean	7.12	4.49	7.03	1.77	2.64	3.10	3.81	2.45	0.77
	Median	4.23	3.30	4.38	1.23	1.77	1.25	2.74	1.56	0.51
	Std-dev.	6.24	3.42	6.65	1.34	2.31	3.46	2.82	2.03	0.57
Feb.	Mean	6.04	4.65	6.93	1.61	2.87	2.94	4.74	2.48	0.69
	Median	4.27	3.66	4.99	1.22	2.14	1.82	4.01	1.70	0.53
	Std-dev.	3.77	3.06	4.91	1.17	2.21	2.62	3.09	2.01	0.50
Mar.	Mean	4.81	4.56	7.56	1.50	3.51	2.76	6.20	2.74	0.84
	Median	3.20	4.25	4.93	1.37	2.30	2.11	5.09	2.04	0.66
	Std-dev.	4.74	3.00	7.56	1.03	3.45	2.47	5.47	2.33	0.55
Apr.	Mean	2.59	2.34	2.93	0.77	0.97	1.90	2.15	1.43	0.54
ŕ	Median	1.79	1.17	1.78	0.40	0.52	0.80	0.87	0.60	0.28
	Std-dev.	2.09	3.52	3.22	1.04	1.20	2.88	3.96	1.96	0.61
May	Mean	0.71	0.98	1.00	0.44	0.54	0.68	0.73	0.63	0.27
	Median	0.57	0.93	0.88	0.39	0.45	0.47	0.56	0.49	0.22
	Std-dev.	0.38	0.64	0.72	0.26	0.35	0.58	0.52	0.41	0.13
Jun.	Mean	0.59	0.99	1.19	0.48	0.53	0.57	0.70	0.58	0.25
	Median	0.55	0.96	0.92	0.40	0.44	0.53	0.70	0.53	0.25
	Std-dev.	0.22	0.56	1.20	0.38	0.21	0.31	0.25	0.29	0.09
Jul.	Mean	0.54	1.07	1.09	0.42	0.51	0.55	0.78	0.58	0.24
	Median	0.54	0.97	0.86	0.42	0.46	0.55	0.78	0.57	0.22
	Std-dev.	0.19	0.60	0.81	0.20	0.17	0.28	0.32	0.30	0.09
Aug.	Mean	0.79	1.31	1.27	0.47	0.57	0.76	1.00	0.82	0.40
C	Median	0.55	1.15	1.01	0.40	0.52	0.60	0.85	0.71	0.34
	Std-dev.	0.53	0.92	0.86	0.29	0.29	0.62	0.60	0.51	0.23
Sep.	Mean	1.28	1.98	2.32	0.15	1.53	1.01	1.87	2.65	0.55
1	Median	1.11	0.91	1.75	0.09	0.76	0.48	1.26	0.57	0.26
	Std-dev.	0.77	2.91	2.69	0.16	2.62	1.65	2.49	6.41	0.71
Oct.	Mean	5.49	2.78	2.78	1.12	1.40	1.82	2.59	2.45	0.75
	Median	2.41	1.47	1.97	0.65	1.05	0.94	1.92	1.24	0.53
	Std-dev.	13.88	2.98	2.41	1.26	1.23	2.40	2.26	2.84	0.66
Nov.	Mean	5.57	5.53	6.47	2.38	3.06	2.56	6.25	3.26	0.96
	Median	3.39	4.98	5.01	2.14	2.13	2.07	4.54	2.01	0.65
	Std-dev.	4.95	4.58	5.77	2.00	2.47	2.22	5.37	3.52	0.85
Dec.	Mean	9.19	4.62	12.46	1.34	4.16	6.39	3.24	2.44	0.88
	Median	7.37	2.38	9.14	0.83	3.56	5.19	1.96	2.39	0.83
	Std-dev.	6.36	4.80	8.88	1.35	2.79	4.41	2.82	1.19	0.42
Annual	Mean	3.73	2.94	4.42	1.04	1.86	2.09	2.84	1.88	0.60
	Median	3.01	1.72	3.62	0.69	1.32	1.67	2.04	0.99	0.26
	Std-dev.	3.70	2.56	2.86	0.94	1.47	1.86	2.37	2.44	0.62

NMHCs vary largely from place to place but the phase of seasonal cycle is almost same. As it has been discussed that strength of seasonal variability in NMHCs is more at Ahmedabad compared to at Osaka, particularly the differences are more during summer months. This result suggests that apart from the OH reactivity transport of various air masses over the region is also important at Ahmedabad. Three-dimensional calculation of OH radical abundance shows the seasonal variation with summer maximum and winter minimum concentrations (Figure 3.6) in the Northern Hemisphere [*Spivakovsky et al.*, 1990]. As pollutants are transported from East Asian and Middle East countries through



**Figure 3.6:** Model calculated zonally and monthly averaged concentrations of OH  $(10^5 \text{ molecule cm}^{-3})$  for January, April, July and October including night hours. Contours are given for 0.1 (dotted lines), 1 (dashed lines), and for values from 5 to 30, with increments of 5 solid lines). Adapted from Spivakovsky et al. [1990].

continental India in the winter season, while pristine clean marine air from the Indian Ocean and the Arabian Sea prevails during the summer monsoon over the Indian subcontinent [*Lelieveld et al.*, 2001].

#### 3.1.5 Interspecies correlation of NMHC species

Non-methane hydrocarbons do not have secondary sources in the atmosphere (atmospheric chemical reactions do not produce NMHCs), the atmospheric sources of these species are always linked to the emission processes near the source regions. Though there are various anthropogenic sources of light NMHCs, the correlation studies of these

compounds are useful in identifying important common sources. For example the correlation studies of acetylene, ethene and propene are used to study the contribution from fossil fuel combustion, as these compounds are abundant in automobile exhaust. The correlation plots of some of the anthropgenically emitted NMHCs pairs are shown in Figure 3.7(a-i). We have used all months data set to discuss the correlation of NMHCS at Ahmedabad. The very good correlation coefficients of  $r^2=0.90$ , 0.84, and 0.94 for ethane vs. propane, ethane vs. i-butane, and propane vs. i-butane respectively indicate their common sources of emissions. Liquefied petroleum gas (LPG) leakage is likely the largest source of atmospheric propane and the butanes [*Blake and Rowland*, 1995], and petroleum-refining activities emit mostly ethane, propane and other alkanes [*Sexton and Westberg*, 1979]. Correlation plot of ethene and propene shows a linear fit with coefficient value of  $r^2= 0.87$ , this could be due to the dominant contribution from automobile exhaust. Moderate or relatively small correlation coefficient values of  $r^2=$ 



**Figure 3.7:** Linear correlation (with coefficient value  $r^2$ ) between various NMHCs (ppbv) species observed during 2002 at Ahmedabad.

0.67, 0.68, 0.50, and 0.68 for ethene vs. n-butane, proapane vs. acetylene, acetylene vs. ethane and acetylene vs. i-butane respectively indicate different dominant sources of these species. Though there are many common sources for some NMHC species, relatively good correlation in some pairs of species can also be attributed to the collocations of their sources. These species are mainly contributed by the local emissions from the urbanized activities at Ahmedabad unlike at Mt. Abu where transport from various regions is important.

#### 3.1.6 Correlation of CO versus NMHCs

Carbon monoxide is emitted primarily from incomplete combustion of fossil fuel and burning of vegetation. There are some common sources of CO and some NMHC species (e.g., ethene, propene, and acetylene) from vehicle exhaust. Thus examination of the



**Figure 3.8:** Linear correlation (with coefficient  $r^2$ ) between CO and various NMHCs species observed simultaneously at Ahmedabad during 2002.

relationship of CO with NMHCs can also provide useful information on their sources and emission signatures. Figure 3.8(a-i) shows scatter plots of CO (hourly average data) and all NMHCs measured simultaneously at Ahmedabad. It can be seen that among the nine NMHCs measured, correlations of CO with ethene, propene, and acetylene are  $r^2$ = 0.83, 0.78, and 0.69 respectively. The good correlation of these NMHCs with CO relative to other NMHC species again confirms their common sources of origin. The C<sub>2</sub>H<sub>2</sub>/CO ratio which is a photochemical indicator is estimated to be 6.36 pptv/ppbv. This value is higher than the reported value of 5.3 pptv/ppbv in Hong Kong under the Asian outflow condition [*Wang et al.*, 2003]. This high value of photochemical tracer also suggests the major influence of freshly emitted localized emissions in the distributions of NMHCs and CO at Ahmedabad. Poor correlation of CO with ethane and propane ( $r^2$ =0.36 and 0.30, respectively) indicate that the vehicular exhaust emissions are not dominant sources for these NMHC species.

#### **3.1.7** Diurnal variation of O<sub>3</sub>

Mean diurnal variations of  $O_3$  for different months of the year 2002 are shown in Figure 3.9. During the day, O<sub>3</sub> concentration starts increasing gradually after sunrise, attains maximum value during noontime and then decreases. The daytime increase in  $O_3$ concentration, which is a pronounced feature of an urban polluted site, is basically due to the photoxidation of the precursor gases such as CO, CH<sub>4</sub>, and NMHCs in presence of sufficient amount of NOx. Being an urban site, NO concentrations at Ahmedabad are generally found to be well above the threshold level (10 pptv) for  $O_3$  production [*Naja*, 1997]. Ozone levels are observed to be low during the nighttime, as there is no phtotoxidation of precursors (causing O<sub>3</sub> production). Also during nighttime the titration of O<sub>3</sub> by surface emission of NO in shallow boundary layer and loss due to surface deposition continues. Detailed study of O<sub>3</sub> variability at Ahmedabad during 1991-1995 has been reported earlier [Lal et al., 2000]. During summer months the diurnal amplitude (5-10 ppbv) of  $O_3$  is found to be small (minimum of ~5 ppbv during June month), on the other hand amplitudes of 20-50 ppbv (maximum of 50 ppbv during November month) were observed during autumn and winter months. Though the nighttime values are low, the minimum O<sub>3</sub> concentrations are observed during early morning hours, near the sunrise time. Amplitudes of diurnal variation in O<sub>3</sub> are higher in winter and lower in summer



**Figure 3.9:** Observed diurnal variation of mean ozone values (ppbv) in different months of year 2002 at Ahmedabad. Vertical bars are  $1\sigma$  variation.

months as observed in NMHCs. However, ozone concentrations are highest during the noon hours.

#### 3.1.8 Solar UVB radiation flux

Solar UVB (280-315 nm) radiation plays an important role in many physical and chemical processes in the atmosphere. It influences the oxidation processes in the troposphere and consequently the budgets of reactive trace gases. The chemical impacts of changing UVB radiation as consequence of the stratospheric O<sub>3</sub> loss have been studied on global scale [*Madronich and Granier*, 1992]. The influence could also be relevant for

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regional air quality since it could alter the concentrations of photo-oxidants in the boundary layer on longer time scales.

Apart from changes in overhead ozone column, UVB radiation is also affected by clouds. In the troposphere, absorption of UVB radiation by  $O_3$  and  $SO_2$  is very efficient due to their long relative path lengths [*Bruhl and Crutzen*, 1989]. On the scale of hours to weeks, clouds exert a large influence on UVB and UVA (315-400 nm) radiation thus photo chemistry above, below and within the cloud layer can get affected. The main influence of higher UVB radiation is on increase in OH radical production. With higher UVB radiation, more  $O_3$  is destroyed leading to OH production, but more peroxy radicals



**Figure 3.10:** Observed diurnal variation of mean UV-B (280-315 nm) radiation flux in different months of the year 2002 at Ahmedabad. Vertical bars are  $1\sigma$  variation.

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Total Flux (mW cm <sup>-2</sup> )	SD	26.84	27.80	31.13	34.40	33.77	24.43	18.33	15.45	24.65	24.85	22.38	19.85
	Median	44.71	45.38	48.91	57.21	57.07	43.96	34.22	35.65	47.31	49.18	40.03	41.32
	Mean	42.07	43.07	46.72	53.84	54.10	42.03	34.88	32.62	44.20	46.30	37.77	37.67
UVB Flux ( $\mu$ W cm <sup>-2</sup> )	SD	4.84	5.04	7.92	9.76	10.31	8.22	6.23	5.94	8.16	6.36	4.36	3.77
	Median	5.57	6.08	8.60	11.85	10.99	7.61	6.10	6.77	9.23	6.40	4.54	3.75
	Mean	5.78	6.43	9.62	12.63	12.42	9.11	7.24	7.15	10.03	7.46	5.44	4.65
Period of study	Months	January	February	March	April	May	June	July	August	September	October	November	December

are formed which in turn either support  $O_3$  destruction or its formation. For the selected fair weather conditions with moderately high NOx concentrations, an increase of surface  $O_3$  was found for increasing UVB radiation. Monthly mean diurnal variation of UVB flux at Ahmedabad is shown in Figure 3.10. The diurnal intensity distributions of both UVB and total solar radiation show gaussian distribution with time. The deviations during summer months are due to rainfall or cloudy sky conditions at Ahmedabad. Monthly statistical data of UVB and total solar radiation have been given in Table 3.2 for the different months of year 2002.

#### 3.1.9 Seasonal variations of O<sub>3</sub>, precursors and solar radiation fluxes

There is very clear and systematic seasonal variation in surface  $O_3$  at Ahmedabad. Higher  $O_3$  concentrations have been found during autumn/winter months and lowest concentrations are found during SW monsoon period. Statistical data of  $O_3$  measurements for different months of year 2002 have been given in Table 3.3, the maximum mean value

Month	Mean	Median	SD	Maximum	Minimum
January	38.4	29.1	15.75	64.3	20.3
February	43.2	34.4	15.06	65.1	26.3
March	40.8	30.8	15.93	64.5	22.6
April	25.5	20.7	9.39	40.5	14.8
May	15.9	13.4	4.10	22.4	11.7
June	13.2	12.0	2.02	16.7	10.4
July	16.8	15.3	4.51	25.0	11.2
August	19.0	16.4	6.61	34.5	12.4
September	17.9	17.1	3.39	23.2	12.4
October	26	16.2	15.56	51.5	9.2
November	30.5	16.7	20.47	62.0	10.3
December	28	17.0	17.67	57.2	11.2

**Table 3.3**: Statistics of ozone (ppbv) observed during different months of year 2002 atAhmedabad.

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of 43 ppbv and minimum of 13 ppbv were observed in February and June months respectively. Change in the wind circulation over this region takes place during autumn, it becomes northeasterly from generally southwesterly during summer period. The northeasterly wind flow brings the air, rich in pollutants to the observational site, causing higher levels of  $O_3$  and its precursors. During June and August months the wind pattern is mainly southwesterly which brings cleaner air from the Arabian Sea and the Indian Ocean. The levels of precursors are not sufficiently high enough to produce  $O_3$  in the daytime. Monthly mean values of  $O_3$ , CO and sum of  $C_2$ - $C_5$  NMHCs along with UVB flux for year 2002 at Ahmedabd are shown in Figure 3.11. The elevated  $O_3$  values in winter months are associated with higher levels of CO and NMHCs precursors, though intensity of solar UVB and total radiation fluxes are less in these months. While during the summer months  $O_3$  and NMHCs precursors levels are low particularly in June, July, and August months, with also a dip in seasonal cycles of total and UVB solar radiation



**Figure 3.11:** Monthly mean sum of  $C_2$ - $C_5$  NMHC species, UV-B flux, ozone and CO during different months of the year 2002 at Ahmedabad. Vertical bars are  $1\sigma$  variation.

fluxes. Ozone and NMHCs values are elevated in autumn season (October, November, and December). The similarity in seasonal cycles in  $O_3$  and precursors indicates that photochemical processes play major role in the seasonal distribution of  $O_3$  at Ahmedabad. Seasonal variations in surface measurements of other  $O_3$  precursor gases (NOx, CO and CH<sub>4</sub>) at Ahmedabad for the period 1991-1995 have been reported earlier [*Lal et al.*, 2000].

### **3.2** Distributions of C<sub>2</sub>-C<sub>4</sub> NMHCs at Mt. Abu

#### 3.2.1 Description of the site, experiments and general meteorology

Air samples were collected at a remote mountaintop called Guru shikhar (24.6°N, 72.7°E, 1680 m asl) at Mt. Abu. This region comes under the southern end of Aravali range of mountains and is the highest in the entire western central Indian region. The main town of Mt. Abu (about 10 km from Guru Shikhar) is situated at a height of 1220 m with a population of 30,000-40,000. Only the observatory staff needed for observation has been staying at the measurement site. Nearest urban city Ahmedabad is about 200 km towards south.

The air sampling at Mt. Abu for the analyses of NMHCs were started in September 2001. But in the present study we have discussed only the data of full year 2002. Whole air grab samples were collected in evacuated glass bottles using an oil free 'Metal Below' compressor. All the bottles were carefully conditioned and leak tested before being sent to Mt.Abu from PRL Ahmedabad. Air samples were sucked from the terrace of the observatory through a three-meter long stainless steel tube. Samples were collected for continuously 24 hours with 1 to 1.5 hours of interval during all the months, so that diurnal and seasonal patterns are studied. Mt. Abu is about 250 km far from the Arabian Sea coast and the Inter Tropical Convergence Zone (ITCZ) is around the latitude of Mt. Abu in summer [*Asnani et al.*, 1993].

The general wind pattern at Mt. Abu is similar to that of Ahmedabad. Figure 3.2 shows the monthly mean wind field lines during 2002, based on the wind data from the NCEP. The site offers cleaner background atmosphere due to the remoteness of the site from any man made activities and also because of higher altitude location. This is the first study of NMHCs distributions in tropical Asia at an elevated site. Ozone measurements do not show daytime in situ photochemical buildup, on the contrary there is a decrease in  $O_3$  during daytime at Mt Abu. Diurnal variation in  $O_3$  shows a significant change in its pattern after northeast monsoon period with a unique double hump in spring. Seasonal variation shows maximum values during late autumn and winter and lowest during summer-monsoon. Background  $O_3$  (33.5 ppbv) and continental  $O_3$  (48.2 ppbv) amounts are estimated using the nighttime data and change in wind patterns in different months for this region. It is shown that boundary layer mixing and unique meteorology over this
region play important roles in the diurnal and seasonal variations in O<sub>3</sub> at this site [*Naja et al.*, 2003].

#### **3.2.2** Diurnal variations of C<sub>2</sub>-C<sub>4</sub> NMHCs

Due to inadequate amount of air samples collected at Mt. Abu we could not detect the pentanes properly during the summer months of measurements. Hence only  $C_2-C_4$  NMHCs distributions are being discussed. Figure 3.12(a-g) depicts the winter, summer, and annual mean diurnal variations in NMHC species at Mt. Abu for the year 2002. Annual mean does not show any systematic variability except higher values with fluctuations during afternoon and evening hours in some species. Similarly, during the summer season we do not observe any kind of diurnal trend, all the NMHCs levels are below their annual mean levels. In winter season apart from elevated values in all NMHCs compared to their annual means, some sharp peaks during afternoon and evening hours (15 to 22 hours IST) are also observed in some species. NMHCs concentrations are slightly higher in early morning hour. Some NMHCs like ethane, propane and acetylene concentrations are much higher than their summer values. But in some species like ethene, propene, and i-butane the values differ slightly during both the seasons of measurements.

As we have discussed that Mt. Abu is a higher altitude station where local emissions of pollutants are very less except due to some tourist buses plying during the daytime. Therefore, transport of NMHC species from various source regions is the main process that controls the observed levels of these species. In the absence of local boundary layer (surface) emissions, difference in the free tropospheric and surface levels are very less for these compounds. During winter season due to strong inversion layer, the sporadic emissions by vehicles are trapped and hence we can observe some peaks during the evening hours. Due to almost no loss by OH radical reactivity and stable nighttime boundary layer, slightly higher concentrations of NMHCs persist till early morning. The evening peaks are prominent in some species, particularly in ethene, propene and acetylene. This feature of diurnal variation in some species confirms that the cause is local emission and that too vehicular as ethene, propene and acetylene are emitted in vehicular exhaust.



**Figure 3.12:** Seasonal (winter and summer months) and annual mean diurnal variations of various  $C_2$ - $C_4$  NMHCs mixing ratios observed during year 2002 at Mt. Abu.

#### **3.2.3** Seasonal variation of C<sub>2</sub>-C<sub>4</sub> NMHCs

Monthly statistical values of each  $C_2$ - $C_4$  NMHCs measured are presented in Figure 3.13(a-g) in the form of box and whisker plots. Like other reported measurements for the Northern Hemisphere the winter season values are maximum and summer season values are minimum in all the species measured at Mt. Abu. Markedly different seasonal patterns are evident for compounds with predominantly anthropogenic sources (ethane, propane, acetylene etc.) compared to species with strong biogenic summertime sources (e.g. ethene and propene). In relatively long-lived species like ethane, propane and acetylene the

strength of variability is higher compared to the highly reactive species like ethene and propene. Statistics of all the  $C_2$ - $C_4$  NMHCs measured during different months of year 2002 at Mt. Abu are given in Table 3.4.



**Figure 3.13:** Box-whisker (mean values are shown as horizontal dotted lines) plots of  $C_2$ - $C_4$ NMHCs mixing ratios representing their seasonal cycles (all the months) observed during year 2002 at Mt. Abu.

Most of the anthropogenic hydrocarbons are removed from the atmosphere primarily by reaction with OH. Rates of removal vary markedly with season, while emissions are largely invariant. It is found that, the seasonal variation of long-range

Months Yr.2002	Statistics	C <sub>2</sub> H <sub>6</sub>	$C_2H_4$	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	i-C <sub>4</sub> H <sub>10</sub>	$C_2H_2$	n-C <sub>4</sub> H <sub>10</sub>
Jan.	Mean	2.16	0.52	0.66	0.28	0.37	0.79	0.82
	Median	2.15	0.42	0.65	0.16	0.19	0.60	0.64
	Std-dev.	0.31	0.30	0.14	0.27	0.39	0.58	0.41
Feb.	Mean	2.00	0.41	0.72	0.23	0.21	0.35	0.52
	Median	1.96	0.34	0.70	0.21	0.20	0.30	0.48
	Std-dev.	0.19	0.14	0.09	0.11	0.04	0.13	0.13
Mar.	Mean	1.52	0.35	0.47	0.18	0.17	0.39	0.37
	Median	1.49	0.30	0.44	0.12	0.14	0.20	0.19
	Std-dev.	0.10	0.28	0.09	0.25	0.05	0.32	0.61
Apr.	Mean	1.33	0.29	0.44	0.16	0.25	0.44	0.29
1	Median	1.25	0.29	0.44	0.16	0.17	0.27	0.18
	Std-dev.	0.30	0.08	0.16	0.04	0.23	0.46	0.41
May.	Mean	0.78	0.26	0.30	0.14	0.23	0.20	0.14
2	Median	0.79	0.23	0.28	0.13	0.18	0.17	0.10
	Std-dev.	0.19	0.09	0.10	0.04	0.16	0.11	0.10
Jun.	Mean	0.60	0.17	0.20	0.08	0.16	0.23	0.15
	Median	0.60	0.16	0.20	0.09	0.10	0.13	0.07
	Std-dev.	0.24	0.04	0.05	0.02	0.13	0.29	0.12
Jul.	Mean	0.52	0.24	0.27	0.12	0.13	0.17	0.07
	Median	0.50	0.23	0.24	0.11	0.12	0.15	0.06
	Std-dev.	0.08	0.05	0.09	0.03	0.04	0.07	0.06
Aug.	Mean	0.53	0.26	0.28	0.13	0.13	0.18	0.07
C	Median	0.52	0.23	0.29	0.11	0.09	0.16	0.05
	Std-dev.	0.09	0.14	0.06	0.06	0.10	0.06	0.06
Sep.	Mean	0.83	0.29	0.33	0.16	0.11	0.25	0.36
•	Median	0.84	0.29	0.29	0.15	0.10	0.23	0.29
	Std-dev.	0.11	0.10	0.11	0.05	0.05	0.17	0.25
Oct.	Mean	1.30	0.22	0.38	0.14	0.18	0.38	0.22
	Median	1.24	0.19	0.33	0.14	0.15	0.27	0.21
	Std-dev.	0.18	0.07	0.16	0.03	0.08	0.37	0.06
Nov.	Mean	1.56	0.38	0.49	0.11	0.21	0.42	0.37
	Median	1.62	0.20	0.52	0.11	0.21	0.32	0.36
	Std-dev.	0.28	0.48	0.23	0.02	0.06	0.22	0.20
Dec.	Mean	1.68	0.61	0.58	0.24	0.30	0.98	0.40
	Median	1.65	0.46	0.49	0.21	0.24	0.61	0.32
	Std-dev.	0.14	0.31	0.17	0.11	0.13	0.71	0.21
Annual	Mean	1.22	0.34	0.46	0.17	0.21	0.41	0.31
	Median	1.23	0.28	0.44	0.13	0.17	0.27	0.21
	Std-dev.	0.58	0.24	0.20	0.14	0.18	0.43	0.35

**Table 3.4:** *C*<sub>2</sub>-*C*<sub>4</sub> *NMHCs data (in ppbv) during different months of year 2002 at Mt.Abu.* 

transport play significant role in the observed seasonal cycles of these compounds, especially in remote regions where the local sources are largely absent. In the winter season the northeast (NE) wind flow influences while during summer season it is the southwest wind over the Indian subcontinent as shown in Figure 3.2. The absence of strong seasonal variability in ethene and propene at Mt. Abu could be due to negligible local anthropogenic emissions, transport of marine airmass from the Arabian Sea during monsoon period and also enhanced local biogenic emissions. Oceans and vegetation are the prominent sources of reactive alkenes [*Bonsang et al.*, 1985, *Goldstein et al.*, 1995a].

# **3.2.4** Comparison of seasonal variations at Mt. Abu and other remote sites

For this comparison the annual surface measurements of  $C_2$ - $C_4$  hydrocarbons are compiled based on the data reported in Laurila and Hakola [1996] for Uto (59°47' N, 21°23' E) and Pallas (67°58' N, 24°07' E); *Bottenheim* [1995] for Lac La Flamme (PQ) Canada; Swanson [2003] for Greenland (72.57°N, 38.48°N) and Penkett [1993] for Atlantic Ocean. All sites are considered remote from urban or anthropogenic inputs and were presented as background concentrations for their specific region. In Figure 3.14(ag), plots are shown for the average mixing ratios for ethane, ethene, propane, propene, ibutane, acetylene and n-butane. In tropical region long-term studies of NMHCs have been rare particularly for remote sites. Except these measurements other data sets are from higher northern hemispheric latitudes where meteorological conditions are completely different from Mt. Abu. Ethane is the dominant compound and it shows large seasonal variation. The annual mean values of ethane are 1522, 1539, 1384, 1886, 1978, and 1233 pptv for Uto, Pallas, Greenland, Atlantic Ocean, LLF (Canada), and Mt. Abu respectively. For anthropogenically emitted light NMHCs, in the northern hemispheric sites summer season values are lowest while winter season values are highest. The mean seasonal ranges (summer-winter) of ethane are 700-2123, 742-2378, 786-2095, 1508-2357, 940-2826, and 533-1887 pptv respectively for Uto, Pallas, Greenland, Atlantic Ocean, LLF (Canada), and Mt. Abu respectively. Comparison shows that not only annual mean but winter and summer seasons mean values are also lowest at Mt. Abu and offers a clean background environment in this region.

Mt. Abu is a tropical elevated site while other sites are in mid to higher latitude ranges, the winter accumulation of ethane at Mt. Abu is not as high as other sites in



**Figure 3.14:** Comparison of seasonal cycles of various  $C_2$ - $C_4$  NMHCs species at Mt. Abu with other published data from other mountaintop and remote regions of the Earth's surface. We have adapted data for Uto, Pallas (Finland) from Laurila and Hakola [1996], Lac la Flamme (Canada) data from Bottenheim et al. [1995]; Greenland data from Swanson et al. [2003] and Atlantic Ocean data from Penkett et al. [1993].

higher latitudes. Also the emission of pollutants in mid latitudinal regions are higher compared to tropical emissions. In tropical region, the efficient convection process dilutes the boundary layer pollutants by lifting up the air masses. Therefore, fast photochemical processing, vertical mixing due to convection, and relatively less emissions of pollutants play very important roles in observed low levels in ethane and in some other light NMHCs at Mt. Abu. Comparisons of strengths (maximum to minimum ratio) in seasonal variabilities of various NMHCs measured at different sites are given in Table 3.5.

Species	Mt. Abu	Ahmedabad	Freserdale <sup>a</sup> (Canada)	Birkenes <sup>b</sup> (Norway)	Keji <sup>c</sup> (Canada)	Happo <sup>d</sup> (Japan)
Ethane	3.43	9.39	2.99	4	2.7	2.55
Ethene	1.92	4.07				1.24
Propane	2.47	6.06	18.4	5	8.4	2.14
Propene	2.10	3.57				0.48
I-butane	1.81	5.64	44.1			3.4
Acetylene	2.64	4.67	10.9	5	6.1	0.79
N-butane	5.98	5.95	41.2	10	10.3	3.24
I-pentane		3.89				2.50
N-pentane		2.57				2.57

**Table 3.5:** *Winter/Summer ratios of NMHCs observed at Mt. Abu, Ahmedabad and other parts of the Northern Hemisphere.* 

(a) Jobson et al. [1994a], (b) Hov et al. [1991], (c) Bottenheim et al. [1995], (d) Sharma et al. [2000]

#### 3.2.5 Interspecies correlation of NMHC species at Mt. Abu

In remote locations, the observed levels of anthropogenically emitted hydrocarbons (light NMHCs) are due to the transport from the distant sources depending upon strengths. Even if sources are common, the chemical signatures of air mass vary a lot due to different transport times and hence different levels of photochemical processing. Hence, identification of sources and their locations are not easy. But in urban centers only freshly emitted air mass dominates and plays an important role in their distributions, before any significant chemical processing takes place. The source characterizations for short-lived species are rather more difficult than the relatively long-lived species like (ethane, propane, and acetylene) in remote sites. Figure 3.15(a-i) represents scatter plots of some important NMHCs measured at Mt. Abu during the year 2002. This data set is for all the months of year 2002. For ethane and propane natural gas leakage is major source while the fractions of butanes are high in petroleum and LPG products. Fossil fuel combustion in automobiles and power plants are known to release large amounts of acetylene, ethene and propene. Also Oceanic and biogenic emissions are important sources of ethene and propene in remote locations. Linear fit correlation coefficient values of some suitable pairs of species can provide hints about the dominant sources in the distributions of NMHCs at Mt.Abu. The moderate correlation coefficient values for ethane vs. propane, ethene vs. propene, and acetylene vs. ethene are 0.65, 0.58, and 0.54,



**Figure 3.15:** Linear correlation (with coefficient value  $r^2$ ) between various NMHCs (*ppbv*) species during year 2002 at Mt. Abu.

respectively. Ethene and propene are poorly correlated with n-butane. Similar correlation studies but data from a given month only show better correlation for the same pairs of species.

Relatively good correlation of ethane and propane indicates common or collocations of their sources. But the good correlation of ethene and propene could be due to both marine emission and fossil fuel combustion. Another good correlation  $(r^2=0.58)$  of ethene and acetylene indicates a major role of combustion related sources of these compounds, but still the correlation is not strong enough to completely ignore the role of other sources like marine emission. The correlation studies from annual data in Figure 3.15(a-i) highlight the differences in photochemical lifetimes between NMHCs and clearly reflect changes in the seasonal trend from the accumulation to decrease in winter and finally slow decrease or steady state in summer. Combined effect of various degree of chemical and dynamical processing of air masses results in moderate correlation of annual NMHCs data compared to individual monthly data.

### 3.3 Comparison of measurements at Ahmedabad and Mt. Abu

We have studied the time series distributions of anthropogenic light NMHCs at two stations Ahmedabad and Mt. Abu. As mentioned earlier, Ahmedabad is a representative of fully urbanized region with large number of industries, being an elevated site with no local emissions Mt. Abu represents a clean background environment. Annual mean values of  $C_2$ - $C_4$  NMHCs measured at Amhmedabad and Mt.Abu are depicted in bar plot (Figure 3.16). It can be seen that Ahmedabad mean values are higher by factors of 3-9 with respect to the mean values at Mt.Abu. The annual mean of Ahmedabad to Mt. Abu ratios are 3.0, 8.8, 9.8, 6.2, 8.9,5.1, and 9.1 for ethane, ethene, propane, propene, i-butane, acetylene, and n-butane respectively. The low mean ratio values in ethane and acetylene are expected due to their relatively longer lifetimes. Due to efficient transports (lifetimes are higher than the transport time) of ethane and acetylene the concentrations are relatively higher for these two compounds even at Mt. Abu.



**Figure 3.16:** Comparison of annual mean values of various NMHCs observed during year 2002 at Mt. Abu and Ahmedabad.

## 3.4 Abundance of individual C<sub>2</sub>-C<sub>4</sub> NMHCs

Figures 3.17(a) and 3.17(b) show the pie diagrams of mean distributions of various  $C_2$ - $C_4$  NMHCs measured at Ahmedabad and Mt. Abu. The percentage contributions of ethane, ethene, propane, propene, i-butane, acetylene, and n-butane are 19.7, 15.5, 23.4, 5.5, 9.8,



**Figure 3.17:** *Pie diagrams representing comparisons of abundance (percentage) of various NMHCs species observed at (a) Ahmedabad (b) Mt. Abu during 2002.* 

11, and 15, respectively at Ahmedabad during the year 2002. While at Mt. Abu the relative contributions in  $C_2$ - $C_4$  NMHCs distribution are 39, 10.8, 14.7, 5.4, 6.7, 13, and 10 % from ethane, ethene, propane, propene, i-butane, acetylene, and n-butane, respectively. Studies show that the contribution of individual NMHC species in the distribution rely on the emission and residence time of a given component. At Ahmedabad the emissions play very important role while for the distribution at Mt. Abu transport (hence lifetime) from the source regions is a key parameters in the distribution of NMHCs. Among all the NMHCs measured, propane dominates over Ahmedabad while it is ethane at Mt. Abu.

# Distributions of $O_3$ , CO and Hydrocarbons over the Bay of Bengal

The Asian region is developing very fast, leading to more energy consumption due to industrialization and urbanization. Fossil fuel combustion is one of the most important sources of energy in automobiles and releases many reactive  $O_3$  precursors like hydrocarbons and CO mainly due to incomplete burning of the fuels. In the tropics not only the fossil fuel burning is important but also other human activities like biomass burning, forest fires etc are important contributors of  $O_3$  precursors. The emissions of CO, non-methane hydrocarbons (NMHCs), NO<sub>X</sub> and SO<sub>2</sub> from Asia strongly depend on the fuel used (coal, oil and biofuels) and the efficiency of industrial and traffic emissions [*Lelieveld et al.*, 2001]. In the whole Asia, about one quarter of the energy use depends on biofuels, whereas in India this fraction is close to 50 %.

As we have discussed in chapter 1 that ozone plays important role in atmospheric chemistry, it is also an effective greenhouse gas especially in the upper troposphere [*Lacis et al.*, 1990]. Additionally, near the surface it can have detrimental effects on human health and crops. This is specially important considering that emissions of  $O_3$  precursors (NOx, CH<sub>4</sub>, CO, volatile VOCs) are strongly increasing in the East Asian countries [*van Aardenne et al.*, 1999].

In this chapter we will discuss the distributions of  $O_3$ , CO, CH<sub>4</sub> and C<sub>2</sub>-C<sub>4</sub> hydrocarbons measured over the Bay of Bengal during the Bay of Bengal Process Studies (BOBPS 2002) and the Bay of Bengal Experiment II (BOBEX II) cruise campaigns. BOBPS field campaign was conducted from 14 September to 12 October 2002 during this period the wind flow was from southwest (SW) direction (Figure 4.1(a)), to study the cleaner atmosphere. While BOBEX II campaign was conducted during 19-28 February 2003. Due to persistence of northeast (NE) wind flow during this period (Figure 4.1(b)) large amount of continental emitted pollutants can get transported from the Asian

countries over the Bay of Bengal. Previous studies over the Indian Ocean, Arabian Sea and Bay of Bengal under major field campaigns INDOEX and BOBEX [*Lal et al.*, 2004] comprising measurements of O<sub>3</sub> and other trace gases took place only during the winter



**Figure 4.1:** Average NCEP wind field flow at 925 mb during (a) BOBPS (14 Sep.-12 Oct. 2002) (b) BOBEX II (19-28 Feb. 2003) over the Bay of Bengal. Color bars depict the magnitudes of wind speed (m/s).

season. One of the main purposes of these campaigns was to study the role of transport by northeast wind flow from India and other North East Asian countries over the Indian Ocean and the Arabian Sea. In this chapter we present the results of  $O_3$  and related trace gas measurements made over the Bay of Bengal, when the wind flows were from SW and NE directions.

### 4.1 Experimental details

BOBPS (cruise no. SK182) and BOBEX II (cruise no. SK188) were conducted using the Ocean Research Vessel (ORV) *Sagar Kanya* over the Bay of Bengal. We performed the in-situ measurements and also collected air samples when the ship speed was at least 6-7 knots per hour to avoid any contamination due to the ship's exhaust. Air samples were sucked in through a 2 m long stainless steel tube in glass canisters of about 300 ml volume using an oil free compressor (Metal bellow, USA) near the bow of the ship. However, we used teflon tube for the inlet line for air sampling for O<sub>3</sub> measurement. A

UV absorption based  $O_3$  analyzer from Dasibi (RS-1008, USA) was used during this cruise campaign.

NMHCs ( $C_2$ - $C_5$ , alkanes, alkenes and alkyne) were measured from the collected air samples using a gas chromatograph (GC) (Hewlett Packard 5890 II) equipped with a flame ionization detector (FID), detailed description of this system is given chapter 2. About 1 to 1.2 L (STP) of the air samples were preconcentrated at liquid nitrogen temperature using a cryotrapping (a stainless steel tube packed with glass beads) procedure. The analyses of CH<sub>4</sub> and CO were performed by another gas chromatograph (Varian Vista, 6000, USA). The reproducibility in NMHCs analyses ranged between 3 to 10% depending upon the compounds. Calibrations of individual NMHCs were performed using calibration mixture from Scott (USA) and MPIC, Germany. Details of measurement methods and calibration procedures of various trace gases have been discussed in chapter 2.

# 4.2 Field expedition during 14 September to 12 October 2002(BOBPS) over the Bay of Bengal

#### 4.2.1 Meteorological conditions

During the September and October months, the southwesterly wind pattern seems to be pertinent over India and surrounding marine regions. This wind pattern in general brings unpolluted marine air from the Indian Ocean over this region (Bay of Bengal). However, sometimes the air passes over the southern region of India and Sri Lanka and gets polluted. While other surrounding marine regions of the Indian subcontinent namely the Arabian Sea and the Indian Ocean are not affected by these continental emissions in this season. We used NCEP wind data to study the distributions of trace gases, in particular for O<sub>3</sub> distribution over the Bay of Bengal and found to be very useful in distinguishing the origins of air masses during the campaign. Apart from wind field analyses we have also incorporated the 7-day back trajectory analyses for three height levels (surface, 500 m and 1000 m) to explain the observed variations. We have used HYSPLIT model [*Draxler and Hess*, 1998] for back trajectory analyses. Statistics of various meteorological parameters measured onboard the ship are given in Table 4.1.

Meteorological	Mean	Std-dev.	Median
Parameter			
Temp(°C)	28.6	1.1	28.6
RH (%)	79.0	7.2	79.0
Pressure (mbar)	1006.7	3.1	1006.9
Wind speed (m/s)	5.5	2.7	5.4
Wind direction (deg.)	212.8	49.7	220.4
$H_2O(g/kg)$	19.29	1.4	19.19
EPT ( <sup>°</sup> K)	350.5	4.1	350.3

**Table 4.1:** Meteorological parameters observed during BOBPS 2002 cruise onboard SagarKanya.

### 4.2.2 Variations in O<sub>3</sub> along the cruise track

The cruise measurements are divided in two parts. During the first part from 14 to 30 Sep. 2002 (DOY (Day of Year) 257-273) the ship cruised in the open ocean (away from **BOBPS (Sep. 14 - Oct. 12, 2002)** 



**Figure 4.2:** Cruise track (with Day of Year information) of ORV Sagar Kanya during BOBPS 2002 (14 September to 12 October, DOY 257-284), which started and ended at Chennai port.

anthropogenic or continental emissions). While during the second part starting from Oct. 1 to 12, 2002 (DOY 274-285) the ship cruised along the east coast of India before it arrived at the Chennai port (Figure 4.2). Statistical reports of measurements of various trace gases like  $O_3$ , hydrocarbons and CO for complete cruise, for the open ocean and coastal tracks have been given separately in Table 4.2. Higher values of almost all the species during open ocean measurements compared to coastal track measurements have been observed.

Species	Mean	Mean	Mean
	(Complete cruise)	(Coastal)	(Open ocean)
O <sub>3</sub> (ppbv)	27±6	27±6	28±6
CO (ppbv)	143±23	135±19	154±25
CH <sub>4</sub> (ppmv)	1.75±0.05	$1.74 \pm 0.04$	$1.75 \pm 0.05$
Ethane (pptv)	561±130	536±110	598±140
Ethene (pptv)	299±170	248±100	377±220
Propane (pptv)	191±70	191±70	192±60
Propene (pptv)	129±50	111±30	154±70
i-butane (pptv)	107±20	105±20	109±20
n-butane (pptv)	145±50	139±50	153±50
Acetylene (pptv)	128±80	94±60	178±100
C <sub>2</sub> H <sub>2</sub> /CO (pptv/ppbv)	$0.86 \pm 0.48$	0.678±0.38	1.12±0.51

**Table 4.2:** *Mixing Ratios (Mean and 1 \sigma variation) of NMHCs, CH*<sub>4</sub>, *CO, O*<sub>3</sub> *and C*<sub>2</sub>H<sub>2</sub>/*CO ratio during BOPBS 2002 campaign.* 

Figures 4.3 and 4.4 show variations in  $O_3$  and other trace gases (daily average of in situ measured  $O_3$  and analyzed trace gases from each sample) against the DOY. The  $O_3$  values of 32-33 ppbv were observed just after the start of the cruise, afterwards it started declining slowly when the ship moved away from the Indian coast towards the southeast direction over the Bay of Bengal. On DOY 260-261, when the ship was at the southern most point of the cruise, lowest daily averaged  $O_3$  values of 17-18 ppbv were observed. Within the next 3-4 days, when the ship turned northward,  $O_3$  values increased to about 34-35 ppbv on DOY 264-265 and higher values persisted till DOY 273 except small variation. After DOY 272 the ship started moving closer to the Indian coast. Just in the beginning of the second part of the cruise on DOY 275,  $O_3$  values suddenly dropped to low values around 18 ppbv and were around 20 ppbv on DOY 276 and 277, respectively. On DOY 278 the  $O_3$  values increased to around 32 ppbv and almost maintained the same level during the rest of the cruise except some fluctuations.



**Figure 4.3:** Time series plots of  $O_{3,1}$ , CO,  $CH_4$  and  $C_2H_2/CO$  values with air sampling locations along the cruise track during BOBPS 2002.



**Figure 4.4:** *Time series of ethane, propane, acetylene, ethene and propene mixing ratios with air sampling locations along the cruise track during BOBPS 2002 campaign.* 

The average wind fields corresponding to various episodes of measurements are depicted in Figure 4.5. In the beginning of the first three days of the cruise the wind fields originated over the Arabian Sea (Figure 4.5(a)) and swept the southern coast of India and Sri Lanka, bringing O<sub>3</sub> and other pollutants along the cruise track. When the ship moved further towards the southern Bay of Bengal the mixing of wind streamlines from south (originated in southern open Indian Ocean) and wind passing through the southern part of India have been observed, causing the gradual decrease in O<sub>3</sub> and other pollutants. On DOY 260 and 261 only air mass originated over the open Indian Ocean with the wind speed between 15-20 m/s coming from south and slightly southwest directions prevailed. For these two consecutive days of O<sub>3</sub> minimum period the ship was located near 7-9°N, 88°E. Further northward along the 88°E longitude, once again the sampled air was a mixture from the open Indian Ocean and from southern India and Sri Lanka, causing gradual increase in O<sub>3</sub> values and finally reaching the maximum value on DOY 264-265 at 12-14°N, 88 °E. For these two days the average wind field (Figure 4.5(b)) streamlines not only swept the southern region but also traversed the north east region of India due to prevailing cyclonic condition centered over the northern Bay of Bengal. The peak value in  $O_3$  on DOY 265 coincided with high values in CO,  $C_2H_2$  and highest  $C_2H_2/CO$  ratio of 2.11 pptv/ppbv, confirming the transport of freshly emitted pollutants from within the continental boundary layer. During the second minimum O<sub>3</sub> episode between DOY 274 and 276 the wind field analyses near the surface show an anti-cyclone condition (Figure 4.5(c)) centered over the northern region of the Bay of Bengal due to this the coastal measurements are corresponding to the sampling of clean marine background air mass. The anti cyclonic condition did not last long and on DOY 278 O<sub>3</sub> values suddenly jumped from 18 ppbv to around 34 ppbv and this high value persisted till the end of the cruise with slight fluctuations near the southeast coast of India. The wind field analyses corresponding to this transition in  $O_3$  value is associated with the drastic change in wind patterns over the Bay of Bengal. After the anti cyclonic condition the wind streamlines originated near the west coast of India over the Arabian Sea and traveled through southern continental regions of India and Sri Lanka sweeping the polluted air mass from there (Figure 4.5(d)).

Study of the 5-minute average  $O_3$  data along with other meteorological data reveal many interesting features in trace gases over the Bay of Bengal. In Figure 4.6, two examples of convective downdraft events associated with sudden change in meteorological tracers namely equivalent potential temperature (EPT) for an air parcel,



**Figure 4.5:** Average wind streamlines at 925 mb level for four selected periods during BOBPS 2002 period, using NCEP reanalysis data.

constituting very good anti correlation with O<sub>3</sub> on 25<sup>th</sup> and 26<sup>th</sup> September (DOY 268 and 269) are represented. On 25<sup>th</sup> September (DOY 268) morning around 8 am IST (Indian Standard Time is 5.5 hours ahead of GMT) O<sub>3</sub> value suddenly got doubled of its value of about 23 ppbv, exactly at the same time EPT value decreased to 351 °K from 355 °K (see Fig. 4). Next day on 26<sup>th</sup> September (DOY 269) another example of such an anti correlation can be seen just before 10:30 hrs, O<sub>3</sub> was around 25 ppbv while corresponding EPT value was 357 °K, after that O<sub>3</sub> increased to 40 ppbv and EPT dropped down to 347-348 °K. Such relations in O<sub>3</sub> and EPT are also found elsewhere [*Betts et al.*, 2002] and are attributed to convective downdrafts of free tropospheric air in the boundary layer.

General meteorological data from Chennai for September and October months show that the EPT values of 345-348 <sup>o</sup>K correspond to an altitude of about 2 km. Not only the EPT but also other meteorological parameters like wind speed and wind direction showed anomaly. Some sharp peaks for very short duration in O<sub>3</sub> are anti correlated with EPT,



**Figure 4.6:** Convective downdraft events during BOBPS 2002, 5-minutes average data of ozone and equivalent potential temperature (EPT) against IST (Indian Standard Time), (a) for September 25, 2002 (b) for September 26, 2002.

temperature and relative humidity on DOY 268, confirming the intrusion of  $O_3$  from the free troposphere. It has been shown that just above the marine boundary layer  $O_3$  increases with altitude [*Zachariasse et al.*, 2000].

The average latitudinal gradients of  $O_3$  are found to be around 1.37 and 0.77 ppbv deg<sup>-1</sup> for open ocean and complete cruise respectively (Figure 4.7(a) and 4.7(b)) while it



**Figure 4.7:** Latitude profiles of  $O_3$  (1° latitudinal average and 1 $\sigma$  variation), CO and CH<sub>4</sub> during BOBPS 2002 campaign. The open symbols and filled symbols plots are for open ocean and complete cruise tracks respectively and straight lines are best linear fits.

was 3 ppbv deg<sup>-1</sup> during the BOBEX 2001 field campaign [*Lal et al.*, 2004] over the Bay of Bengal. During the INDOEX 1998 and 1999 campaigns, the average latitudinal gradients of O<sub>3</sub> were 2.7 and 1.7 ppbv deg<sup>-1</sup>, respectively over the Arabian Sea (5-20 °N). This shows that gradient in O<sub>3</sub> was minimum during BOBPS 2002.

#### 4.2.3 Variations in CO along the cruise track

Carbon monoxide distribution (Figure 4.3) shows exactly similar trend like O<sub>3</sub> except for some days along the coastal track measurements. Over the Bay of Bengal, the maximum CO value was 210 ppbv while minimum value was 108 ppbv. In the beginning of the cruise CO values were around 127 ppbv and decreased slowly when the ship moved towards the southern region over the Bay of Bengal and attained a low value of about 110 ppbv between DOY 260 and 261 coinciding with minimum value in O<sub>3</sub>. From the southern most point of the cruise track the northward measurements showed increasing trend in CO. The highest CO value of 210 ppbv was observed on DOY 264 and 265. Afterwards it decreased to around 170 ppbv and varied slightly without any trend till DOY 273 showing almost similar trend to the variation in O<sub>3</sub>. Between DOY 274 and 275 of measurements, CO values dropped rapidly and attained the lowest value of 108 ppby, coinciding again with minimum value in O<sub>3</sub>. From the beginning till DOY 277, CO and O<sub>3</sub> showed similar trends and variations, thereafter CO did not show any relation with O<sub>3</sub> till the end of the cruise. CO measurements made at Srinkarin (14.37°N, 99.1°E) in rural Thailand during 1997-2000 showed the influence of southwest monsoon from the Indian Ocean [*Pochanart et al.*, 2003]. Over the southern region of the Bay of Bengal (<10 °N) the minimum CO value of 110 ppbv could be due to the air mass from the southern Indian ocean MBL on DOY 260.

Figure 4.7(c) and 4.7(d) depict the latitudinal distributions of CO along the open ocean track and for the complete cruise measurements respectively. The open ocean average gradient value of 3.86 ppbv deg<sup>-1</sup> is higher than the complete cruise value of 2.7 ppbv deg<sup>-1</sup>. That means the gradient along the coastal region is lower compared to open ocean. Which could be masked by transport from different regions along the coast. The maximum in CO value was observed at 12.5 °N latitude. During the BOBEX 2001, the latitudinal gradient of CO was about 6.46 ppbv deg<sup>-1</sup> and during the INDOEX 1999 campaign it was around 4 ppbv deg<sup>-1</sup> [*Chand et al.*, 2001]. So, like O<sub>3</sub> gradient the CO gradient is also lowest during this period.

#### 4.2.4 Variations in CH<sub>4</sub> along the cruise track

The distribution of  $CH_4$  shows relatively large variation (1.67 to 1.86 ppmv) over the Bay of Bengal (Figure 4.3). On DOY 257  $CH_4$  values were around 1.72 ppmv and decreased slowly to a minimum value of 1.67 ppmv on DOY 259, after this minimum it showed

increasing trend except some low values near DOY 263. It reached very high values near DOY 269 and persisted till DOY 273 when it got maximized, except a dip near DOY 271. The duration of broad peak is coinciding with the cruise days along 20 °N and values fallen down sharply on either side of these track days. After DOY 273, there is a decreasing tendency but with fluctuations. Similar broad peak during DOY 269 to 273 is also seen in ethane. This could be due to the nearness of Kolkata and Dhaka regions from the north most part of the cruise track.

Figures 4.7(e) and 4.7(f) show the latitudinal dependence of CH<sub>4</sub> along the open ocean track and for the complete cruise measurements respectively. Its latitudinal gradient is 10.65 ppbv deg<sup>-1</sup> in the open ocean and is slightly higher than the gradient for the complete cruise value of 9.6 ppbv deg<sup>-1</sup>. In CH<sub>4</sub> also, the coastal region of the Bay of Bengal shows lower gradient than the open ocean like in CO. The average gradient over the Bay of Bengal during BOBEX campaign was 9.4 ppbv deg<sup>-1</sup>. Latitudinal gradient of CH<sub>4</sub> over the Bay of Bengal seems to be higher than other reported measurements, for example during the INDOEX 1999 campaign the latitudinal gradients of CH<sub>4</sub> were 2.3 ppbv deg<sup>-1</sup> [*Chand et al.*, 2001] and 1.7 ppbv deg<sup>-1</sup> [*Muhle et al.*, 2002] only. The maximum mixing ratio of CH<sub>4</sub> value was observed at around 20°N latitude over the Bay of Bengal. High gradient values in CH<sub>4</sub> can be due to stronger local continental sources. Apart from fuel combustion activities CH<sub>4</sub> emissions from large wetlands and paddy fields are important in Bangladesh and Burma. The latitudinal gradient in CH<sub>4</sub> is higher while gradients in O<sub>3</sub> and CO are lower compared to other reported values over the Bay of Bengal and other nearby marine regions.

#### 4.2.5 Variations in NMHCs along the cruise track

The distribution plots of some NMHCs are shown in Figure 4.4. The location and sampling time information regarding the maximum and minimum values of these compounds and other trace gases are given in Table 4.3. In the beginning of the cruise, ethane values were around 590 pptv, which decreased slowly till a minimum value of 376 pptv near DOY 259. After this it showed increasing trend and became maximum (913 pptv) near DOY 273. Again a minimum value of around 377 pptv was observed on DOY

Table 4.3: Locations and DOY information of maximum and minimum values of various trace species measured during BOBPS

2002.	

Species	Maximum	роү	Latitude(N)	Longitude(E)	Minimum	р0Υ	Latitude(N)	Longitude(E)
O <sub>3</sub> (ppbv)	43	265.50	19.02	88.15	13	274.76	16.73	83.59
CO (ppbv)	210	264.15	12.45	88.00	108	281.26	12.63	81.00
Methane (ppmv)	1.86	272.27	19.68	86.55	1.67	259.25	8.12	86.57
Ethane(pptv)	913	272.27	19.68	86.55	376	258.92	8.97	85.54
Ethene(pptv)	992	264.73	13.99	88.00	108	262.87	11.98	88.00
Propane(pptv)	399	284.00	12.06	80.69	114	284.11	12.38	80.58
Propene (pptv)	300	264.73	13.99	88.00	99	258.92	8.97	85.53
i-butane(pptv)	152	264.96	14.50	88.00	77	284.01	12.06	80.69
n-butane (pptv)	346	270.50	20.02	88.00	93	282.38	11.95	81.03
Acetylene (pptv)	420	264.73	13.99	88.00	16	281.43	12.39	81.00

275 afterwards it varied between 400 and 700 pptv till the end of the cruise. The distribution of ethane is similar to that of  $CH_4$  including coincidences in their maximum and minimum values, mainly due to their transport from common sources. Propane does not show much variation, during the entire cruise its value was just around 190 pptv.

Alkenes (ethene and propene) are highly reactive and hence are short-lived compounds in the atmosphere. In contrast to the alkanes, ethene and propene may also have local sources in the surface ocean waters perhaps from biological activity [*Bonsang and Lambert.*, 1985, *Rudloph and Johnen.*, 1990]. In the first part of the cruise from the beginning till DOY 268 ethene and propene showed higher values with large variability compared to those observed during the later part of the cruise. Higher values of ethene and propene over the southern Bay of Bengal may be due to larger local emissions as well as transport from the polluted continental landmass. Distributions of alkenes are different from alkanes as they show small-scale variations. These small-scale variabilities mostly in ethene may be due to its embedded diurnal cycle. Figure 4.8 shows composite diurnal variations of ethene and propene based on all the samples, which were collected at



**Figure 4.8:** Composite diurnal variations of alkenes (ethene and propene) based on the measurements of different dates of BOBPS 2002 campaign.

different times on different days. Alkenes mixing ratios were observed slightly lower in the afternoon and early evening than those at late night or in the early morning over remote Atlantic Ocean [*Rudloph and Johnen.*, 1990]. While a study over north Atlantic coastal site by *Lewis et al.* [1999] reports peak concentrations of alkenes at around the

local noon. From our measurements in Figure 4.8, ethene and propene values are higher during 6 to 16 hrs (local time) compared to night and early morning hours. The diurnal variation in ethene is quite clear than in propene. Solar radiation (photo oxidation) seems to play major role in the production of alkenes in the marine environment.

At the start of the campaign on DOY 257, acetylene concentration was around 128 pptv later it decreased to a minimum on DOY 259. After DOY 264, acetylene showed rapid increase and attained a maximum value of 420 pptv on DOY 265. After this peak it maintained the 200 pptv level with slight fluctuation till DOY 273. Just after DOY 273 acetylene values started dropping and reached the lowest values on DOY 275. Overall the distribution of acetylene is similar to that of ethane and  $CH_4$  except some anomalies. The maximum value in acetylene coincided with the maximum values in CO and also in alkenes just after DOY 264.

#### 4.2.6 Latitudinal variations of NMHCs

The latitudinal dependence of measured NMHCs for the open ocean cruise track (data collected along 88°E only) are given in Figure 4.9. In general NMHCs species, which are having anthropogenic sources, show a significant decrease from north towards south over the Bay of Bengal. Ethane, one of the dominant and longest lived NMHCs species, shows on an average latitudinal gradient of 29 pptv deg<sup>-1</sup> with good linear fit correlation ( $r^2 =$ 0.76). While the gradient in propane is very small of about 8 pptv  $deg^{-1}$  with linear fit correlation coefficient value of  $r^2 = 0.30$  only. The latitudinal gradients of butanes namely i-butane and n-butane are 1.7 pptv deg<sup>-1</sup> and 5.0 pptv deg<sup>-1</sup> respectively, which are similar to the gradients observed over other regions of the globe [Rudloph and Johnen., 1990, Lewis et al., 1999]. Alkenes over the Bay of Bengal do not show any systematic latitudinal variation, even though the Bay of Bengal region is surrounded by continental environment compared to the Pacific, Atlantic, and Indian Oceans. It is mainly due to the prevailing natural (oceanic) emission of these compounds over the Bay of Bengal. However, occurrence of higher values of ethene, propene and acetylene near 14 °N latitude also suggest contribution by rapid transport of pollutants from the southern part of India. Acetylene decreases from north towards south by 14 pptv deg<sup>-1</sup>.



**Figure 4.9:** Latitudinal scatter plots of NMHCs species with their best linear fits during BOBPS 2002 campaign.

#### 4.2.7 Correlation among various trace gases

Figure 4.10 shows the correlations of some NMHCs with CO. Figures 4.10(a) and 4.10(b) show reasonable correlation ( $r^2 = 0.51$  and 0.60) of ethane and acetylene with CO, mainly due to their common sources over the continent in respectively. A relatively better correlation of acetylene and CO indicates their combustion related common sources over the continent. However, it does not show any significant correlation with propane, ethene,



propene, i-butane and n-butane, which are also from marine sources and are of short life times.

**Figure 4.10:** (*a*) Correlation plot ( $r^2$  is correlation coefficient of linear fitting) of ethane and CO, (b) Correlation plot of acetylene and CO during BOBPS 2002 campaign.

Figures 4.11(a) and 4.11(b) show correlation plots of some NMHCs and CH<sub>4</sub>. Like correlations with CO, ethane and acetylene show better correlations ( $r^2 = 0.64$  and 0.24) with CH<sub>4</sub> compared to other NMHCs. A good correlation between ethane and CH<sub>4</sub> indicates their common continental sources like natural gas, paddy fields and wetlands. Propane shows slightly better correlation with CH<sub>4</sub> as compared to CO while butanes are



**Figure 4.11:** Correlation plots ( $r^2$  is correlation coefficient of linear fitting) of (a) ethane and CH<sub>4</sub>, (b) acetylene and CH<sub>4</sub> and (c) CH<sub>4</sub> and CO during BOBPS 2002 campaign.

poorly correlated. Among various correlation combinations ethene and propene are the

Methane shows best correlation with ethane while CO shows best correlation with acetylene compared to correlations with other NMHCs. Figure 4.11(c) shows a poor correlation (coefficient  $r^2 = 0.30$ ) between CO and CH<sub>4</sub>. This indicates that they do not have common sources.

#### 4.2.8 C<sub>2</sub>H<sub>2</sub>/CO ratio a tracer for the "age" of the air mass

Acetylene  $(C_2H_2)$  and CO have comparable atmospheric cycles. Both are largely combustion products and are removed by the reaction with OH in the atmosphere. Owing to the difference in their lifetimes against OH (OH reactivity for  $C_2H_2$  is three times faster than for CO), photochemical aging of an air mass after its emission leads to faster decrease of C<sub>2</sub>H<sub>2</sub> and hence the value of C<sub>2</sub>H<sub>2</sub>/CO ratio [Muhle et al., 2002]. Therefore, C<sub>2</sub>H<sub>2</sub>/CO ratio can be used as an indicator of the age of air mass, as discussed in chapter 1. In particular, the  $C_2H_2/CO$  ratios (pptv/ppbv) less than 0.5 are generally considered to be representative of aged air mass and the ratios greater than 1.0 are indicative of fresh emissions of only few days old [Gregory et al., 1996]. Variation of C<sub>2</sub>H<sub>2</sub>/CO ratio is depicted in Figure 4.3. The C<sub>2</sub>H<sub>2</sub>/CO ratio show values greater than 1.0 pptv/ppbv in most of the sampled air masses for the first half of the cruise (DOY 257-273) in the open ocean, indicating transport of fresh emissions. Except some cases for instance near DOY 260, the  $C_2H_2/CO$  value is much less than 1.0, when pristine marine air mass arrived from the southern Indian Ocean. Study of back trajectory analyses during the sampling of air masses in open ocean are in very good agreement with observations as they originated or at least swept the south Indian continent or Sri Lanka bringing freshly emitted pollutants. Also relatively higher surface wind speed (10-20 m/s) helped in faster transport of air mass containing many short-lived reactive NMHCs. While along the coastal track (eastern coast of India, DOY 274-285), observations show frequent sampling of air masses having C<sub>2</sub>H<sub>2</sub>/CO ratios less than 0.5 except for locations near north most position of track and during the last 2 to 3 days of cruise near Chennai. Measurements along the east coast of India show influence of transport of the aged air masses from open ocean. Otherwise fresh air mass with elevated values of NMHCS and other anthropogenicallyemitted species would have dominated due to nearness of emission sources. Also the concentrations of NMHCs and other species like CH<sub>4</sub> and CO along the coast are lower compared to the measurements during DOY 257-273. These  $C_2H_2/CO$  ratios along the coast are also supported by the back trajectory analyses as the sources of these trajectories are mostly in the remote marine regions away from continental influence even though cruise track being closer to the continent. The ship was close to Chennai port (one of the metropolitan cities in India) during the last 2 to 3 days of the campaign (DOY 282-285). Hence the measurements show sudden increase in  $C_2H_2/CO$  ratio values from less than 0.5 to above 1.0. Rather more important factor is the back trajectories at 3 different levels (surface, 500 and 1000m), all passed through or over the Chennai region during the last 3 days of observations. In general these observed  $C_2H_2/CO$  ratios are supported by the 7-day back trajectory analyses. Some examples are given below.

#### 4.2.9 Back trajectory analyses for some special events

The back trajectory plots corresponding to some important features of observations of trace gases are shown in Figure 4.12 at the three different height levels. For minimum in O<sub>3</sub> along with many other species near DOY 260 the back trajectory plot in Figure 4.12(a) shows the origin of all trajectories over cleaner southern region of the Indian Ocean and they were confined within the MBL before they arrived near the measurement locations. As we can see in Figure 4.12(b) that just after DOY 264 the  $O_3$ , CO, acetylene and alkenes along with C<sub>2</sub>H<sub>2</sub>/CO ratio (2.1 pptv/ppbv) values were maximized. The trajectories during this period originated over the Arabian Sea and passed through the polluted zones of Mumbai and Chennai bringing the freshly emitted pollutants. For DOY 272 measurements, the trajectories passed through the continental Sri Lanka and just over Chennai and traveled along the east coast of India (Figure 4.12(c)) contributing in maximum values of ethane and CH<sub>4</sub> near elevated background regions (closet to Kolkata) for these gases. Within 7-day the two lower level trajectories swept across the southern states of India namely Kerala and Tamil Nadu where lots of wetlands and paddy fields are there. Wetlands and paddy fields are natural sources of CH<sub>4</sub> and ethane also. In Figure 4.12(d) the trajectories are corresponding to minimum values of  $O_3$ ,  $CO_3$ , ethane and acetylene near DOY 275. The trajectories at two low levels originated over southern region of the Arabian Sea (far away from the coast) and were confined over the open marine regions till the day of measurement.



**Figure 4.12:** Seven day back trajectories of air parcels arriving at observation sites (15m, 500m and 1000m altitudes) (a) on DOY 260, showing minimum in  $O_3$ ,  $CH_4$  and ethane (b) on DOY 264, showing maximum in  $O_3$ , CO,  $C_2H_2$ , ethene and propene (c) on DOY 272, showing maximum in  $CH_4$  and ethane and (d) on DOY 275, showing a minimum in  $O_3$  and many other gases during BOBPS 2002 campaign.

# 4.3 Field expedition during 19-28 February 2003 (BOBEX II) over the Bay of Bengal

The Bay of Bengal Experiment (BOBEX II) was conducted during 19-28 February 2003, onboard the ORV *Sagar Kanya*. The ship started from Chennai (13°N, 80.2°E) on 19 February and returned to land at Tuticorin (8.75°N, 78.22°E) on 28 February 2003 (Figure 4.13). Onboard measurements of O<sub>3</sub> were made by using a Dasibi (RS 1008) analyzer. Air samples were collected in glass bottles using a metal bellow compressor. These



BOBEX-II (Feb 19 - Feb 28, 2003)

**Figure 4.13:** Cruise track during BOBEX II campaign over the Bay of Bengal. The day numbers (DOY) are marked at respective locations on the cruise track.

collected samples were analyzed for CH<sub>4</sub>, CO, and various light NMHCs using gas chromatographic techniques. Statistical data of various meteorological parameters observed during the entire cruise campaign over the Bay of Bengal are given in Table 4.4.

Parameter	Mean value	Median	Std-dev.
Temp (°C)	25.8	25.8	1.7
RH (%)	66.6	67.0	4.9
Pressure (mbar)	1010.7	1010.6	1.8
Wind speed (m/s)	3.7	3.5	1.3
Wind direction (deg.)	113.5	123.8	47.2
$H_2O(g/kg)$	14.0	14.67	2.2
EPT (°K)	334.3	336.6	8.2

**Table 4.4:** Meteorological parameters observed during BOBEX II 2003 cruise on board Sagar Kanya.

#### **4.3.1** Variations in O<sub>3</sub> along the cruise track

Figure 4.14(a) depicts the temporal and spatial variations of hourly averaged ozone mixing ratio observed during the entire cruise campaign over the Bay of Bengal. Ship locations (latitude, longitude) along the cruise track are also plotted against day of year (DOY) 2003 (Figure 4.14(d)). Ozone mixing ratios show large range (20-50 ppbv) of variability. Ozone values were around 22 ppbv near the Chennai port and it increased rapidly when ship moved away from the shore. High O<sub>3</sub> values of around 40 ppbv were observed just after DOY 50 and then decreased to 30 ppbv before DOY 51. The average O<sub>3</sub> value during these two days of measurements is 33 ppbv. Ozone again decreased from 32 to 25 ppbv during DOY 51-52. There was a sharp increase in O<sub>3</sub> values as it increased from 25 ppbv to 52 ppbv within one day, peak value occurred around DOY 53. Ozone showed rather slow fall as values are around 40 ppbv on DOY 54. For measurements during DOY 54-57, O<sub>3</sub> values vary between 30-40 ppbv. During these three days, measurements were along 82.2°E southward over the Bay of Bengal including coastal region of Sri Lanka. Ozone level started increasing when ship moved along the northwest (NW) direction towards the Tuticorin port.

### 4.3.2 Variations in CH<sub>4</sub> and CO along the cruise track

Figure 4.14(b) depicts the variations in  $CH_4$  during the entire field campaign over the Bay of Bengal. Maximum of 1.85 ppmv was observed near the northern tip of the cruise track while it showed a minimum value of 1.65 ppmv near the southern tip over the Bay of



**Figure 4.14:** Time series variations of hourly averaged  $O_3$  and other gases observed during the BOBEX II (2003) cruise campaign along with latitude (solid line) and longitude (dashed line) information.

Bengal. Measurements during the first few days of the campaign do not show large variations, as CH<sub>4</sub> values are observed to be between 1.70 to 1.75 ppmv during DOY 49.5-52.2. Like  $O_3$ , mixing ratios of CH<sub>4</sub> show sharp rise (transition) as its values were around 1.70 ppmv on DOY 52.2 and then a maximum of 1.85 ppmv on DOY 52.7. After this maximum, CH<sub>4</sub> values started decreasing with slow rate of around 92 ppbv/day (7% of mean per day) compared to its rise and the values were around 1.75 ppmv near DOY 54. Variations in CH<sub>4</sub> during DOY 54-57 show rather slow decreasing trend of 38 ppbv/day till a minimum value of 1.65 ppmv near DOY 57. The Ship sailed along the NW direction on the last day of the campaign (between DOY 57-58). During this period, measurements show increase in CH<sub>4</sub> values. Mean value of 1.72 ppmv was observed during the entire campaign.

Figure 4.14(c) shows the time series variation in CO values over the Bay of Bengal. Except some small variations in its distribution, the variability in CO is more or less similar to that in O<sub>3</sub> and CH<sub>4</sub> mixing ratios. Carbon monoxide also shows large range (126-293 ppbv) of variation in its values over this region. Slightly increasing tendency is observed in CO values as it increased from 175 ppbv to 220 ppbv during DOY 49.5-50.2. Carbon monoxide did not vary significantly and values were around 200 ppbv during DOY 50.2-52.2. After this there was a sharp rise in its values and it maximized around DOY 53, which coincides with maxima values in O<sub>3</sub> and CH<sub>4</sub>. Unlike CH<sub>4</sub>, the declining trend (36% per day of mean) in CO is rather faster, CO resumes its before peak value of about 200 ppbv just after the peak on DOY 54. This fast decreasing trend in CO continues till DOY 54.7 when the values were around 155 ppbv. Then there was slow decrease during DOY 54.7-57 over the southern portion of the Bay of Bengal. A minimum value in CO of 126 ppbv was observed near DOY 57. Again there was an increase in its values during the last day of measurements. Similar increasing trends are also observed in O<sub>3</sub> and CO. The mean CO value of 193 ppbv is observed during the entire cruise campaign.

#### 4.3.3 Variations in C<sub>2</sub>-C<sub>4</sub> NMHCs along the cruise track

Time series variations in ethane and acetylene mixing ratios are depicted in Figure 4.15(a). Both the species show similar patterns in their distributions over the Bay of Bengal. Variability in these two NMHCs species shows better resemblance with  $O_3$  compared to the variations in CH<sub>4</sub>, and CO species during the entire cruise campaign. These species also show large variations in their absolute values, as maximum values of


**Figure 4.15:** Time series variations of  $C_2$ - $C_4$  NMHCs species and a tracer ratio  $C_2H_2/CO$  observed during BOBEX II (2003) field campaign over the Bay of Bengal.

2088 and 1388 pptv and minimum values of 622 and 134 pptv were observed in ethane and acetylene, respectively. Like  $O_3$ ,  $CH_4$  and CO, peaks in ethane and acetylene also show sharp rise and slow fall in their mixing ratios. Ethane and acetylene values are low

during DOY 51-52. During these two days the ship sailed northward between 13 to 17 °N latitudes along 87°E longitude over the central region of the Bay of Bengal.

Time series variations in relatively short-lived species namely propane, i-butane, and n-butane are shown in Figure 4.15(b). Distribution patterns of these species show large fluctuations yet trends are similar to those of ethane and acetylene particularly in propane the peak is more pronounced. From the beginning till DOY 54 mixing ratios of these NMHCs were elevated, except on DOY 51-52 when relatively lower values were observed in these species. Measurements of these compounds did not show any kind of trends and observed to be constant during DOY 54-57. After DOY 57 increasing trends were observed in propane and butane. The mean values of 239, 115 and 98 pptv were observed in propane, i-butane, and n-butane, respectively over the Bay of Bengal.

Figure 4.15(c) shows time series variations in ethene and propene, almost similar variations can be seen in these species. In the beginning, ethene and propene values were stable at around 200 and 100 pptv levels till DOY 50. While elevated values were observed in both the species, mixing ratios are just below 300 and 200 pptv levels for ethene and propene, respectively between DOY 50-50.8. Like other trace species, ethene and propene mixing ratios showed lower values as these were below 200 and 100 pptv, respectively during DOY 51-52. Unlike other species, alkene species did not show sharp transitions though values were slightly elevated for the measurements during DOY 52-53. During DOY 53-57 mixing ratios did not vary significantly and values were about 200 and 100 pptv levels in ethene and propene, respectively. After DOY 57 their values showed rapid increase toward the end of campaign.

Various statistical data including maxima and minima values with their spatial and temporal information derived for all the species measured during the entire cruise campaign are given in Table 4.5.

#### 4.3.4 Discussion

As we have seen from the wind field analyses that wind flow used to be from the NE direction during this field campaign (BOBEX II) over the Bay of Bengal. Due to this wind flow, pollutants are transported from various continental regions over the entire Bay of Bengal and this reflected in pronounced variability in various trace species measured over the Bay of Bengal. Emissions inventory of trace gases has already been discussed in chapter 1. Asian emissions show strong regional differences [*Woo et al.*, 2003].

Table 4.5: Median, mean, standard deviation, maximum and minimum values of various trace species along with location and DOY information during BOBEX II (2003) field campaign over the Bay of Bengal.

Compounds	Median	Mean	Std-dev.	Max.	DOY	Latitude	Longitude	Min.	DOY	Latitude	Longitude
O <sub>3</sub> (ppbv)	34	34	6.4	52	53.06	18.98	86.60	21	51.58	15.09	86.97
CO (ppbv)	194	193	40	293	53.00	18.99	86.60	126	56.67	6.93	82.13
CH4 (ppmv)	1.72	1.72	0.04	1.85	52.67	18.91	87.00	1.65	56.58	7.22	82.17
$C_2H_6$ ( pptv)	1106	1181	362	2088	52.83	19.48	86.99	622	52.09	16.96	87.02
$C_2H_4$ (pptv)	182	198	60	516	57.33	5.92	79.95	137	54.21	15.44	83.96
C <sub>3</sub> H <sub>8</sub> (pptv)	206	239	100	591	52.83	19.48	86.99	131	56.00	9.40	82.17
C <sub>3</sub> H <sub>6</sub> (pptv)	94	106	50	408	52.50	18.35	87.00	54	50.88	13.00	86.50
i-C4H10 (pptv)	102	115	42	264	53.75	16.81	85.97	84	57.50	09.9	79.52
$n-C_4H_{10}$ (pptv)	57	98	123	892	49.67	13.10	81.86	52	55.50	11.24	82.17
C <sub>2</sub> H <sub>2</sub> (pptv)	373	471	276	1338	52.75	19.23	87.00	134	51.33	14.21	87.00
C <sub>2</sub> H <sub>4</sub> /C <sub>3</sub> H <sub>6</sub>	1.99	2.04	0.59	3.86	52.58	18.63	87.01	0.59	51.33	15.43	87.00
C <sub>2</sub> H <sub>2</sub> /CO (pptv/ppbv)	2.15	2.33	0.88	4.84	52.83	19.48	86.99	0.63	51.33	14.21	87.00

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These differences reflect in large part due to differences in the contribution of fossil fuels, biofuels, and biomass burning.

For each individual sampling location, 7-day back trajectories (ending at 15 m, 500 m, and 1000 m asl) were calculated with the Hybrid Single-Particle Langrangian Integrated Trajectories (HYSPLIT) program [*Draxler and Hess*, 1998] to track the origin of the probed air masses. Making use of the back-trajectories and measurements of chemical composition, various source regions are grouped in the following categories.

- 1. Asian continental tropical (AsiaCT), the air mass originating over India, Bangladesh, and Burma regions.
- 2. Asian continental extra-tropical (AsiaCX), the airflow passing over the Arabian Peninsula.
- 3. Asian marine tropical (AsiaMT), characterized as having passed over marine regions.

We have also incorporated  $C_2H_2/CO$  ratio, which is used as qualitative estimates of the age of various air samples. In Figure 4.15(d)  $C_2H_2/CO$  (pptv/ppbv) ratio is plotted against DOY for measurements over the Bay of Bengal. Mean values of trace species and their derived quantities for various air masses (various episodes) are given in Table 4.6.

#### 4.3.5 Air masses observed during DOY 49.5-51

For this period of measurements some of the 7-day back-trajectories are plotted in Figure 4.16(a). These trajectories originated over the northwest regions of India and transported locally emitted pollutants from Delhi, Kolkata and some parts of Bangladesh before subsiding near the measurement locations over the Bay of Bengal. Air masses also spent 3-4 days within the MBL over the Bay of Bengal and could have diluted the pollutants. We have assigned the air masses to be of AsiaCT type, measured during DOY 49.5-51. The mean mixing ratios of  $O_3$ , CO and ethane in this AsiaCT regime were 32 ppbv, 200 ppbv and 1130 pptv, respectively. The chemical tracer  $C_2H_2/CO$  ratio value of 2.14 pptv/ppbv for this period indicates transport of recently emitted pollutants from the continent into the MBL (Marine Boundary Layer) of the Bay of Bengal.

#### 4.3.6 Air masses observed during DOY 51-52

Except for some long lived trace gases measurements of all the species show sharp decreases in mixing ratios for this period of observation over the Bay of Bengal. Figure

**Table 4.6:** Mixing ratios (mean and  $1\sigma$  variation) of trace species measured during different periods of BOBEX II (2003) cruise campaign over the Bay of Bengal.

<u>BOBEX II</u>	7 YOU	49-51	DOY :	51-52	DOY	52-55	DOY	55-57	DOY :	57-58
	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV	AVG	STDEV
O <sub>3</sub> (ppbv)	32	4	26	4	38	7	35	3	28	3
CO (ppbv)	200	14	203	10	237	34	150	13	166	15
CH4 (ppmv)	1.73	0.015	1.72	0.010	1.77	0.035	1.68	0.019	1.68	0.020
C <sub>2</sub> H <sub>6</sub> (pptv)	1130	119	718	67	1539	330	1040	132	933	156
C <sub>2</sub> H <sub>4</sub> (pptv)	232	44	162	20	195	38	169	18	264	117
C <sub>3</sub> H <sub>8</sub> (pptv)	190	28	164	25	293	116	188	39	245	109
C <sub>3</sub> H <sub>6</sub> (pptv)	122	37	72	14	120	68	86	22	111	34
i-C4H10 (pptv)	122	54	84	з	117	38	93	13	123	72
n-C <sub>4</sub> H <sub>10</sub> (pptv)	299	210	42	18	81	39	43	22	71	57
C <sub>2</sub> H <sub>2</sub> (pptv)	427	78	268	58	776	285	300	68	290	95
C <sub>2</sub> H <sub>4</sub> /C <sub>3</sub> H <sub>6</sub> (pptv/pptv)	1.81	0.30	2.4	0.19	1.9	0.67	1.91	0.38	2.35	0.52
C <sub>2</sub> H <sub>2</sub> /CO (pptv/ppbv)	2.13	0.32	1.3	0.30	3.3	0.75	1.98	0.35	1.73	0.45

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4.16(b) shows the 7-day back trajectories plots for this period of measurements over the Bay of Bengal. Source regions of these trajectories were located over the Bangladesh and Burma regions only. But the height information of these trajectories indicates long travel time (5-6 days) of the air parcel within the MBL over the Bay of Bengal. Not only the transport from very limited continental region but also the dilution of pollutants due to mixing with relatively clean marine air resulted in observed low levels of various trace species. Also relatively lower mean  $C_2H_2/CO$  ratio value of 1.3 pptv/ppbv compared to AsiaCT type air masses justifies the decreased mixing ratios of trace species observed during this period. Good agreement in back-trajectory analyses, chemical tracer ratios and chemical characterization (absolute values) indicates sampling of AsiaMT type of air masses over the Bay of Bengal during DOY 51-52. The mean mixing ratios in O<sub>3</sub>, CO and ethane in this AsiaMT regime were 26 ppbv, 203 ppbv and 718 pptv, respectively. Air parcels sampled during this period seem to be depleted in anthropogenically emitted ethene and propene while mixing ratios are below detection limit particularly for anthropogenically emitted reactive NMHCs species like butanes. Some short-lived NMHCs like ethene and propene also have oceanic sources [*Plass-Dulmer et al.*, 1995; Lewis et al., 1999]. During this episode of measurements the mean mixing ratios of ethene and propene were around 162 and 72 pptv, respectively. The observed slope value of 2.4 pptv/pptv for ethene and propene stands in agreement with values determined by on-line measurements over the Atlantic Ocean of 2.5 in SH and 2.9 in the NH [Rudolph and Johnen, 1990]. Therefore, one can assume that observed mean values of ethene and propene are representative of marine background levels of these compounds over the Bay

of Bengal.

#### 4.3.7 Air masses observed during DOY 52-55

During DOY 52-55 elevated mixing ratios with maxima around DOY 53 in all trace species were measured over the northern region of the Bay of Bengal. Observed peaks are not symmetric with respect to time (DOY) as their increases are sharp while tailing in the fall side of the peaks. For these days of observations, back trajectories are shown in Figure 4.16(c). Air parcels originated from the mid-latitude continental of the NH (mainly from Arabian Peninsula, Middle East, and Europe) and were advected to the sampling site via southeast in the free troposphere before descending over the Bay of Bengal. The strongest pollution event was caused by the long-range transport from the Middle East



**Figure 4.16**: Back trajectory (ending at 500 m) plots for periods (a) DOY 49-51, (b) DOY 51-52, (c) DOY 52-55 and (d) DOY 55-58 during BOBEX II (2003) field campaign over the Bay of Bengal.

and SE Europe. Highest mean  $C_2H_2/CO$  tracer ratio value of 3.3 pptv/ppbv also suggests rapid transport of recently emitted or less photochemically processed pollutants over the Bay of Bengal. After the peak day, the source regions of various trajectories moved southeastward and this resulted in the gradual decrease in the mixing ratios of trace species. Air parcels transported from extra-tropical NH continental regions are grouped in AsiaCX type. Ozone levels reached up to 52 ppbv and the average mixing ratios are 38 ppbv, 237 ppbv, and 1539 pptv, respectively for O<sub>3</sub>, CO and ethane. Similar events of elevated values in various trace species are also observed during INDOEX 1999 field campaign over the Arabian Sea [*Muhle et al.*, 2002; *Burkert et al.*, 2003]. During the INDOEX 99 campaign (in AsiaCX regime) highest mixing ratios in ethane, acetylene, CH<sub>4</sub> and O<sub>3</sub> were observed to be 1866 pptv, 325 pptv, 1.82 ppmv and 53 ppbv, respectively. This event over the Arabian Sea was not attributed to biomass burning, since the typical marker acetonitrile was minimum [*Wisthaler et al.*, 2002].

#### 4.3.8 Air masses observed during DOY 55-57 and 57-58

During DOY 55-57 and DOY 57-58 source regions were located over the southern region of Pakistan and western region of India (mostly over the Gujarat province), 7-day back trajectories are shown in Figure 4.16(d). Air parcels transported via the central region of the Indian subcontinent descended over the measurement locations over the Bay of Bengal including the east coast of Sri Lanka. The trajectory height information also indicates long transport time (3-4 days) within the MBL of the Bay of Bengal. A  $C_2H_2/CO$  tracer ratio of 1.98 pptv/ppbv suggests the moderate age of air parcels. The observed mean values in O<sub>3</sub>, CO and ethane are around 35 ppbv, 150 ppbv, and 1040 pptv during DOY 55-57 over this region. During DOY 57-58 the ship was located near the western coast of Sri Lanka and sharp increases were observed in all the trace gases for this day of measurement sites are due to additional pollutant supply from the continental Sri Lanka. Mean mixing ratios in O<sub>3</sub>, CO, and ethane are around 28 ppbv, 166 ppbv, and 933 pptv during DOY 57-58. Depending upon the origin of back trajectories, air parcels are of AsiaCT type during these two episodes.

#### 4.3.9 Comparison of measurements over the Bay of Bengal

The distributions of  $O_3$  and anthropogenically emitted trace gases like CO, CH<sub>4</sub> and NMHCs have been studied in different seasons over the Bay of Bengal. Measurements of various trace gases are made during the three field campaigns (BOBEX, BOBPS, and BOBEX II) over this region. These measurements are extensive and covered large portion of the Bay of Bengal. Measurements show large differences in absolute values and variability in various trace gases observed during all these cruise campaigns over this region.

Measurements of  $O_3$ , CO and CH<sub>4</sub> trace species are made during all the three cruise campaigns. Mean mixing ratios of  $O_3$ , CO, and CH<sub>4</sub> observed during these campaigns (2001-2003) are shown in Figure 4.17. The mean values in  $O_3$  mixing ratios are around 42, 27 and 34 ppbv while CO values are around 217, 143 and 193 ppbv during BOBEX, BOBPS and BOBEX II field campaigns, respectively. Methane is a long -lived trace gas and is well mixed within the troposphere. Except an unusually high value of 1.92 ppmv during BOBEX 2001, methane does not show significant seasonal differences as its mean



**Figure 4.17:** A comparison of mean values of  $O_3$ , CO and CH<sub>4</sub> during three different cruise campaigns (2001-2003) over the Bay of Bengal.

values are 1.75 and 1.72 ppmv during BOBPS and BOBEX II field campaigns, respectively. Comparison of latitudinal gradients observed in  $O_3$ , CO, and CH<sub>4</sub> during BOBPS and BOBEX II campaigns are shown in Figure 4.18(a-c). Distributions of anthropogenically emitted NMHCs show north to south decreasing trends during both the seasons. Figure 4.18(e-f) shows the latitudinal gradients for ethane, propane and acetylene during two different seasons over the Bay of Bengal. The mean C<sub>2</sub>H<sub>2</sub>/CO tracer ratio values of 0.86 and 2.33 pptv/ppbv were observed during BOBPS and BOBEX II



**Figure 4.18:** Comparison of latitudinal variations in O3, CH<sub>4</sub>, CO and NMHCs during BOBPS and BOBEX II (2003) field campaigns over the Bay of Bengal.

Measurements of various light NMHCs were made during the last two cruises (BOBPS and BOBEX II) only. Figure 4.19 shows box-whisker plots of various NMHCs, representing some statistical parameters of their measurements during the two distinct seasons over the Bay of Bengal. It can be seen very clearly that the seasonal differences are more in relatively long-lived NMHC species, while no significant differences are observed in reactive (short-lived) NMHCs over the Bay of Bengal. The mean values in ethane are around 561 and 1181 pptv while in acetylene the values are around 128 and 471 pptv during the summer (BOBPS campaign) and winter (BOBEX II campaign) seasons, respectively.



**Figure 4.19:** Box-whisker plots of  $C_2$ - $C_4$  NMHCs species during BOBPS (filled box) and BOBEX II (empty box) campaigns over the Bay of Bengal.

### 4.4 Comparison with previous measurements

During the BOBEX 2001 [Lal et al., 2004] and the INDOEX 1999 [Muhle et al., 2002] field campaigns, measurements of various trace gases were made over the Bay of Bengal and the Arabian Sea. Both BOBEX and INDOEX field campaigns were conducted in February and March months. Over the Bay of Bengal during BOBEX our measurements were extensive covering the large portion while measurements were only for the southern portion (south of 10°N) during INDOEX 1999. Table 4.7 gives mean values of various trace gases for the Bay of Bengal, Indian Ocean and also for the Arabian Sea. The large differences in absolute values and variability of compounds measured during the above campaigns can be seen over the Bay of Bengal. It is mainly due to their large gradients over this region. Present measurements (BOBPS 2002) also show lower concentrations of many compounds over the southern portion. The mean values of ozone and CO measured over this region (42.2 and 217 ppbv, respectively during BOBEX 2001) and the Arabian Sea (43.9 ppbv and 217 ppbv, respectively during INDOEX 1999) were higher than the BOBPS measurements. One of the important reasons for these differences is the prevailing meteorological conditions over the Bay of Bengal as during February and March months NE wind flow brings lot of pollutants from India and other northeast Asian countries over this region as mentioned earlier. Being in the tropical region the second but also important reason may be the suppressed biomass burning and forest fire emissions during the wet season of BOBPS 2002 compared to the dry months (February and March) of other campaigns.

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Species	INDOEX (1999)	INDOEX (1999)	BOBEX (2001)
	(Bay of Bengal)	(Arabian Sea)	(Bay of Bengal)
O <sub>3</sub> (ppbv)	$22.4 \pm 1.5$	$43.9\pm8$	$42.2\pm12.0$
CO (ppbv)	$162.9\pm3$	$217\pm42$	$217\pm31$
CH <sub>4</sub> (ppmv)	1.77	$1.73\pm0.05$	$1.92\pm0.05$
Ethane (pptv)	370		
Propane (pptv)	$17.1\pm0.9$		
Acetylene (pptv)	$138.5\pm9$		
C <sub>2</sub> H <sub>2</sub> /CO (pptv/ppbv)	$0.86\pm0.14$		

**Table 4.7:** *Mixing Ratios (Mean and 1 \sigma variation) of trace species measured during other field campaigns.* 

# CHAPTER 5

# Study of O<sub>3</sub> and Water Vapor Distributions over Madras and Delhi

Atmospheric chemistry is dominated by the cycles of  $O_3$  and water vapor. It is known that the photochemical formation of  $O_3$  from its precursors is the major source of tropospheric  $O_3$  [*Crutzen*, 1979, 1988; *Fishman and Crutzen*, 1977]. In the gas phase chemistry, the photolytic dissociation of  $O_3$ , in the presence of water vapor provides the primary source of the hydroxyl (OH) radical which initiates the oxidation of the majority of trace gases. The nitrogen oxides (NO, NO<sub>2</sub>), also controlling the OH concentrations, play a central role in the photochemical formation of  $O_3$  in the tropopshere. It is interesting to note that these chemicals are responsible for the destruction of  $O_3$  in the stratosphere. Moreover, water vapor is the predominant greenhouse gas [*Ramanathan et al.*, 1985; *Wigley*, 1987] and, in combination with the exchange of latent heat, it is an essential factor in atmospheric energetics.

Long-term  $O_3$  observations have shown significant differences from station to station. For instance, trends in tropospheric  $O_3$  are found as follows: (1) higher (1-2%yr-1) over western Europe, since the beginning of industrial era; (2) smaller (0.5-1% yr-1) over the eastern coast of United States in summer for 1970-1991; and (3) no change over Canada [*Marenco et al.*, 1998 and references there in]. Much lower or insignificant increases are observed in the southern hemisphere, while the  $O_3$  trend at the tropics is obviously influenced by biomass burning emissions which may result in regional increases of  $O_3$  and CO concentrations because of rising deforestation rates [*Kirchhoff*, 1996]. In the upper troposphere, there are no systematic indications of  $O_3$  changes over the last two decades, certainly due to larger natural variability of  $O_3$  near the tropopause.

There have been attempts by other authors to group  $O_3$  profiles in terms of certain criteria, *Newell et al.* [1999] characterized four layer types in terms of combinations of  $O_3$  and water vapour characteristics, defined as either enhanced (+) or reduced (-). They

assigned sources to each and were able to calculate the percentage occurrence of each layer type based on data from the MOZAIC (Measurements of OZone and Water Vapor by Airbus In-Service AirCraft) and PEM (Pacific Exploratory Mission) programs. The layer types are defined as follows, with the percentage occurrence indicated in brackets after each type:  $O_3+/H_2O+$  indicative of continental pollution (11-15%);  $O_3+/H_2O-$  characterized by stratospheric air (50-54 %);  $O_3-/H_2O+$  due to convection from the boundary layer (15-19%); and  $O_3-/H_2O-$  indicative of subsiding air originally raised in deep convection over oceans (17-18%).

Some typical climatological  $O_3$  profiles in the tropics are shown in Figure 5.1 which are shaped like an "S" with a minimum at the surface, a maximum at 330 K (~6.5km), another minimum at 345 K (11.2 km), and a subsequent increase toward the tropopause. A simple model can reproduce these features whose only free parameter is



**Figure 5.1:** The mean annual dependence of ozone mixing ratio on potential temperature measured at different sites in the tropics. Figure adapted from Folkins et al. [2002].

mean  $O_3$  mixing ratio of air detraining from deep convective clouds. The first order climatological  $O_3$  profile in the tropics arises from a balance between vertical advection, deep convection, and chemistry [*Folkins et al.*, 2002]. The factors that determine the vertical variation of  $O_3$  in the tropics can be grouped together into seven categories: (1) in

situ production/destruction, (2) deep convective outflow, (3) vertical advection, (4) shallow convection, (5) eddy exchange with the midlatitudes/lowermost stratosphere, (6) convective downdrafts, and (7) vertical mixing near the tropical tropopause associated with convective overshooting [*Sherwood and Dessler*, 2001] and Kelvin waves [*Fujiwara et al.*, 1998]. Shallow convection refers to the mixing occurring along the sides of deep convective updrafts or that associated with shallow dissipating convective plumes. Vertical advection refers to the O<sub>3</sub> tendency arising from the slow radiatively driven vertical motions in the tropics.

#### 5.1 Tropical tropospheic O<sub>3</sub>

Tropical region is a large contributor to the global  $O_3$  budget. Moreover, it plays a key role in controlling the chemistry and climate of the tropical troposphere. Human activities increase O<sub>3</sub> concentration in the troposphere through emissions from fossil fuel combustion and biomass burning [Crutzen et al., 1979, 1985; Logan et al., 1981]. This will especially be the case in future in the tropics where the economic activity is growing strongly with possible strong impact on chemistry and climate [IPCC, 2001]. The detailed characteristics of O<sub>3</sub> in the tropical troposphere remain unsolved because of a lack of comprehensive observations. There are only few tropical ozone-sounding stations that make O<sub>3</sub> measurements on a routine basis. The number of ozonesonde stations in the tropics, particularly the northern tropics, is limited compared to that in the northern midlatitudes [Logan, 1999]. Simulations of the tropical tropospheric O<sub>3</sub> distributions are hampered by a lack of knowledge of transport processes such as deep convection, stratosphere-troposphere exchange (STE), and long-range transport from the source regions. In the previous chapter we have studied the long-range transport of polluted air masses from Middle East and European countries over the Bay Bengal. It is also seen that the trajectories of these air masses pass through the free troposphere over continental India. Therefore such transports can have impacts in the vertical distributions of various trace gases over the region. The main aim of this work is to study how transport processes affect the tropospheric O<sub>3</sub> distribution over the Indian subcontinent.

#### 5.2 The MOZAIC Program

#### 5.2.1 Scientific Objectives

The MOZAIC program was initiated in 1993 by European scientists, aircraft manufacturers, and airlines to collect experimental data. The MOZAIC data combined with meteorological data are being used to (1) establish a quasi-global climatology of the large scale distributions of O<sub>3</sub> and water vapor in the UT/ LS near the tropopause; (2) establish the vertical and temporal distributions of O<sub>3</sub> and water vapor at various locations (airports) distributed over the continents; (3) investigate the seasonal and geographical variations of the measured distributions in relation to their natural and anthropogenic sources, STE, and horizontal and vertical air circulation; and (4) to validate chemistry and transport models [*Marneco et al.*, 1998]. Ozone and water vapor sensors were installed on board five long -range commercial aircraft (Airbus A340's) of four participating airlines. The MOZAIC project, in operation since August 1994, is a EU (European Union) supported project for the automatic measurements of O<sub>3</sub> and water vapour on board AIRBUS A340 aircraft on scheduled flights. MOZAIC is sponsored by major European airlines: Air France (1 aircraft), Austrian Airlines (1 aircraft), Lufthansa (2 aircraft) and Sabena/Air France (1 aircraft).

#### 5.2.2 MOZAIC measurements over India

The MOZAIC data are invaluable for investigation of the seasonal and geographical variations of  $O_3$  and water vapor in relation to the main chemical and physical processes

	199	6	199	7	199	8	199	9	200	0	200	1
Season												
	D	Μ	D		D	Μ	D	Μ	D	Μ	D	Μ
				Μ								
JFM	2	4	11	9	1	5	0	0	10	0	2	11
AMJ	19	5	0	6	7	4	12	0	6	0	15	5
JAS	9	5	0	8	3	4	9	0	6	0	0	8
OND	7	8	0	8	2	2	3	0	11	0	6	0

 

 Table 5.1: Number of MOZAIC measurements over Delhi (D) and Madras (M) during 1996-2001.

occurring in the atmosphere. During the ascent and descent of the aircraft above airports, vertical profiles are recorded. MOZAIC measurements of vertical  $O_3$ , water vapor and many meteorological parameters over the Indian subcontinent consists of measurements at three metropolitan cities, namely Madras (12.99°N, 80.15°E), Delhi (28.56°N, 77.11°E) and Mumbai (Bombay) (19.09°N, 72.87°E). In this study we have discussed the distributions of  $O_3$  and water vapor over Madras and Delhi only since relatively large and regular database are available for these two sites. Figure 5.2 represents the total number of observations over Madras and Delhi. Number of vertical observations made during various seasons of 1996-2001 period over Madras and Delhi is given in Table 5.1. We have not discussed the measurements made over Mumbai due to irregular and lack of enough database. Madras is a coastal city and maritime air masses influence the location oftenly. The northeast monsoon is the principal while the southwest monsoon is the



**Figure 5.2:** Bar plot representing the total number of MOZAIC measurements over Madras and Delhi during 1996-2001 period.

secondary rainy season for this place (Figure 5.3). Delhi is a land locked subtropical station, except summer monsoon season, dry climate persists during most of the time of year. The southwest summer monsoon is the principal rainy season for this place (Figure 5.4).



**Figure 5.3:** Rainfall (mm) variations, measured at Madras during 1996-2001 period. Data taken from India Meteorological Department (IMD), India.

## 5.3 Variability in wind fields over India

The observed seasonal changes in the wind flow over the continental India or SE Asia are associated with onset and withdrawn of monsoon. A monsoon seasonal change is characterized by a variety of physical mechanisms, which produce strong seasonal winds, a wet summer and dry winter. The main characteristics are differences in land/sea temperatures, location within the ITCZ region, and intense convective storms. The summer monsoon circulation is generally visualized as large-scale convergence of mass and moisture over the Indian sub-continent and adjoining South East Asian land mass in the lower levels and a strong upper level divergence aloft. Surface heating during summer favors enhanced convection over land, which is fueled by moist inflow at low



**Figure 5.4:** *Rainfall (mm) variations, measured at Delhi during 1996-2001 period. Data taken from India Meteorological Department (IMD), India.* 

levels. We have utilized NCEP (National Center for Environmental Prediction) wind fields data to derive the wind streamline flow over India and surrounding marine regions. Figures 5.5, 5.6, 5.7 and 5.8 show the general mean wind streamline plots during JFM, AMJ, JJA, and OND months respectively at four different pressure levels of 925 mb, 700 mb, 400 mb, and 250 mb. In winter season wind flow at 700 mb is NW over Delhi while its a NE over Madras. But the upper troposphere over both the stations are influenced by westerly wind flow, as shown in plots for 250 mb during JFM months. Wind field streamlines are from SW direction at 925 mb level over Madras and Delhi during summer season (JAS months). While opposite wind flow prevails in the upper troposphere over Delhi and Madras, those are westerly and easterly over Delhi and Madras respectively at 250 mb during summer season. In general, westerly wind flow prevails in the middle and



**Figure 5.5:** Mean wind fields at four different pressure levels during January, February and March (JFM) months of 2002 over continental and surrounding marine regions of India. Color bar represents the magnitude of wind speed. Data adapted from NCEP.

upper troposphere throughout the year over Delhi. While wind patterns over Madras show large seasonal variations in the entire troposphere.

## 5.4 Vertical distribution of O<sub>3</sub> in the tropics

The tropical continental boundary layer (CBL) is an important source region of photochemically produced  $O_3$ . Biomass burning and fossil fuel combustion generate CO, CH<sub>4</sub> and nonmethane hydrocarbons. The variations at the tropics reflect the heterogeneity of this region, arising from  $O_3$  precursor sources (biomass burning), sinks (photolysis, photochemistry), and convective processes. The combination of last two processes is



**Figure 5.6:** *Mean wind fields at four different pressure levels during April, May and June (AMJ) months of 2002 over continental and surrounding marine regions of India. Color bar represents the magnitude of wind speed. Data adapted from NCEP.* 

responsible for the very low  $O_3$  concentrations found in upper layers: (1) increases in photochemical destruction of  $O_3$  in the presence of high humidity, through the following reactions:

$$O_3$$
+hv  $\Rightarrow O(^1D)+O_2$   
 $O(^1D)+H_2O \Rightarrow 2OH$   
 $O_3$ +HO<sub>2</sub>  $\Rightarrow OH+2O_2$   
 $O_3+OH \Rightarrow O_2+HO_2$ 



**Figure 5.7:** *Mean wind fields at four different pressure levels during July, August and September (JAS) months 2002 over continental and surrounding marine regions of India. Color bar represents the magnitude of wind speed. Data adapted from NCEP.* 

and (2) vertical transport, to high altitude, of these ozone-poor air masses from the marine boundary layer as described by *Davies et al.* [1998]. On the other hand deep convection appears to be one of the most effective mechanisms for transporting  $O_3$  and  $O_3$  precursors (CO, NOx, hydrocarbons) to the free troposphere [*Chatfield and Crutzen*, 1984]. Relatively fresh emissions can be vented to the middle or upper troposphere in a matter of minutes. When boundary layer NO has been diluted through convective transport,  $O_3$  is produced more efficiently on a per-molecule basis than in a highly polluted boundary



**Figure 5.8:** *Mean wind fields at four different pressure levels during October, November and December (OND) months of 2002 over continental and surrounding marine regions of India. Color bar represents the magnitude of wind speed. Data adapted from NCEP.* 

layer [*Liu et al.*, 1987]. Lateral transport from a source in the upper troposphere or perhaps the lower stratosphere, or  $O_3$  and its precursors from a very photochemically active source region have also been observed to play important role in the distributions. An important factor in transport studies is the lifetime of  $O_3$ . Ozone is photodissociated by short wave solar radiation (< 340 nm) into electronically excited  $O(^1D)$  atoms. Reaction of these with water vapor form OH radicals. Thus the lifetime of  $O_3$  is basically determined by the amount of water vapor and solar radiation. The lifetime of  $O_3$  increases from 2 to 5 days in the moist tropical marine boundary layer (MBL) to approximately 90



**Figure 5.9:** Contour plots representing the annual variations (monthly mean data) of ozone, water vapor and temperature over Madras during 1996.

days in the free troposphere [*Fishman et al.*, 1991]. Thus once  $O_3$  is lifted from the boundary layer, it can be transported far away from its source regions.

# 5.5 Annual variations in O<sub>3</sub>, water vapor and temperature over Madras during 1996-1998

#### 5.5.1 Variability over Madras during 1996

Monthly mean data have been used to study the seasonal distribution in O<sub>3</sub>, water vapor and temperature over Madras. Figures 5.9(a), 5.9(b) and 5.9(c) show seasonal variations in  $O_3$ , water vapor concentration and temperature respectively over Madras for 1996. It can be seen from these plots that O<sub>3</sub> and water vapor show large annual variability. Ozone values are always below 30 ppby during all the months within the boundary layer. In the free troposphere (from 1 to 8 km heights) O<sub>3</sub> values varied between 40 to 50 ppbv without any significant vertical gradients during winter months (January, February and March). A patch of elevated O<sub>3</sub> values of 50-70 ppbv is observed in middle troposphere between 3 to 8 km altitudes during April to June months. Ozone values are very low near the surface and in the upper troposphere during August to November months (summer and autumn seasons). It shows steady increasing trend, as its values were 10-15 ppbv, 10-20 ppbv, 20-30 and 30-40 ppbv for 0-2 km, 2-4 km, 4-6 km and 6-8 km height ranges, respectively. Being a coastal city, the lower troposphere is always influenced by high water vapor concentrations. Except for January, February, and December months the middle and upper tropospheric regions are also influenced by high water vapor content and relative humidity values are found to be more than 50%. Very high values of water vapor concentrations were observed during March and April months, which seem to be an unusual event, as we do not observe same for 1997 and 1998.

As we have discussed that Madras is an urbanized region and there is always large emission of  $O_3$  precursors (pollutants). High  $O_3$  during daytime while low during night is the common feature of a typical urban region. Decrease of  $O_3$  near sunset is the result of surface deposition and the formation of a stable surface inversion layer that prevents  $O_3$ from being transported from aloft. Since MOZAIC measurements are always taken during night hours,  $O_3$  values are always very low within the boundary layer. In the lower and mid-troposphere high concentrations of  $O_3$  in the spring season could be due to the longrange transport of pollutants by northwesterly winds associated with the winter monsoon circulation bringing air from the Asian continent [*Hastenrath et al.*, 1985]. The presence of higher  $O_3$  concentrations in the mid-troposphere at this time of the year may be due to the uplift farther north by convection. Conversely, summer minima with mean concentrations as low as 15 ppbv in the period from July to November over Madras are observed. This is related to monsoon circulation advecting clean air from the southwest over the Indian Ocean to ITCZ region, which is well north of equator in the summer months. This is also the period when higher and frequent rainfall was observed at Madras.

#### 5.5.2 Variability over Madras during 1997 and 1998

Figures 5.10(a), 5.10(b) and 5.10(c) show the seasonal variations in  $O_3$ , water vapor concentration and temperature respectively over Madras for 1997 year. The observed broad features in the seasonal distribution of  $O_3$  are similar to that of 1996 year. For instance during both the years  $O_3$  values are maximum in the spring season while minimum during summer monsoon. Both anthropogenic and natural processes (emission as well as transport) control the distribution of  $O_3$  in the troposphere and these processes may change from year to year. Though main features are repeated yet some differences can be observed. In the mid-troposphere during spring season not only  $O_3$  mixing ratio but spatial (vertical) extent is relatively lower compared to those in 1996. There is early occurrence of low  $O_3$  during summer monsoon circulation as it started from June in 1997 while it was from July during 1996. In the upper troposphere (6-8 km altitudes)  $O_3$  values range from 30 to 40 ppbv in 1996 and 50 to 60 ppbv during 1997. Except higher water vapor concentration during February, March and April months it shows similar vertical trends like that have been seen during 1996 over Madras.

Figures 5.11(a), 5.11(b) and 5.11(c) show the seasonal variations in  $O_3$ , water vapor concentration and temperature respectively over Madras for 1998 year. November and December months data are missing due to non-availability of measurements. Seasonal variability in  $O_3$  for 1998 data is similar to observations during 1996 and 1997. The higher vertical extent of very high  $O_3$  (values up to 80 ppbv) during spring season of 1998 compared to 1996 and 1997 for same period is a clear difference in the annual distribution patterns. Seasonal variation in water vapor concentration during 1998 is similar to 1996.

In general,  $O_3$  and water vapor show just opposite seasonal variations, though water vapor distribution is very much localized compared to  $O_3$ . Similar annual patterns in  $O_3$  and water vapor are repeated during different years except some small-scale differences.



**Figure 5.10:** Contour plots representing the annual variations (monthly mean data) of ozone, water vapor and temperature over Madras during 1997.



(a) Ozone (ppbv), Madras 1998

Figure 5.11: Contour plots representing the annual variations (monthly mean data) of ozone, water vapor and temperature over Madras during 1998.

# 5.6 Annual variations in O<sub>3</sub> and water vapor over Delhi during 1996 and 1998

#### 5.6.1 Variability over Delhi during 1996

Figures 5.12(a) and 5.12(b) depict the seasonal variations in  $O_3$  and water vapor concentrations, respectively over Delhi for 1996. Near surface  $O_3$  values are between 40-60 ppbv during all the months of the year. Higher  $O_3$  mixing ratios (60-80 ppbv) are observed just above the boundary layer during the spring season. In the mid-troposphere (from 1 to 5 km altitudes)  $O_3$  values varied between 60-80 ppbv with an exception of small patch of 40-60 ppbv during winter and spring seasons (January to June months). But at elevated heights (8-10 km)  $O_3$  varies from 80-100 ppbv during winter season. Maximum  $O_3$  values of 100-150 ppbv were observed in the middle and upper troposphere (6-10 km) over Delhi during the spring season only. Ozone mixing ratios vary from 40-60 ppbv in the lower and middle troposphere while in the upper troposphere values are 60-80 ppbv during August, September and October months. Ozone starts increasing again in November month, as its values are 60-80 and 80-100 ppbv in the middle and upper troposphere respectively.

Water vapor distribution also reflects pronounced seasonal variation over Delhi during 1996. Surface water vapor concentrations are 6-9 g/kg for January to May months. It starts increasing thereafter, and maximum concentration of 24-27 g/kg is observed during August month. Afterwards there is again decreasing trend and becomes minimum (3-6 g/kg) during November and December months. In the free troposphere water vapor concentrations are very less during winter and spring months. While relatively very high concentrations are observed in the lower and middle troposphere during the summer season. During this period only (summer monsoon circulation) substantial rainfall is observed at Delhi.

Distribution of tropospheric  $O_3$  exhibits pronounced seasonal variation, which reflects the influence of both photochemistry and S/T exchange (peaking in spring) [*Thouret et al.*, 1998]. The influence of stratospheric contribution combined with the photochemical cycle can explain why the rise in  $O_3$  concentrations starts in spring. *Carmichael et al.* [1998] showed with model results that near-surface  $O_3$  in the springtime over East Asia is



**Figure 5.12:** Contour plots representing the annual variations (monthly mean data) of ozone, water vapor and temperature over Madras during 1996.

strongly influenced by continental outflow of precursors and strong downward transport of ozone-rich air from the stratosphere. The occurrences of high  $O_3$  tongues in the upper troposphere follow the propagation of dry air with low relative humidity, suggesting that  $O_3$  is of stratospheric origin rather than anthropogenic resulting from photochemical production from its precursors. The exchange of stratospheric  $O_3$  in the upper and middle troposphere was linked to the stratospheric folding associated with subtropical East Asia jet. The summer minimum in  $O_3$  over Delhi is a result of influence of the monsoon circulation carrying ozone-poor air masses from the Arabian Sea and Indian Ocean over the continent during this period. The convective processes can also lift ozone-poor air from the planetary boundary layer to upper heights.

#### 5.6.2 Variability over Delhi during 1998

Figures 5.13(a) and 5.13(b) depict the seasonal variations in  $O_3$  and water vapor concentrations, respectively over Delhi for 1998. Some broad features observed in the seasonal distributions of  $O_3$  for 1998 are similar to that of 1996. For instance  $O_3$  value shows maximum in the upper troposphere during the spring and minimum near the surface during the summer monsoon season. Ozone values are 40-60 ppbv within the boundary layer and middle troposphere (from surface to 1 km altitude) during February, March and April months of 1998 year. But these values are higher for the same period during 1996. Water vapor concentrations seem to be higher during February, March and April months of 1998 compared to 1996.

# 5.7 Average seasonal variations of O<sub>3</sub>, relative humidity and temperature over Madras during 1996-2001

To study the seasonal distribution of  $O_3$  along with some meteorological parameters over Madras, we have used MOZAIC data from 1996 to 2001 period. All these data sets are categorized in four groups as JFM (January, February and March), AMJ (April, May and June), JAS (July, August and September) and OND (October, November and December) months. Mean vertical profiles of  $O_3$ , relative humidity and temperature are shown in Figures 5.14(a), 5.14(b) and 5.14(c), respectively. During JFM months  $O_3$  value increases rapidly with height within the boundary layer, it varies from 15 ppbv at surface to above 40 ppbv at 1 km altitude. In the free troposphere  $O_3$  does not show any significant trend and it varies between 40- 50 ppbv up to 10 km altitude. Similar to JFM months  $O_3$  also increases rapidly at lower heights in AMJ (spring season) months, but unlike JFM months the increasing trend continues in middle troposphere also, until a maximum value of 60 ppbv at 6 km of altitude. For data points between 1 to 6 km the linear fit correlation value is  $r^2=0.89$  while the gradient in  $O_3$  is about 3.5 ppbv/km. After this peak it shows slightly



**Figure 5.13:** *Contour plots representing the annual variations (monthly mean data) of ozone, water vapor and temperature over Madras during 1998.* 

decreasing tendency, at 10 km height  $O_3$  value is about 48 ppbv. In summer season (JAS)  $O_3$  is steady near the surface, in boundary layer it is around 15 ppbv. Between 2 to 7 km an excellent linear fit correlation value of  $r^2$ =0.98 gives a gradient of 4 ppbv/km in  $O_3$ . The increasing trend disappears after 7 km altitude and almost constant value of 32 ppbv is observed up to 10 km level. The variation during OND months is similar to that observed during JAS except that it continues to increase in the upper troposphere and its level is higher by about 5 ppbv. Ozone shows a gradient of 4 ppbv/km



**Figure 5.14:** *Mean vertical profiles (1996-2001, MOZAIC data) of (a) ozone, (b) relative humidity and (c) temperature grouped in different months of the year over Madras.* 

for linear fit correlation (coefficient  $r^2$ = 0.92) between 1 to 7 km data. Average O<sub>3</sub> values throughout the height are in ascending order for JAS, OND, JFM and AMJ months of measurements.

Vertical distribution pattern of relative humidity profiles show just opposite trends of what has been seen in  $O_3$  for the respective seasons or periods over Madras. Relative humidity shows large fluctuations with height in each season as compared to that in  $O_3$ . For all the seasons, the humidity is above 70% near the surface. In winter JFM months the relative humidity in the free troposphere is much less than the other seasons. Temperature profiles do not show much seasonal variation, particularly in the middle troposphere. There is slight seasonal variation within the boundary layer (up to 2-3 km). Due to surrounding marine region of the Bay of Bengal seasonal changes are hampered as we have discussed that high water vapor concentrations are observed over the Madras in the troposphere.

The mid-tropospheric maxima in the  $O_3$  profiles over Madras are result of convective activity. The lifetime of  $O_3$  is short in the MBL. Convection vents ozone-poor air from MBL to upper troposphere [*Lelieveld and Crutzen*, 1994]. This ozone- poor air at upper levels is only slowly mixed back to lower troposphere levels by subsidence in the cloud-free part of the troposphere. At mid-tropospheric levels the convective detrainment is often small. This ozone-poor air can develop in upper troposphere and in the MBL while the middle troposphere remains relatively unaffected. This resulted as increased  $O_3$  values in the middle troposphere.

# 5.8 Average seasonal variations of O<sub>3</sub>, relative humidity and temperature over Delhi during 1996-2001

Mean vertical profiles of  $O_3$ , relative humidity and temperature grouped in different months are shown in Figures 5.15(a), 5.15(b) and 5.15(c), respectively over Delhi. In JFM months  $O_3$  increases with height within the boundary layer over Delhi. It can be seen that in the free troposphere  $O_3$  variability is very less and values are around 50 ppbv without any significant gradient. While during spring months (AMJ) the boundary layer  $O_3$  values vary between 50 to 60 ppbv. Ozone increases linearly with a rate of 4 ppbv/km between 2 to 7 km of altitudes. Ozone increases very slowly between 7 to 10 km and attains the highest values of 70-75 ppbv during AMJ period of measurements. In the summer (JAS) months the boundary layer  $O_3$  value increases rapidly from less than 10



**Figure 5.15:** *Mean vertical profiles (1996-2001, MOZAIC data) of (a) ozone, (b) relative humidity and (c) temperature grouped in different months of the year over Delhi.* 

ppbv near surface to 25-30 ppbv. In the middle troposphere  $O_3$  shows linear increasing trend similar to what has been seen over Madras. Linear fit shows higher increase rate (6.5 ppbv/km) in  $O_3$  over Delhi than Madras for 1 to 7 km of altitudes. After a peak value of 65 ppbv  $O_3$  value declines in the higher heights. Overall the patterns of  $O_3$  variability are similar over Madras and Delhi for JAS period. Ozone vertical profile during OND months shows a distinct pattern, just above above 1 km height it decreases up to 3 km and then it increases slowly in the mid and upper tropospheric regions. In the free troposphere  $O_3$  varies between 45 to 50 ppbv.

Vertical distribution trends in  $O_3$  (increasing) and relative humidity (decreasing) are important only up to altitude of 7 km only. Seasonal variations in temperature profiles do not show much variation in gradient but the background values are different for different seasons over Delhi. Background temperature values are maximum in summer while minimum during winter season, the difference is more than 10 C for any given height. Except during the summer monsoon period (JAS months) water vapor content is relatively less throughout the year over Delhi and this could play very important role in the observed seasonal variation in temperature over Delhi.

## 5.9 Case study analysis using individual profiles

At any particular location there can be large day-to-day variability in the vertical structure of  $O_3$ . Not only do the altitudes and magnitudes of maxima and minima change but the vertical structure appears very irregular, sometimes exhibiting marked stratification, with a single or multiple peaks, and other times exhibiting a uniform profile and absence of structure, indicative of well mixed atmosphere.

Each O<sub>3</sub> profile is a unique response to photochemical and dynamic process operating. Hence a study of its profiles in terms of its structure, particularly the magnitude and altitudes of maxima and minima, depth and the vertical gradient of O<sub>3</sub> should reveal insights into these processes. Traditionally, mean profiles averaged by season or year together with some measure of variability about these means, have been analyzed. Examples of such studies that have focused on constructing O<sub>3</sub> climatology for particular locations include *Kirchhoffs et al.* [1991], *Diab et al.* [1996], *Fortuin and Kelder* [1998], *Thouret et al.* [1998], *Logan* [1999] and *Thompson et al.* [2003]. On the other hand, case study analysis has been widely used to gain an understanding of processes operating. Examples in which the focus has been on dynamic processes particularly stratospheric-
tropospheric exchange (STE) include, *Merrill et al.* [1996], *Cooper et al.* [1998], *Folkins et al.* [1999], *Randriambelo et al.* [1999], *Zachariasse et al.* [2000], *Scott and Cammas* [2002] and *Kim et al.* [2002]. Others in which strong photochemical forcing was present, include *Fujiwara et al.* [1999] and *Longo et al.* [1999]. The drawback of case study analysis is that, whilst an understanding of process is gained, there is little contribution to our knowledge of the frequency of occurrence of such events or their relative importance in the overall  $O_3$  budget.

We first describe the observed features in  $O_3$  and relative humidity in the troposphere and then use trajectory analysis (HYSPLIT model) to reveal the transport features associated with air masses. Back trajectories represent the large-scale circulation and may be used to suggest potential source regions, though origin of a specific air parcel can not be determined exactly.

# 5.9.1 Profiles over Madras

## (a) July 25, 1997

Vertical profiles of O<sub>3</sub>, relative humidity and temperature on 25 July 1997 have been shown in Figure 5.16(a). This  $O_3$  profile is representative of the wet season. In the lower troposphere vertical profile of O<sub>3</sub> shows constant values of around 15 ppbv, enhanced relative humidity values of 80-90% near surface increases with altitude and it is more than 110% at 6 km altitude. Very high relative humidity in the middle troposphere could be due to the presence of thick cloud layers, suggesting deep convection over the region. Between 6 and 7 km of altitudes O<sub>3</sub> value increases from 20 to 30 ppbv and is constant in the upper troposphere, while relative humidity profile shows decreasing trend in the upper troposphere. The minimum O<sub>3</sub> concentrations in middle and upper troposphere were about 15-20 ppby. Such low levels of  $O_3$  are prevalent in the free troposphere over the maritime continent [Fujiwara et al., 2000]. Back trajectory analyses at three altitudes of 2, 4 and 8 km have been shown in Figure 5.17(a). All the trajectories arriving over Madras have originated within the marine boundary layer (MBL) over southern Indian Ocean. Trajectories were confined within the marine boundary layer and deep convection lifted the air masses just hours before the measurements (see lower panel of Figure 5.17(a)). Due to deep convection entire troposphere is well mixed which reflected in observed minimum and maximum values in O<sub>3</sub> and relative humidity respectively over Madras. Lifting of ozone-poor MBL air, with additional O<sub>3</sub> depletion that may occur in

clouds, may have caused these minima [*Kley et al.*, 1996]. Similar minima have been found over the Indian Ocean due to lifting of ozone-poor MBL air by convective cells of the Inter Tropical Convergence Zone (ITCZ) [*De Laat et al.*, 1999; *Taupin et al.*, 1999].

# (b) October 17, 1997

Vertical profiles of  $O_3$ , relative humidity and temperature observed over Madras on 17 October 1997 have been shown in Figure 5.16(b). Ozone profile shows large range of



**Figure 5.16:** Vertical profiles of ozone (dark, solid lines), relative humidity (dashed lines) and temperature (gray solid lines) on four selected dates of measurements over Madras.

variation in the troposphere over Madras. Ozone value at the surface is around 10 ppbv and shows linear increasing trend in the lower troposphere (up to 5.5 km altitude) while very high relative humidity is constant at 90% level with some small scale fluctuation. There is sharp increase in  $O_3$  when the values of around 45 ppbv at 5.5 km altitude becomes 80 ppbv at 7 km altitude while between this altitudes relative humidity decreases from 90 to 30%. Peak  $O_3$  value of 82 ppbv is observed between 7 to 8.5 km altitude where relative humidity is minimum (10%). Figure 5.17(b) shows back trajectory plots at altitudes 2.5, 5 and 9 km over Madras for 17 October 1997. Back trajectory arriving at 2.5 km altitude originated over the SE Asia region containing Thailand, Laos, Combodia and Vietnam. In October month, biomass burning is not so intense, transport of anthropogenic emitted O<sub>3</sub> precursors in the lower troposphere could have caused the increasing trend in O<sub>3</sub> over Madras. While back trajectories calculated at 5 and 9 km altitudes reveal their origin in the lower troposphere of the Indonesian region. It has been reported that during October-December, 1997 there was extensive forest fire over Indonesia. This could have transported O<sub>3</sub> and its precursors over Madras. We have not noticed such enhancements in O<sub>3</sub> distributions during October and November month of 1998 over Madras. Chan et al. [2003] reported substantial O<sub>3</sub> enhancement over many parts of tropical SE Asia and the subtropical south China region including Hong Kong in mid autumn and early winter (October-December) of 1997, when many forest fires occurred in the Indonesian region. In this case, O<sub>3</sub> enhancements were caused by the large scale-scale outflows of O<sub>3</sub> and other pollutants from the Indonesian region and were related to abnormal meteorological conditions that associated with the strong El Nino phenomenon.

# (c) January 02, 2001

Vertical profiles of  $O_3$  mixing ratio, temperature and relative humidity on Jan.02, 2001 over Madras are shown in Figure 5.16(c). In the lower troposphere (from surface up to 5 km)  $O_3$  is almost constant and fluctuates between 20-30 ppbv while corresponding humidity profile shows decreasing trend and varied between 40-90%. The small-scale fluctuations in  $O_3$  and relative humidity are perfectly anti-correlated. In the middle troposphere at 5 km altitude  $O_3$  suddenly increased (from 25 to above 65 ppbv) and this ozone-rich layer persisted up to 7.5 km altitude where it again sharply decreased to 25 ppbv level. Relative humidity values associated with this high  $O_3$  layer are below 10%. In the upper troposphere  $O_3$  decreases with height while RH starts increasing, at 10 km level



**Figure 5.17:** Seven-day back trajectory plots and their back day information indicating the source and history of air masses at different altitudes for four selected dates of measurements over Madras.

 $O_3$  is below 20 ppbv while relative humidity value is about 60%. Back trajectory analyses were calculated at the three altitudes of 3, 6 and 9 km (Figure 5.17(c)). For 3 and

9 km of altitudes trajectories were originated in the free troposphere over the surrounding marine regions and show little subsidence over Madras. Paths of these trajectories do not show any influence of continental air mass before they arrived over Madras. Transport of air masses from the marine free troposphere could have brought low  $O_3$  and high relative humidity in the lower and upper troposphere. While trajectory arriving at 6 km altitude show continental influence as it originated in the free troposphere of western portion of Africa and subsided over Madras region. The combination of high  $O_3$  and low relative humidity might be due to convectively lifted CBL (Continental Boundary Layer) air that has subsided [*Zachariasse et al.*, 2000].

### (d) April 26, 2001

Vertical profiles of ozone, relative humidity and temperature obseved over Madras on 26 April 2001 have been shown in Figure 5.16(d). Vertical distributions of O<sub>3</sub> and relative humidity show steps like structures. Due to strong temperature inversion ozone-rich air parcel does not enter into the boundary layer, surface O<sub>3</sub> value is below 10 ppbv while relative humidity values vary from 40 to 80% within the boundary layer. Just above the boundary layer O<sub>3</sub> values increased drastically and remained elevated (50-75 ppbv) up to 3.5 km altitude reverse to this relative humidity values decreased down to 10% and remained low up to 3.5 km altitude. Ozone again decreases to 20 ppbv level accompanied by simultaneous increase in relative humidity (10 to 70%) in the middle troposphere between 3.5 to 4.5 km of altitudes. Just like above boundary layer, between 5 to 7 km altitudes O<sub>3</sub> again shoots up to elevated values of 60-70 ppbv while relative humidity value becomes extremely low (below 5%). While in the upper troposphere there is a decrease in O<sub>3</sub>, a layer of moderate O<sub>3</sub> values of about 35 ppbv and 15% relative humidity was observed between 7 and 9 km of altitudes. Finally, O<sub>3</sub> comes down to a free tropospheric background value of about 20 ppbv with relative humidty exceeding 40% level between 9 and 11 km of altitudes. Though we have analyzed back trajectories at various altitudes, Figure 5.17(d) shows the trajectory plots only at 3.0, 4.5 and 8 km altitudes. For O<sub>3</sub> maximum near 3 km altitude back trajectory analysis shows the origin of air mass over the eastern continental boundary over Africa and passed through Arab countries and northwest India. Continental areas over central Africa are shown to be responsible for the low to mid-tropopsheric enhancement in spring [Diab et al., 2003]. In spring season apart from biomass burning other anthropogenic pollutants are transported over the Indian Ocean via continental India. During minima in O3 values near 4.5 km trajectory originated in the upper troposphere over the Atlantic Ocean, this would have caused the occurrence of low  $O_3$  and high relative humidity values while before subsiding over Madras it also passed over the Bay of Bengal. For moderate  $O_3$  value of 35 ppbv near 8 km trajectory analysis shows the origin of the air mass in the lower troposphere over the Indian Ocean very close to the continental India. This would have diluted the high  $O_3$  layer (5 to 7 km altitudes), lying just beneath this layer. Trajectories arriving in the upper troposphere at 9 km and higher altitudes originated over the Southeast Indian Ocean and could have transported the ozone poor and wet air masses over the Madras. This transport could be due to the presence of easterly jet and is characterized by ozonepoor and wet layer between 9-14 km over the tropics [*Fujiwara et al.*, 2003].

# 5.9.2 Profiles over Delhi

## (a) May 28, 1999

Vertical profiles of O<sub>3</sub>, relative humidity and temperature observed on 28 May 1999 over Delhi are shown in Figure 5.18(a). Lower troposphere (below 5 km ) seems to be well mixed as O<sub>3</sub> values remained constant at 70 ppbv after sharp increase in the boundary layer value of 30 ppby. While constantly low relative humidity values of around 15% are observed over this region. At 5 km altitude O<sub>3</sub> values jumps from 70 ppbv to around 130 ppbv accompanied by decrease in RH value to 5%. Above this altitude relative humidity remains extremely low and is constant up to 10 km altitude. We can see a layer of O<sub>3</sub> between 5 and 7.5 km altitudes with a peak value of 145 ppbv at 7 km altitude. After this enhanced layer O3 value is around 80 ppbv and decreases slowly in the upper troposphere. The profile looks like a superimposition of enhanced  $O_3$  layer with the background value of 70 ppbv in the free troposphere. This enhanced  $O_3$  layer in  $O_3$  is isolated by very strong inversion in temperature and gradient is almost disappeared for altitude range corresponding to layer in O<sub>3</sub>. This layer can be attributed to stratospheric in origin without any ambiguity. To investigate the regions of this ozone-rich layer we have calculated back trajectory analyses at 5, 6 and 9 km of altitudes and they are shown in Figure 5.19(a). Trajectories arriving at below and above the ozone-rich layer altitudes (5 and 9 km) were originated in the free troposphere of continental regions of North Africa and passed through Middle East countries before descended over Delhi. These would have transported the O<sub>3</sub> and its precursor gases, emitted from biomass burning and other anthropogenic activities. While trajectories at 6 km altitude originated over northeast flange of America at 12 km altitude which is in fact a lower stratospheric region at 45N latitude. Study of some profiles shows influences of stratospheric originated air mass in the upper troposphere over Delhi in the spring season. Exchange of  $O_3$  from the stratosphere can occur due to the filamentation around the subtropical jet (STJ) [*Appenzeller et al.*, 1997]. Shear-induced differential advection can cause tracer surface to stretch which leads to quasi-horizontal laminae-like tracer structure [*Appenzeller et al.*,



**Figure 5.18:** Vertical profiles of ozone (dark, solid lines), relative humidity (dashed lines) and temperature (gray solid lines) on four selected dates of measurements over Delhi.

1997]. The presence of layers with ozone and water vapor mixing ratios significantly different from the background atmosphere introduces changes in the radiative cooling and heating rates, which are strongly dependent on these gases [*Stoller et al.*, 1999]. We observed heating in the layer region, as temperature is constant at -10 C instead of decreasing with altitude and hence heating at the top of the layer. This heating stops the vertical mixing and isolates the layer.

# (b) March 14, 2000

Vertical profiles of O<sub>3</sub>, relative humidity and temperature observed on 14 March 2000 over Delhi are shown in Figure 5.18(b). Ozone increases rapidly in the boundary layer and its value is 60 ppbv at 1 km altitude while relative humidity decreases from around 55% to 10% within the 2 km from the ground. Study of a set of profile reveal that 50-60 ppbv O<sub>3</sub> levels constitute background over Delhi during March month. In the middle troposphere many sharp peaks in O<sub>3</sub> are embedded over the background level. While in the upper troposphere occurrence of sharp peaks have disappeared and O<sub>3</sub> shows constant value of 50-55 ppbv with slightly elevated relative humidity level compared to dry middle troposphere. Sharp peaks in  $O_3$  are observed for 2,4, 5 and 7 km of altitudes but among these O<sub>3</sub> value is maximum for 5 km peak with 115 ppbv. Back trajectory analysis plots for 3, 5.5 and 9 km altitudes are shown in Figure 5.19(b). Trajectories arriving at the lower mid-tropospheric altitudes over Delhi have all originated over continental regions of North America and passed though Europe and Middle East countries. Back trajectory for  $O_3$  peak at 5.5 km altitude has originated in the free troposphere while source regions of trajectories arriving below this altitude are in the lower troposphere over the midlatitude. Thus transport of ozone-rich dry air masses from higher mid latitudinal continental zones could have resulted in the various peaks and O<sub>3</sub> and completely dry air mass over Delhi. While air masses originated over tropical regions and by passing through tropical Atlantic Ocean and Africa influenced the upper troposphere as we observed moderate O<sub>3</sub> values with about 20% RH values.

# (c) November 29, 2000

Vertical profiles of  $O_3$ , relative humidity and temperature observed on 29 November 2000 over Delhi are shown in Figure 5.18(c). This is a distinct example in the sense that  $O_3$  does not show any relation with humidity however we have seen very strong anticorrelation between these two gases over Madras and Delhi. Ozone values vary from 20 to 30 ppbv while elevated RH values of 70-90% are observed in the boundary layer. Temperature profile shows an inversion at 2 km altitude due to this relative humidity decreases drastically from above 85% to below 20% while  $O_3$  does not show sharp



**Figure 5.19:** Seven-day back trajectory plots and their back day information indicating the source and history of air masses at different altitudes for four selected dates of measurements over Delhi.

change just over the boundary layer. Vertical distribution of  $O_3$  does not show any trend and vary between 30 to 40 ppbv while relative humidity shows large variability of 15-90% in the middle and upper troposphere. In the lower troposphere an RH layer of 20% is accompanied by 40 ppbv  $O_3$  between 2 and 4 km of altitudes. While in the middle troposphere another layer of 90% RH value is accompanied by 35 ppbv  $O_3$  value between 6 and 8 km of altitudes. Without any change in  $O_3$ , relative humidity profile shows increasing trend in the upper troposphere. Back trajectory plots for 3, 6 and 9 km altitudes are shown in Figure 5.19(c). Air masses originated over southern portion of Europe and traveled across Middle East and this could have resulted in dry layer at 3 km altitude however  $O_3$  is relatively low. Trajectory arriving in the middle troposphere at 6 km (layer with very high RH values) originated in the free troposphere of tropical Atlantic Ocean and passed over the central Africa.

# (d) October 03, 2001

Vertical profiles of O<sub>3</sub>, relative humidity and temperature observed on 3 October 2001 over Delhi are shown in Figure 5.18(d). Ozone values are very low in the lower troposphere as it varies between 10-20 ppbv up to 4 km altitude except a sharp peak at 3 km altitude. While enhanced values of relative humidity are observed in the lower troposphere as it varies within 70-100%, a minimum in O<sub>3</sub> value is accompanied by 100% relative humidity value just below 4 km altitude. There are sharp and simultaneous changes in O<sub>3</sub> and relative humidity just below 5 km altitude. As can be observed from the  $O_3$  and relative humidity profiles that  $O_3$  increases from 10 to 80 ppbv while relative humidity decreases from 75% to 5% between 4 and 5 km. Transition region (4 to 5 km) in  $O_3$  and relative humidity is also marked by a strong inversion in temperature and this could have acted as barrier for the vertical mixing of lower tropospheric air masses with middle or upper troposphere. Middle troposphere is influenced by extremely dry and ozone-rich air mass, O<sub>3</sub> value is around 80 ppbv with less than 5% relative humidity between altitudes of 5 and 7.5 km. Ozone and relative humidity profiles reveal increasing and decreasing trends, respectively in the upper troposphere however decrease in O<sub>3</sub> occurs earlier than relative humidity. Figure 5.19(d) shows back trajectories plots at 2, 6 and 9 km of altitudes for this particular measurement over Delhi. In the lower troposphere, 10-day (only 7-day trajectories are shown) back trajectory originated over the southern Indian Ocean and was confined within the boundary layer. This must had transported the clean humid marine air with low O<sub>3</sub> in the lower troposphere over Delhi.

While trajectory analysis at 6 km altitude reveals the source of air mass in the upper troposphere of continental Africa and traversed through the Middle East. Through this channel only ozone-rich and dry masses from upper troposphere would have got transported over Delhi. Trajectory arriving in the upper troposphere at 9 km altitude had originated over the Bay of Bengal and passed through the Arabian Peninsula during last the 10 days. Transport of tropical upper marine air mass via this route resulted in observed trends of  $O_3$  and relative humidity. Since path of trajectory never come down below 8 km altitude, changes in  $O_3$  and relative humidity were gradual in the upper troposphere over Delhi. Such profiles in  $O_3$  and relative humidity can be attributed to the advection processes without any convection. Strong inversion in temperature in the mid-troposphere also supports the convection free dynamical process in distribution of  $O_3$  and water vapor over Delhi.

# Summary and Future Scopes

# 6.1 Trace gases at Ahmedabad and Mt. Abu

There is lack of study related to the tropospheric chemistry in the tropical region. Over the Indian region, only limited measurements of  $O_3$  and some of its precursors (mostly CO, CH<sub>4</sub> and NO<sub>x</sub>) have been reported earlier. However, till recent years there have been no systematic simultaneous measurements of surface  $O_3$  and its important precursors like NMHCs over this region. Realizing the importance in the photochemical production of  $O_3$ and large local emissions, measurements of NMHCs along with  $O_3$ , CO and CH<sub>4</sub> at Ahmedabad and Mt. Abu have been made during 2002

Ahmedabad (23°N, 72.6°E) is an urbanized city having numerous industries and a thermal power plant. In the winter months due to the prevailing NE wind flow, mostly the Asian continental emitted pollutants are transported over the study region. On the other hand, due to the SW wind flow relatively cleaner marine air masses are transported in the summer months. Air samples collected during all the months of year 2002 at a remote mountain top Guru Shikhar, Mt. Abu (24.6°N, 72.7°E, 1680 m asl) were analyzed for C<sub>2</sub>-C<sub>4</sub> NMHCs. The general wind pattern at Mt. Abu is similar to that of at Ahmedabad as these stations are only 200 km far from each other.

Large diurnal variability in  $C_2$ - $C_5$  NMHCs were observed during all the months of year 2002 at Ahmedabad. The diurnal variations are more pronounced in the winter months compared to the summer months. The pattern of diurnal variability in  $C_2$ - $C_5$  NMHCs differed from species to species. However, throughout the year, NMHCs show higher values in the evening and night hours and lower values in the afternoon. Relatively short lived species like ethene and propene, which are emitted from vehicular exhaust, show higher values in the morning traffic hours also. We have also discussed the diurnal variations in  $O_3$ , CO and CH<sub>4</sub> and these are compared with diurnal patterns of NMHCs.

Similar to NMHCs, the amplitudes of diurnal variation n  $O_3$  are higher in the winter months while lower in the summer months. In general diurnal distributions of NMHCs do not show any significant variability at Mt. Abu. Sharp peaks in some species during afternoon and evening hours are observed in the winter season only.

Apart from large diurnal variability, the annual distributions of these species also show substantial seasonal variations. Similar to other reported measurements of NMHCs the winter season high and the summer season low values are observed at Ahmedabad. Annual distribution of O<sub>3</sub> shows very clear and systematic seasonal variation. Higher O<sub>3</sub> values have been observed in the autumn/winter months while lower values are observed in the summer months. The maximum monthly mean value of 43 ppbv and minimum of 13 ppbv were observed during February and June months, respectively. To compare the monthly mean NMHCs data at Ahmedabad with the measurements made at other urban sites, we have also studied the reported C<sub>2</sub>-C<sub>5</sub> NMHCs data for Osaka (Japan). It is observed that amplitude of seasonal variations (maximum to minimum ratio) is higher at Ahmedabad compared to at Osaka. Particularly, the differences are more during the summer month, yet the phases of seasonal variations are quite similar at both sites. Like seasonal variations observed at Ahmedabad almost all the NMHC species studied at Mt. Abu also show the winter season maxima and minima in the summer season. Markedly different seasonal patterns are evident for compounds with predominantly anthropogenic sources (ethane, propane, acetylene etc.) compared to other species with strong summertime biogenic sources (e.g. ethene and propene). The strength of variability in relatively long lived species like ethane, propane and acetylene are higher compared to the highly reactive species like ethene and propene at Mt. Abu. We have compared this NMHCs data with reported data from the other remote sites. Comparisons show annual mean values in all species are lowest at Mt. Abu therefore this site offers a clean background environment in the tropical Asia. In the tropical regions, the efficient convection process dilutes the boundary layer pollutants by lifting up the air masses. Finally, fast photochemical processing, vertical mixing due to convection and less local emissions of pollutants resulted in observed low levels of light NMHCs at Mt. Abu. Study of seasonal variations and comparisons with respective similar sites of measurements hint the significant role of general wind circulation apart from the seasonality in OH radicals at Ahmedabad and Mt. Abu. In the winter season the NE wind flow transports the polluted air mass while in the summer season the SW wind flow bring the clean air masses over the sites.

The interspecies correlations in some NMHC species are studied for the identification of dominant sources. Very good correlation values of  $r^2 = 0.90$ , 0.84 and 0.94 in ethane vs. propane, ethane vs. i-butane and propane vs. i-butane, respectively indicate their common sources, most likely from natural gas leakage/emission at and around Ahmedabad. Another good correlation value of  $r^2 = 0.87$  between ethene and propene could be due to the dominant contribution from automobile exhaust for these species. Among the nine NMHCs measured, the correlation values of CO with ethene, propene and acetylene are  $r^2 = 0.83$ , 0.78 and 0.69, respectively. The good correlation of these NMHCs species with CO again confirms their common sources of emissions. Carbon monoxide is mostly emitted from the incomplete combustion of fossil fuel. The chemical tracer C<sub>2</sub>H<sub>2</sub>/CO ratio, which is a photochemical indicator, is estimated to be around 6.36 pptv/ppbv. This high value of photochemical tracer also suggests the major influence of fresh emissions in the distributions of  $O_3$  precursors at Ahmedabad. Relatively good correlation between ethane and propane observed at Mt. Abu indicates the role of transport from common or collocated source regions. Similarly, the good correlation observed between ethene and propene could be due to fossil fuel combustion and oceanic emissions. A moderate correlation value ( $r^2 = 0.58$ ) between ethene and acetylene indicates major role of combustion related sources of these compounds as oceanic emission does not contain acetylene. Still this correlation is not strong enough to completely ignore the role of biogenic sources like marine emissions.

The annual mean values of  $C_2$ - $C_4$  NMHCs species at Ahmedabad are higher by factors of 3-9 with the mean values measured at Mt. Abu. The large local emissions play very important role in the distributions of various NMHCs at Ahmedabad. Transport of pollutants from various source regions is the key atmospheric process in determining the observed distributions of NMHCs at Mt. Abu. Among all the NMHCs species measured propane dominates at Ahmedabad while it is ethane at Mt. Abu.

# 6.2 Trace gases over the Bay of Bengal

The Bay of Bengal Process Studies (BOBPS) cruise campaign was conducted during 12 September-14 October 2002 while the BOBEX II cruise campaign was conducted during 19-28 February 2003 over the Bay of Bengal. During both the cruise campaigns measurements of  $O_3$  along with meteorological parameters were performed continuously along the cruise track. Air samples collected during these campaigns were analysed for

CO, CH<sub>4</sub> and NMHCs. The main purpose of the BOBPS campaign was to study the distributions and quantification of  $O_3$  and related trace species in wet season (summer monsoon) over this region. In September and October 2002 period winds from south and southwest directions prevailed and these wind patterns brought pristine marine air mass and also the continental emissions over different locations of the Bay of Bengal. However, the BOBEX II campaign was to study the distributions and quantification of  $O_3$  and related trace species in the winter season. Due to persistent northeast (NE) wind flow, large amounts of pollutants get transported from the Asian countries over the Bay of Bengal.

The minimum levels observed in these species were traced to the sampling of pristine marine air masses from the southern Indian Ocean. Elevated levels of O<sub>3</sub> and other pollutants were observed even during the September-October period whenever the continental influenced air parcels from India or Sri Lanka were sampled. In general, higher average values of O<sub>3</sub> and other trace species are observed over the northern region (>10°N) compared to the southern region (<10°N) of the Bay of Bengal. We have used  $C_2H_2/CO$  ratio as a tracer of the age (indicator of photochemical processing) of various air masses. Fast transport of freshly emitted pollutants (high wind velocity of 10-15 m/s and high  $C_2H_2/CO$  ratio value = 2.11 pptv/ppbv) from the Indian sub-continent (Chennai region) were observed over the open marine region at 14°N and 88°E. Similarly, measurements along the open ocean track at 88°E showed higher values of many trace species compared to the measurements along the east coast of India. Ozone, CO, CH<sub>4</sub> and some long lived NMHCs showed decrease in their mixing ratios from north to south. The average latitudinal gradient in CO (2.7 ppbv deg<sup>-1</sup>) is similar while gradient in CH<sub>4</sub> (9.4 ppbv deg<sup>-1</sup>) is much higher compared to the gradients observed for these compounds in earlier campaigns (INDOEX 1998 and 1999) over the Indian Ocean and Arabian Sea. In the present study latitudinal gradient in ozone is 0.77 ppby deg<sup>-1</sup> over the Bay of Bengal while for similar latitudinal range (5-20°N), during the INDOEX 1998 and 1999 campaigns the observed gradients were 2.7 and 1.7 ppbv deg<sup>-1</sup> respectively over the Arabian Sea [Chand et al., 2001; Muhle et al., 2002].

To study the transport and for chemical characterization of various air masses the wind field streamlines, 7-days back trajectories and a tracer  $C_2H_2/CO$  ratio are found to be very useful. Combined study of 5-minutes averaged data of  $O_3$  and a meteorological quantity EPT (Equivalent Potential Temperature) reveal the convective downdrafts of free tropospheric air masses at some locations along the cruise track. Ethane and acetylene

show good correlations with  $CH_4$  and CO respectively, which could be due to their common sources over the continent. On the other hand methane and CO show poor correlation suggesting different sources of emissions over the continent.

Based on the back trajectories and measurements of chemical composition of air parcels various source regions are grouped as: AsiaCT (Asian continental tropical), AsiaCX (Asian continental extra-tropical) and AsiaMT (Asian marine tropical). The chemical tracer ratio C<sub>2</sub>H<sub>2</sub>/CO is also incorporated, as earlier, to probe the sampled air masses. Ozone and its precursor gases show lowest values in the AsiaMT type parcel. In such cases the air parcels spent relatively longer travel time within the marine boundary layer (MBL). The mean mixing ratios of O<sub>3</sub>, CO and ethane were 26 ppbv, 203 ppbv and 718 pptv, respectively have been observed in the AsiaMT parcels. The lowest mean C<sub>2</sub>H<sub>2</sub>/CO ratio value of 1.3 pptv/ppbv justifies the decreased mixing ratios of various trace gases in this air mass. The observed ratio of 2.4 pptv/pptv in ethene and propene in AsiaMT type of parcel stands in agreement with values of around 2.5 pptv/pptv determined from marine fluxes. Air parcels originated from the mid-latitude continental of the Northern Hemisphere (mainly from Arabian Peninsula, Middle East and Europe) advected to sampling sites over the Bay of Bengal are recognized as AsiaCX type. In the AsiaCX type parcel the highest levels of almost all the trace species were observed. The mean mixing ratios of 38 ppbv, 237 ppbv and 1539 pptv were observed in O<sub>3</sub>, CO and ethane values, respectively. The highest mean C<sub>2</sub>H<sub>2</sub>/CO tracer ratio value of 3.3 pptv/ppbv also suggests the rapid transport of freshly emitted or less photochemically processed pollutants. In the moderately aged air masses of AsiaCT type, the mean mixing ratios in O<sub>3</sub>, CO and ethane were 32 ppbv, 200 ppbv and 1130 pptv, respectively over the Bay of Bengal.

The large variability in almost all trace gases were observed during both the seasons of measurements over this region. The mean values in  $O_3$ , CO and some long lived NMHCs are higher in the winter season compared to the wet season. In the wet season (SW wind flow) the mean mixing ratios in  $O_3$ , CO and ethane were 27 ppbv, 143 ppbv and 561 pptv while during the winter season their values were 34 ppbv, 193 ppbv and 1180 pptv, respectively. The mean chemical tracer  $C_2H_2/CO$  was observed to be significantly higher during the winter season compared to its value in the summer season, this affirmed the transport of freshly emitted pollutants during the winter season over the Bay of Bengal. Comparison of  $O_3$ , CO and CH<sub>4</sub> measurements over the Bay of Bengal with other surrounding marine regions of Indian subcontinent (Arabian Sea and Indian



**Figure 6.1:** A comparison of mean values of  $O_3$ , CO and CH<sub>4</sub> observed over the Bay of Bengal with (a) the mean values measured over the Arabian Sea (AS) and the Indian Ocean (IO) and (b) mean values over Pacific Ocean (PO) and Atlantic Ocean (AO).

Ocean) under Asian outflow regime in the winter season (during BOBEX 2001, INDOEX 1998 and 1999) are shown in Figure 6.1(a). Similarly, comparison with the reported measurements over the Pacific Ocean [*Browell et al.*, 2001] and the Atlantic Ocean [*Parrish, et al.*, 1993] are presented in Figure 6.1(b). The Bay of Bengal region is most polluted compared to other marine regions.

# 6.3 Vertical distributions of O<sub>3</sub> and water vapor over Madras and Delhi

The tropical region is a large contributor to the global  $O_3$  budget, it plays key role in controlling the chemistry and climate of tropical troposphere. The detailed characteristics of  $O_3$  in the tropical troposphere are poorly known because of lack of comprehensive observations. We have observed the long-range transport of polluted air masses from

Middle East and European countries over the Bay of Bengal. It is also seen that the trajectories of these air masses pass through the free troposphere over the continental India. Therefore, such transports can also have impacts in the vertical distributions of various trace gases over this region. We have studied the vertical distributions of ozone and water vapor over Madras (12.99°N, 80.15°E) and Delhi (28.56°N, 77.11°E) using MOZAIC (Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft) data for 1996-2001 period. The main aim of this work is to study how transport processes affect the vertical distributions in the troposphere over the Indian subcontinent.

Monthly mean data were used to study the annual distributions of  $O_3$ , water vapor and temperature during 1996, 1997 and 1998 over Madras. Large seasonal variability is observed in  $O_3$  and water vapor. In the lower and mid-troposphere, high concentrations of  $O_3$  in the spring season could be due to the long-range transport of pollutants by northwesterly winds associated with the winter monsoon circulation. This circulation transports the ozone-rich polluted air masses from the Asian continent. Conversely, summer minima with mean concentration as low as 15 ppbv during July to November period are observed over Madras. This is related to summer monsoon circulation, advecting clean and moist air from the Indian Ocean.

Elevated  $O_3$  values of around 100-150 ppbv were observed in the middle and upper troposphere (6-10 km) during the spring season over Delhi. Ozone mixing ratios were around 40-60 ppbv in the lower and middle troposphere while in the upper troposphere values were around 60-80 ppbv during August, September and October months. Occurrences of high  $O_3$  tongues in the spring season follow the propagation of dry air with low relative humidity, suggesting that  $O_3$  is from higher heights, probably of stratospheric origin. The summertime low values over Delhi are attributed to summer monsoon circulation, advecting ozone-poor air mass from the Arabian Sea and the Indian Ocean over the continent during this periods. The convective processes lift the advected ozone-poor air masses from the planetary boundary layer (PBL) to the upper heights.

In general,  $O_3$  and water vapor show just opposite seasonal variations, though water vapor distribution is very much localized compared to  $O_3$ . Similar annual patterns in  $O_3$  and water vapor are repeated during different years except some small-scale differences.

Case study of vertical profiles over Madras and Delhi reveals significant day-today variability in the vertical structure of  $O_3$  and relative humidity. These studies also revealed influences of convection and advection of various air masses from within the troposphere. Prevalence of particular type of air mass in determining the distributions of  $O_3$  and relative humidity varied with seasons over both the stations. In some cases influence of stratospheric originated air masses in the spring season, especially over Delhi have been identified using back trajectory analyses. Impacts of Indonesian forest fires in the vertical distributions of  $O_3$  during 1997 were also detected over Madras.

Vertical distributions of ozone and water vapor show very irregular, sometimes exhibiting marked stratification, with a single or multiple peaks, and other times exhibiting a uniform profile and absence of structure, indicative of well mixed atmosphere.

In general, vertical distributions over Delhi show higher background  $O_3$  values than Madras in the troposphere, while reverse is true for water vapor. Dynamics play major role in the seasonal distribution over Madras and Delhi. In the lower and middle regions of the troposphere, low  $O_3$  values with high water vapor concentrations in the summer monsoon season are pronounced over Madras than Delhi. While in the upper region of the troposphere, high  $O_3$  values with very low amount of water vapor in the spring season are pronounced over Delhi than Madras. In the spring season, elevated  $O_3$ levels over both the stations reflect the influence of photochemical production from precursors. Back trajectory analysis suggests that this enhancement resulted from the transport. Air masses arriving at the altitudes of  $O_3$  peaks in the middle troposphere appear to have passed over the regions of biomass burning which occurs at this time of year (March and April months).

# 6.4 Future outlook

Due to fast industrial development and economic growth of the Asian region, the emissions of various pollutants have been projected to increase. Asia will be the most important sources of anthropogenic emissions to the global troposphere. Extensive research is needed to better understand the effects of NMHCs and other pollutants (CO, CH<sub>4</sub>, NOx etc.) emissions on environment and climate in the tropical region.

Asian outflow is influenced by intercontinental transport also. Anthropogenic pollution originating from Europe, Africa and Middle East has been found to significantly contribute to high altitude Asian outflow. Therefore, it is also important to study the vertical distributions of trace gases. NMHCs play important role in atmospheric chemistry. Vertical distributions of these gases are important to assess their impacts at

different heights in the Asian tropical troposphere. A balloon-borne cryogenic whole air sampler can be used to obtain vertical profiles of these gases.

Hydrocarbons also have several applications in the study of the composition of an air mass. They can be used to study the history of the photochemical, transport, and removal processes in an air mass. When air masses that contain fresh emissions undergo rapid transport, they can arrive at remote regions and still have great potential for photochemistry because the trace gases would not have been significantly altered during the fast transport. Ship-borne measurements of O<sub>3</sub>, CO and hydrocarbons in different seasons are needed to study over the other marine regions around India. So far measurements of trace gases are not carried out during summer (SW monsoon) period over the Arabian Sea. Transport processes have different pathways over the Arabian Sea compared to that over the Bay of Bengal during both the seasons. Emphasis should also be given to the measurements of some anthropogenic halocarbons along with O<sub>3</sub> and its precursor gases. Measurements of halocarbons along with NMHCs can be used to draw the information about the specific sources of emissions and their transport over the remote regions.

Apart from balloon-borne measurements of various trace gases aircraft's can be used for online measurements and air sample collection at various altitudes over India. Use of aircraft will be helpful in extensive spatial coverage of measurements.

Numerical models in combination with field measurements have proven to be useful tools in studying the complex interactions of chemical species and meteorology in the atmosphere. Development of photochemical air quality model that will be helpful to predict spatially and temporally resolved ambient pollutant concentrations like NMHCs. A network of stations for long term, simultaneous measurements of ozone and its precursor gases will be important to account the regional contributions in the model simulations.

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# List of Acronyms and Abbreviations

BOBEX	Bay of Bengal Experiment
BOBPS	Bay of Bengal Process Studies
CMDL	Climate Monitoring Diagnostics Laboratory
EPT	Equivalent Potential Temperature
EPA	Environmental Protection Agency (United States)
GC-FID	gas chromatograph-flame ionization detector
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory Model
INDOEX	Indian Ocean Experiment
IPCC	Intergovernmental Panel on Climate Change
MBL	marine boundary layer
MOZAIC	Measurements of Ozone and Water Vapor by Airbus In-Service
	Aircraft
NASA	National Aeronautics and Space Administration
NCEP	National Center for Environmental Prediction (NOAA)
NMHCs	nonmethane hydrocarbons
NOAA	National Oceanic and Atmospheric Adminstration
ORV	Oceanic Research Vessel
PAN	peroxyacetyl nitrate
PRL	Physical Research Laboratory
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
UV-B	Ultraviolet- B radiation (280-315 nm)
WMO	World Meteorological Organization (UN)
VOCs	volatile organic compounds