### Study of Trace Gases and Related Meteorological Parameters in Lower Atmosphere

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**Faculty of Science** 

by

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## CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "**Study of trace gases** and related meteorological parameters in lower atmosphere" by Shuchita Srivastava under my guidance. She has completed the following requirements as per Ph.D. regulations of the University

- (a) Course work as per the university rules.
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- (d) Published/accepted minimum of one research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

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## **DECLARATION**

I Ms. Shuchita Srivastava, D/o Mr. Vimal Chand Srivastava, resident of D-105, PRL residences, Navrangpura, Ahmedabad – 380009, hereby declare that the research work incorporated in the present thesis entitled "Study of trace gases and related meteorological parameters in lower atmosphere" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

Date:

•

Shuchita Srivastava

## Dedicated to

 $\mathcal{M}y$ 

# Loving Parents

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## <u>Abstract</u>

The distribution of ozone is highly variable in the lower troposphere and is controlled by the photochemical production, boundary layer dynamics and transport from different regions. Effects of these processes on the distribution of ozone are investigated using balloon, ship and airborne measurements of  $O_3$  and its precursors together with various meteorological parameters over different Indian locations and surrounding marine regions.

Effects of regional pollution and long range transport have been studied on the distribution of ozone measured using balloonborne sensors in the lower troposphere over Ahmedabad using back-trajectory based residence time analysis. The regionally polluted air-mass dominates over Ahmedabad within the boundary layer (lower 2 km) with ~ 40% and ~ 21% higher levels than average ozone in summer and spring respectively. This difference is only ~ 8-11% in the lower free troposphere (2-4 km). The long range transport (LRT) plays a significant role in the lower free troposphere with 32% higher ozone levels than average values during May-July months.

A layer of enhanced ozone (~ 65-70 ppbv) is found between 0.5 and 3 km range over northern Bay of Bengal (BoB) in spring 2006 based on ship based ozonesonde observations. The layer was found drier and warmer than air of southern BoB showing the influence of continental air mass. Identification of the source regions for high ozone levels has been made using potential source contribution function (PSCF). This technique has identified the Northern Indian Region (NIR) as the source of high ozone plume. The mixing ratios of ozone are found 25% higher in the NIR air-mass than average ozone over northern BoB between 0.75 and 2.5 km. Effect of LRT is evident between 2.5 and 3.25 km with 16% higher levels than average ozone. However, such kind of increase in ozone has not been observed over Arabian Sea.

The distribution of ozone and its precursors are also investigated over different land-marine interfaces during an aircraft campaign in January, 2009. The polluted plumes rich in these gases are found over northern BoB and south-east BoB which are attributed to originate from the Indo-Gangetic Plain and South East Asia respectively. The vertical and horizontal mixing of these gases, their inter-correlations, age and photochemical processing of air masses etc. are studied in detail.

Key Words: Ozone, regional pollution, long range transport, Indo Gangetic Plain, Bay of Bengal, Arabian Sea

## Contents

Acknowledgements	V
Abstract	vii
List of Figures	xiii
List of Tables	xvii

Chapter 1: Introduction	. 1
-------------------------	-----

1.1 Tropospheric ozone	2
1.1.1 Importance	3
1.1.1.1 Radiative forcing	3
1.1.1.2 Oxidizing capacity of the atmosphere	4
1.1.1.3. Effects on human health and plants	5
1.1.2 Sources and Sinks	7
1.1.2.1 Photochemical production and loss	7
1.1.2.2 Loss of ozone by dry deposition	9
1.1.2.3 Flux from the stratosphere	9
1.1.3 Trends of tropospheric ozone	10
1.2 Precursors of ozone	12
1.2.1 Carbon monoxide	12
1.2.2 Methane	12
1.2.3 Non-Methane Hydrocarbons	13
1.3 Atmospheric dynamics in the troposphere	15
1.3.1 Atmospheric boundary layer	16
1.3.2 Land-Sea breeze circulation	
1.3.3 Long range transport	19
1.4 Study of trace gases over the Indian subcontinent	21
1.5 Objectives and chapter details of the thesis	22

Chapter 2: Experimental techniques	25
------------------------------------	----

2.1 Techniques for ozone measurements	. 25
2.1.1 Photometric technique for ozone measurement	. 27
2.1.2 Electrochemical technique for ozone measurement	. 31
2.1.2.1 Electrochemical Concentration Cell (ECC) sensor	. 32
2.1.2.2 Radiosonde	. 34
2.1.2.3 Global Positioning System (GPS)	. 35
2.1.2.4. V2C interface	. 35
2.1.2.5. Ground based reciever system	. 35
2.1.2.6. Preparation and launch of Ozonesonde	. 36
2.2 GC technique for CO and $CH_4$ measurements	. 37
2.3 GC technique for NMHCs measurements	. 39
2.4 Satellite based measurements of CO, NO <sub>2</sub> and fire	.41
2.4.1 CO observations by Measurements Of Pollution In The Troposphere	
(MOPITT)	. 42
2.4.2 NO <sub>2</sub> observations by Ozone Monitoring Instrument (OMI)	. 42
2.4.3 Fire detection by Advanced Along-Track Scanning Radiometer (AATSR)	. 43

#### Chapter 3: Distribution of ozone in the lower troposphere over Ahmedabad 45

3.1 Site description and meteorology	47
3.2 Surface ozone and mixed layer height over Ahmedabad	49
3.2.1 Distribution of surface ozone over Ahmedabad	49
3.2.2 Seasonal variation of mixed layer height over Ahmedabad	50
3.3 Vertical distributions of ozone, temperature and relative humidity	57
3.4 Back-trajectories and geographical sectors	60
3.5 Residence time of air-masses	65
3.5.1 Seasonal and frequency distribution of residence time	66
3.5.2 Seasonal variation of mean altitude of trajectories	68
3.6 Dependence of ozone on residence time over Western India	70
3.7 Contribution of different air-masses	73

3.7.1 Regionally polluted air-mass	73
3.7.2 Marine air-mass and influence of long range transport	75
3.8 Surface ozone at Ahmedabad	76
3.9 Comparison with other sites	

#### Chapter 4: Ozone and its precursors over Bay of Bengal & Arabian Sea

4.1 Cruise track and meteorological conditions	84
4.2 Vertical distribution of ozone	88
4.2.1 Structure of marine boundary layer	88
4.2.2 Vertical distributions of ozone over Bay of Bengal & Arabian Sea	90
4.2.3 Identification of source regions: Potential Source Contribution Function	95
4.2.4 Residence time analysis	99
4.2.5 Satellite derived CO and NO <sub>2</sub>	101
4.2.6 Comparison with MOZART model	103
4.2.7 Comparison with other measurements	105
4.3 Surface measurements of trace gases during ICARB	108
4.3.1 Spatio-temporal variations of $O_3$ , $CH_4$ , CO and NMHCs	108
4.3.2 Latitudinal variations of trace gases	113
4.3.3 Comparison with other measurements	116

#### Chapter 5: Distribution of ozone and its precursors over land & marine interface 119

5.1 Experimental details and meteorological conditions	120
5.2 Longitudinal variations of ozone and its precursors	124
5.2.1 Longitudinal variation over Vishakhapatnam	124
5.2.2 Longitudinal variation between Chennai and Port Blair	128
5.3 Spatial distributions of ozone and its precursors over BoB	130
5.3.1 Photochemical processing in IGP and SEA plumes	134
5.3.2 Age of IGP and SEA plumes	135

5.4 Vertical distributions of ozone and its precursors	137
5.5 Interspecies correlation of various trace species	142
5.6 Comparison with other measurements	144

Chapter 6: Summary and Future Plan	146
6.1 Distribution of ozone in the lower troposphere over Ahmedabad	146
6.2 Ozone and its precursors over Bay of Bengal & Arabian Sea	148
6.3 Ozone and its precursors over land & marine interface	150
6.4 Future scope	152

References	155
List of Acronyms and Abbreviations	175
List of publications	177

## List of Figures

Figure 1.1	Global mean radiative forcing (W m <sup>-2</sup> ) due to greenhouse gases and	
	aerosol for the period from 1750 to 2005	4
Figure 1.2	Effect of seasonal average ozone mixing ratios on agricultural crop yields	6
Figure 1.3	Increase in spring time free tropospheric (3-8 km) ozone over western	
	North America for period 1984–2008	11
Figure 1.4	Diurnal evolution of the atmospheric boundary layer over land	17
Figure 1.5	Conceptual depiction of the interaction between the coastal sea breeze	
	circulation and the land plume over the marine region during day time	18
Figure 1.6	Long range transport over Ahmedabad, India.	20
Figure 2.1	Absorption spectrum of ozone and response of UV detector	28
Figure 2.2	Schematic diagram of a single beam ozone analyzer	29
Figure 2.3	Schematic diagram of a dual beam ozone analyzer	29
Figure 2.4	Calibration curves of ESA and 2B ozone analyzers	31
Figure 2.5	Schematic of ECC ozonesonde	33
Figure 2.6	Vaisala RS80 radiosonde and Garmin GPS	34
Figure 2.7	Balloonsonde transmission and receiving system overview	36
Figure 2.8	Balloon with ozonesonde payload during ascent	37
Figure 2.9	Schematic of gas chromatograph for CO and $CH_4$	38
Figure 2.10	A typical GC chromatograph for CO and $CH_4$	39
Figure 2.11	The schematic of GC and sample injection system for NMHCs	40
Figure 2.12	A typical NMHC GC chromatograph	41
Figure 3.1	Location of observational site Ahmedabad	47
Figure 3.2	Synoptic wind field (925mb) over Indian region	48
Figure 3.3	Virtual potential temperature and specific humidity profiles over	
	Ahmedabad	50
Figure 3.4	Seasonal variation of mixed layer top over Ahmedabad	53
Figure 3.5	Monthly variation of temperature at 100 m altitude and ABL over	
	Ahmedabad	54
Figure 3.6	Monthly variation of ozone, CO and ventilation coefficient over	
	Ahmedabad	56
Figure 3.7	Seasonal variation of vertical distribution of ozone over Ahmedabad	58
Figure 3.8	Contour plots: annual variation of relative humidity over Ahmedabad	59
Figure 3.9	Contour plots: annual variation of temperature over Ahmedabad	59

Figure 3.10	The seven days back trajectories arriving at Ahmedabad at 1 km altitude	
	during different months	60
Figure 3.11	Altitude variation of seven days back trajectories arriving at Ahmedabad	
	at 1 km altitude during different months	61
Figure 3.12	The seven days back trajectories arriving over Ahmedabad at 3 km	
	altitude during different months	62
Figure 3.13	Altitude variation of seven days back trajectories arriving at Ahmedabad	
	at 3 km altitude during different months	63
Figure 3.14	Spatial coverage of back trajectories over the classified sectors	64
Figure 3.15	Seasonal variation of residence days of trajectories over the classified	
	sectors	66
Figure 3.16	Variations in percentage of trajectories having different residence days	
	over the classified sectors	67
Figure 3.17	Seasonal variation of mean altitudes of trajectories over the classified	
	sectors	69
Figure 3.18	Seasonal variation of ozone mixing ratios with residence days over	
	western Indian region	71
Figure 3.19	Variation of solar radiation over Ahmedabad	72
Figure 3.20	Monthly distribution of average ozone and regionally polluted ozone in	
	the boundary layer and lower troposphere	74
Figure 3.21	The seasonal variation of regionally polluted and background levels of	
	ozone in the boundary layer and lower troposphere	75
Figure 3.22	The seasonal distribution of (a) average ozone with seasonal variation of	
	marine ozone in boundary layer and (b) average ozone with seasonal	
	variation of LRT ozone in the lower troposphere.	76
Figure 3.23	The variation of surface ozone mixing ratios with residence days over WI	
	region in day time and night time during different seasons	77
Figure 3.24	The seasonal variation of regionally polluted ozone, marine ozone and	
	background ozone over Ahmedabad	79
Figure 4.1	ICARB: Cruise track	85
Figure 4.2	Variation of meteorological parameters during campaign	86
Figure 4.3	Synoptic wind fields over Bay of Bengal and Arabian Sea	87
Figure 4.4	Vertical profiles of virtual potential temperature and specific humidity	
	over the study region	89
Figure 4.5	Vertical profiles of ozone over Bay of Bengal and Arabian Sea	91

Figure 4.6	Difference in average profiles of ozone, specific humidity and	
	temperature between the Northern and southern (a) Bay of Bengal and	
	(b) Arabian Sea	94
Figure 4.7	Total Potential Source Contribution Function map over the study region	97
Figure 4.8	Spatial coverage of the classified sectors	99
Figure 4.9	Vertical distributions of ozone in air-masses of different regions	100
Figure 4.10	MOPITT derived CO distributions for the study period	102
Figure 4.11	OMI derived NO $_2$ column distributions for the study period	103
Figure 4.12	Comparison of ozone profiles obtained from ozonesonde and MOZART	
	model for different balloon flights days.	104
Figure 4.13	Vertical distribution of ozone over BoB, AS, Chennai and Delhi in the	
	lower 4 km	106
Figure 4.14	Variation of surface ozone and its precursor gases over BoB and AS	109
Figure 4.15	Seven days back-trajectories over the study region at 500 m amsl	111
Figure 4.16	Correlation of ozone, CO, $CH_4$ and few NMHCs over the study region	112
Figure 4.17	Latitudinal variations of $O_3$ , CO, ethane and n-butane over the study	
	region	114
Figure 5.1	Air sorties: location and trajectory	121
Figure 5.2	Typical aircraft flight profile for multi-level and bi-level sorties	122
Figure 5.3	Synoptic wind field over the study region	124
Figure 5.4	Longitudinal variation of $O_3$ , CO, CH <sub>4</sub> , ethane and n-butane over	
	Vishakhapatnam for bi-level sortie	125
Figure 5.5	Vertical distribution of potential temperature and relative humidity over	
	different marine locations	126
Figure 5.6	Schematic depiction of aircraft path during bi-level sortie, variation of	
	atmospheric boundary layer and marine boundary layer over east of	
	Vishakhapatnam	127
Figure 5.7	Longitudinal variation of $O_3$ , CO, ethane, propane and n-butane at 750	
	m, between Chennai and Port Blair	129
Figure 5.8	Spatial distributions of $O_3$ , CO, CH <sub>4</sub> and various NMHCs at 750 m over	
	Bay of Bengal	130
Figure 5.9	Spatial and altitude variation of back trajectories at 750 m over	
	Vishakhapatnam and Port Blair	132
Figure 5.10	Spatial distribution of fire locations observed by Advanced Along Track	
	Scanning Radiometer (AATSR) during the study period	133
Figure 5.11	Pie diagram showing the percentage abundance of several NMHCs over	
	east of Vishakhapatnam and south of Port Blair	134

Figure 5.12	Correlation plot of CO with acetylene over Vishakhapatnam and Port			
	Blair	135		
Figure 5.13	Vertical distributions of ozone, CO and $CH_4$ over the study region	138		
Figure 5.14	Vertical distributions of alkanes over the study region	139		
Figure 5.15	Vertical distributions of alkenes and acetylene over the study region	140		
Figure 5.16	Vertical distribution of virtual potential temperature, relative humidity,			
	wind speed and wind direction over Vishakhapatnam and Port Blair	141		
Figure 5.17	Correlation plots of CO with methane, ethane and n-butane over			
	Hyderabad, Vishakhapatnam, Port Blair and Mangalore for multi-level			
	sorties	143		

## List of Tables

Table 1.1	Ozone standards for the selected countries	6
Table 1.2	NMHCs: emission, sources, lifetime and reaction rate coefficients with	
	OH radical	14
Table 2.1	Specifications of ozone analyzers	30
Table 3.1	The background ozone and rate of increase in ozone with increasing	
	residence days in the boundary layer and lower troposphere for	
	different seasons over WI region.	73
Table 3.2	Background surface ozone, night time surface ozone and rate of	
	increase of surface ozone during four seasons at Ahmedabad	78
Table 4.1	Average ozone (ppbv) with $\pm1\sigma$ value observed over different altitudes	
	and different marine segments during ICARB 2006	93
Table 4.2	The latitudinal gradients of few trace gases during different campaigns	
	over marine regions surrounding Indian subcontinent	115
Table 4.3	Comparison of mixing ratios of ozone and its various precursor gases	
	over BoB and AS during different cruise campaigns	116
Table 4.4	Comparison of ozone and its various precursors over Northern Bay of	
	Bengal and Hissar.	117
Table 5.1	Details of air sorties conducted during W-ICARB	123
Table 5.2	The average levels of few trace gases measured between 0-3 km during	
	INDOEX 1999 and WICARB 2009.	144

## **Chapter 1**

#### Introduction

The atmosphere is a thin and fragile envelop of air surrounding the earth. It is composed primarily of nitrogen N<sub>2</sub> (78%), oxygen O<sub>2</sub> (21%) and argon Ar (0.93%) gases, known as the major constituents. The remaining gases represent about 1% of the atmosphere and can be subdivided into minor (in the range of ppmv, like CO<sub>2</sub>, helium, neon etc) and trace constituents (in the range of ppbv to pptv, like O<sub>3</sub>, CO, N<sub>2</sub>O, NMHCs). Despite their low abundances, most of these species have significant effects directly or indirectly on global change through heat retention (greenhouse effect) to sustain the ecosystem and also potentially harmful local effects through increased levels of pollution.

The thermal structure of the atmosphere is divided into various layers based on the specific vertical temperature gradients. Its lower most part "troposphere" extends from the surface to about 18 km in the tropics and about 6 to 8 km near the poles, and is characterized by a decreasing temperature with increasing altitude (lapse rate ~  $6.5^{\circ}$ C km<sup>-1</sup>). Although it represents only a tiny part of the whole atmospheric volume, this is the region where most of the anthropogenic and all the biogenic emissions are released. It can essentially be regarded as a continually mixing chemical vessel where composition is dependent on several factors such as temperature, solar radiation, weather, moisture and emitted pollutants. The stratosphere, which is present just above the troposphere, extends up to 50 km. The temperature increases in this region with altitude due to absorption of solar radiation by the ozone layer. The ozone mixing ratio is in the range of 0.5 to10 ppmv (90% of total atmospheric ozone) in the stratosphere and it peaks around 25 km approximately [*Seinfeld and Pandis*, 2006]. This layer protects biota on the earth from potential damage by absorbing the harmful solar ultraviolet-B radiation. In the troposphere, despite its very low mixing ratios (< 150 ppbv, 10% of total ozone), ozone is a pollutant, a potential greenhouse gas and a major oxidant. It has become increasingly apparent in recent years that anthropogenic activities have a significant impact on the stratospheric ozone loss and tropospheric ozone enhancement.

#### **1.1 Tropospheric ozone**

The increasing human activities have resulted in an enormous growth of pollutants in the lower troposphere since the advent of industrial era (since 1750 onwards). Air pollution has been defined as "the presence of substances in the ambient atmosphere, resulting from the activity of man or from natural processes, causing adverse effects to man and the environment" [Weber, 1982]. The combined mixing ratio of all the "reactive" pollutant gases in the lower atmosphere is found to be less than 0.001% (10 ppmv), even in highly polluted urban environments. Despite their small concentrations, these species have disproportionate detrimental effects as air pollutants in the atmosphere [Hewitt and Jackson, 2003]. Minor and trace constituents like carbon-dioxide, ozone, water vapour and many others influence the radiation budget of the atmosphere and therefore linked to the physical climate system. Few of them determine the "oxidizing capacity" of the atmosphere and hence indirectly define the lifetime of many biogenic and anthropogenic trace gases. The tropospheric ozone is one of the important species which determines the oxidizing power of the atmosphere by being the primary source of OH [Seinfeld and Pandis, 2006]. The tropospheric

ozone budget is governed by three different processes namely: vertical transport of ozone rich stratospheric air into the troposphere, in-situ photochemical production and loss, and dry deposition on the earth's surface. Established correlations between high ozone concentrations, and lower crop yield and human health degradation emphasize for many federal regulations on ozone.

#### **1.1.1 Importance**

#### 1.1.1.1 Radiative forcing

The average temperature of the earth is increasing due to increasing amount of greenhouse gases. These gases are evaluated in terms of their radiative forcing (RF). It is a measure of change in energy balance of the Earth-atmosphere system when the abundance of greenhouse constituents is altered. Radiative forcing is usually quantified as the rate of energy change per unit area (W m<sup>-2</sup>) of the globe as measured at the top of the atmosphere. Human activities have exerted a substantial warming influence (positive radiative forcing) on climate by adding the greenhouse gases in the atmosphere since the pre-industrial era. Tropospheric ozone is one of the potential greenhouse gases and absorbs the terrestrial radiation at 9.6  $\mu$ m wavelength. Each additional molecule of ozone is 1200-2000, 217 and 22 times more effective than an additional molecule of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> respectively in global warming [*Ramanathan et al.*, 1985; *Schwarzkopf and Ramaswamy*, 1993; *Myhre et al.*, 2001].

The increase in tropospheric ozone has caused a change in radiative forcing which is estimated by a number of recent model studies [*Hauglustaine and Brasseur*, 2001; *Mickley et al.*, 2001; *Mickley et al.*, 2004; *Wong et al.*, 2004; *Liao and Seinfeld*, 2005; *Shindell et al.*, 2005]. The best estimate for the RF of tropospheric ozone, based on chemistry transport model and general circulation model simulations, is +0.35 W m<sup>-2</sup>, taken as the median of the radiative forcing values reported by above mentioned studies with a 5 to 95% confidence interval of +0.25 to +0.65 W m<sup>-2</sup>. A multi-model experiment (10 global models) was organised through the "Atmospheric Composition Change: an European



**Figure 1.1:** Global mean radiative forcing (W  $m^{-2}$ ) due to greenhouse gases and aerosol for the period from 1750 to 2005 [IPCC, 2007].

NeTwork" (ACCENT) [*Gauss et al.*, 2006]. This showed the normalised adjusted radiative forcing of  $+0.032 \pm 0.006$  W m<sup>-2</sup> DU<sup>-1</sup> for tropospheric ozone with a medium level of scientific understanding [*IPCC*, 2007].

#### 1.1.1.2 Oxidizing capacity of the atmosphere

The oxidation capacity of the troposphere is controlled by the action of ultraviolet radiation shorter than 320 nm (UV-B) on ozone. This leads to the formation of hydroxyl (OH) radicals, which despite its low abundance, reacts with several trace gases. Ozone determines the oxidation capacity of the troposphere and is of utmost importance for maintaining its chemical composition. About 80% of total atmospheric oxidation occurs in the troposphere [*Spivakovsky et al.*, 2000]. The concentrations of tropospheric ozone and hydroxyl radical are expected to increase in polluted regions due to increasing emissions of CO, CH<sub>4</sub>, NMHCs, NO<sub>x</sub> etc from anthropogenic sources and decrease in clean remote tropospheric environments. Altogether, this may lead to an overall decrease in the

oxidation efficiency of the atmosphere [*IPCC*, 2001], contributing to a gradual build up of several long lived trace gases.

#### 1.1.1.3. Effects on human health and plants

Ozone reacts with the human body tissues causing inflammation of the lung. It acts as a strong respiratory irritant at higher levels. Breathing ozone rich air leads to serious health consequences, like

- 1. Premature death
- 2. Shortness of breath and chest pain
- 3. Wheezing and coughing
- 4. Increased susceptibility to respiratory infections
- 5. Increased risk of asthma attacks
- 6. Eye irritation, headache and nausea
- 7. Reduced functioning of immune system

Several nations have established official limits, called national ambient air quality standards, on the levels of ozone at surface. India has not yet set any such standard (Table 1.1).

Elevated levels of  $O_3$  can adversely affect vegetation by way of reduced crop yield [*Grunhage et al.*, 1999] and acute injury on broad-leafed plants including bleaching, chlorosis, and necrosis spots etc. [*Krupa et al.*, 1989]. In Europe, the critical levels of ozone are expressed as the accumulative exposure in hours above a threshold concentration of 40 ppbv, abbreviated as AOT40 [*Fuhrer et al.*, 1996]. The AOT (accumulated ozone threshold) indices have shown to have a linear relationship with the negative grain yield. In a separate study, the reduction in crop yields caused by higher levels of ozone exposure has been studied by Environmental Protection Agency (EPA). At a seasonal

Region /	Value	Averaging	Description	
Country		period (hr)		
Australia	80 ppbv	4		
Canada	65 ppbv	8	Fourth highest annual value averaged over three years. To be achieved by 2010.	
China	60 ppbv	1	This limit is for Class I (residential) area. Higher limits are set for Class II and Class III (industrial) areas.	
European Union	60 ppbv	8	Not to be exceeded more than 25 times per calendar year averaged over three years. To be achieved by 2010.	
India	India has no	India has not yet set a standard or guideline for ozone.		
Japan	60 ppbv	1		
Mexico	110 ppbv	1	Daily maximum	
United States	80 ppbv	8	Fourth highest annual value averaged over three years.	

Table 1.1: Ozone standards/ Guidelines for selected countries [Reid, 2007].



**Figure 1.2:** Effects of seasonal average ozone mixing ratios on agricultural crop yields [Adams et al., 1989; Chameides et al., 1999].

average ozone of 75 ppbv, soybean yields dropped to  $\sim 60\%$  of normal (Figure 1.2). Wheat and corn dropped to  $\sim 60\%$  of normal at an exposure to 100 ppbv [*Adams et al.*, 1989; *Chameides et al.*, 1999].

#### 1.1.2 Sources and Sinks

#### 1.1.2.1 Photochemical production and loss

Ozone governs the chemistry of the atmosphere despite its low abundance in the troposphere. Previously, it was assumed that ozone is transported from the stratosphere and destroyed on the earth's surface [*Regener*, 1949]. Later, *Crutzen* [1973] and *Chameides and Walker* [1973] proposed the concept of in situ ozone production by the oxidation of CO and hydrocarbons in the presence of NO as given below

$$O_3 + hv (\lambda < 320 \text{ nm}) \longrightarrow O_2 + O(^1D)$$
(R1.1)  
$$O(^1D) + H_2O \longrightarrow 2OH$$
(R1.2)

followed by the chain mechanism in NO rich environment,

$CO + 2O_2 + hv$	$\rightarrow$	$CO_2 + O_3$	(R1.8)
$O + O_2 + M$	$\rightarrow$	O <sub>3</sub> +M	(R1.7)
NO <sub>2</sub> + hv ( $\lambda$ < 420 nm)	$\rightarrow$	NO + O	(R1.6)
$HO_2 + NO$	$\rightarrow$	$NO_2 + OH$	(R1.5)
$H + O_2 + M$	$\rightarrow$	$HO_2 + M$	(R1.4)
$\rm CO + OH$	$\rightarrow$	$CO_2 + H$	(R1.3)

or followed by the chain mechanism in NO deficient environment,

<b>O</b> <sub>3</sub> + <b>CO</b>	$\rightarrow$	$O_2 + CO_2$	(R1.10)
H + O <sub>2</sub> + M	$\rightarrow$	$HO_2 + M$	(R1.4)
CO + OH	$\rightarrow$	$CO_2 + H$	(R1.3)
$O_3 + HO_2$	$\rightarrow$	$OH + 2O_2$	( <b>R1.9</b> )

Reaction R1.5 dominates the urban and its downwind locations whereas reaction R1.9 plays a major role in remote marine environments. These two reactions are

the rate determining reactions which results in the production or destruction of ozone depending on the critical or threshold level of NO. The rate constants of reaction R1.5 and R1.9 are  $8.6 \times 10^{-12}$  and  $2.0 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> respectively.

Production rate of ozone =  $k_{R1.5}$  [HO<sub>2</sub>][NO] Destruction rate of ozone =  $k_{R1.9}$  [HO<sub>2</sub>][O<sub>3</sub>]

For net photochemical production of ozone,

 $k_{R1.5}$  [HO<sub>2</sub>][NO] >  $k_{R1.9}$  [HO<sub>2</sub>][O<sub>3</sub>] [NO] >  $k_{R1.9}$  [O<sub>3</sub>]/  $k_{R1.5}$ [NO] >  $0.23 \times 10^{-3}$  [O<sub>3</sub>]

Thus, critical limit of NO depends on the ambient levels of ozone. The ambient concentration of NO should be higher than this critical limit for the net photochemical production of ozone.

The ozone production is dominated by Non-Methane Hydrocarbons (NMHCs) in the urban areas. The reaction mechanism is similar to that of CO as shown below [*Brasseur et al.*, 1999].

RH+4O <sub>2</sub> + hv	$\rightarrow$	<b>R'CHO+H<sub>2</sub>O+2O<sub>3</sub></b>	( <b>R1.18</b> )
$2 \times (O(^{3}P) + O_{2} + M)$	$\rightarrow$	O <sub>3</sub> + M)	(R1.17)
$2 \times (NO_2 + hv)$	$\rightarrow$	$NO + O(^{3}P))$	(R1.16)
$HO_2 + NO$	$\rightarrow$	$NO_2 + OH$	(R1.15)
$RO + O_2$	$\rightarrow$	$HO_2 + R'CHO$	(R1.14)
$RO_2 + NO$	$\rightarrow$	$NO_2 + RO$	(R1.13)
$R + O_2 + M$	$\rightarrow$	$RO_2 + M$	(R1.12)
RH + OH	$\rightarrow$	$R + H_2O$	(R1.11)

NMHCs are denoted by RH for simplicity. The carbonyl compounds (aldehyde or ketone) are denoted R'CHO, where R' denotes an organic fragment having one

carbon atom fewer than R. This should be noted that critical limit of NO will be different if we include all the production processes by CO,  $CH_4$  and NMHCs. The critical limit of [NO]/[O<sub>3</sub>] ratio ranges from  $0.23 \times 10^{-3}$  to  $4.0 \times 10^{-3}$  for the production of ozone depending on the environments.

On the other hand, in highly polluted region where NO is high, ozone loss may occur due to following titration reaction.

 $O_3 + NO \rightarrow NO_2 + O_2$  (R1.19)

#### 1.1.2.2 Loss of ozone by dry deposition

The dry deposition is the transport process of gaseous or particulate species directly onto the earth's surface in the absence of precipitation. The turbulent transfer of ozone in the surface layer is traditionally parameterized in terms of ozone deposition velocity  $(v_d)$ , defined as

$$F = -v_d x [O_3]$$

where F is the turbulent ozone flux in the surface layer and  $[O_3]$  is the mean ozone concentration at the reference height (10 m or less). The deposition velocity depends on the level of atmospheric turbulence, the chemical properties of the depositing species and the nature of the surface. The typical deposition velocity of ozone reported on continental surface is 0.4 cm/sec and on marine/ice/snow surface is 0.07 cm/s [*Seinfeld and Pandis*, 2006].

#### **1.1.2.3 Flux from the stratosphere**

Distribution of ozone in the troposphere is also affected by the downward transport from the stratosphere [*Levy et al.*, 1985; *Holton and Lelieveld*, 1996; *Marcy et al.*, 2004]. The global rate of air exchange between the stratosphere and the troposphere (STE) is controlled by extra tropical wave forcing. Upward transport mainly occurs in the tropics whereas downward transport occurs in mid and high latitudes through small scale features like tropopouse folding or

processes related to synoptic scale frontal systems. Typical tropopause fold is an event by which tropospheric and stratospheric air can mix quasi-horizontally. Sometimes, STE event can deeply penetrate into the troposphere and reach the surface. In extra-tropical region of northern hemisphere, the mean STE contribution to surface  $O_3$  can be up to 30-40% in winter and spring and less than 20% in summer and autumn. The STE contribution in the extra-tropical southern hemisphere is up to 30-50%, whereas in the tropical region it is only about 10-15%. Transport from the stratosphere contributes most significantly to ozone in the upper troposphere, where the lifetime of ozone is relatively long due to low abundance of water vapor. Further, STE contributes to tropospheric ozone at mid and high latitudes in winter when photochemistry is slow and lifetime of ozone is highest i.e. at those latitudes and seasons where radiation and oxidation processes are least active.

#### **1.1.3 Trends of tropospheric ozone**

In the troposphere, the amount of ozone has increased substantially due to anthropogenic emission of precursor gases like carbon monoxide, hydrocarbons and nitrogen oxides. The assessment of long term change in tropospheric ozone is difficult due to sparse observations. Trends in tropospheric ozone have been estimated by using available ozonesonde data over northern middle and high latitudes [WMO, 2003; Naja et al., 2003; Naja and Akimoto, 2004; Tarasick et al., 2005 and Oltmans et al., 2006]. An increase in ozone in the lower troposphere (750 to 550 hPa) of 12 to 15% at Sapporo (43.05°N, 141.3°E) and Tsukuba (36.05°N, 140.1°E) and 35% increase over Kagoshima (31.6°N, 130.6°E) have been observed between 1970-1985 and 1986-2002 periods in Japan [Naja and Akimoto, 2004]. A positive trend of 5% per decade in ozone is observed during 1990 to 2004 over another Japanese site Naha (26.2°N, 127.7°E) between 700 and 300 hPa whereas this trend is negative between surface and 700 hPa [Oltmans et al., 2006]. Ozonesonde observations over Canada show decreasing trends in tropospheric ozone between 1980 to 1990 and increasing trend during 1991 to 2001 [Tarasick et al., 2005].



**Figure 1.3:** Increase in spring time free tropospheric (3-8 km) ozone over western North America for period 1984–2008. Green line and data points are median and yellow data points are means. The blue and red lines and data points indicate the  $95^{th}$ ,  $67^{th}$ ,  $33^{rd}$  and  $5^{th}$  percentile [Cooper et al., 2010].

In the tropical region, *Diab et al.* [2004] have reported an increase of 10 ppb in the upper troposphere during winter over Irene (25.9°S, 28.2°E), South Africa. Significant increase in free tropospheric ozone (7.7 to 11.3 km) is reported in the tropics with  $1.12 \pm 0.05$  ppbv/yr in northern hemisphere and  $1.03 \pm 0.08$  ppbv/yr in southern hemisphere during 1994 to 2003 [*Bortz and Prather*, 2006]. A very recent study over western north America has shown an increase of  $0.63 \pm 0.34$  ppbv/yr in background mid tropospheric (3-8 km) ozone in spring season during 1995-2008 (Figure 1.3) [*Cooper et al.*, 2010]. Over the Indian region (Ahmedabad), *Naja and Lal* [1996] have reported an increase of 1.45% per year. The positive trend of tropospheric ozone is of great concern at present due to its contribution to global warming and climate change.

#### **1.2 Precursors of ozone**

The photochemical formation of ozone takes place due to the oxidation of CO, CH<sub>4</sub> and various non-methane hydrocarbons, in the presence of NO and sunlight. As discussed earlier, CO, CH<sub>4</sub> and NMHCs emissions supply the "fuel" for the ozone production whereas  $NO_x$  and  $HO_x$  play the role of catalyst. The ozone yield is different for different "fuels", 1 for CO, 3.5 for CH<sub>4</sub> and 10-14 for NMHCs. The major production and loss processes and budgets of these species are given below in detail.

#### 1.2.1 Carbon monoxide

Carbon monoxide plays an important role in the tropospheric chemistry via controlling the OH radical abundance through chemical reaction [*Logan et al.*, 1981]. Reaction with CO constitutes 70% of total loss of OH. It is produced by the oxidation of methane and non-methane hydrocarbons and also released from the incomplete combustion of fossil fuels and biomass burning. The global lifetime of CO is two months in the troposphere. This gas is not well mixed in the atmosphere and its highest concentrations are found in the industrialized area in the northern hemisphere, where the anthropogenic sources are most intense. The levels of CO are 60-70 ppbv in the southern hemisphere and 120-180 ppbv in the northern hemisphere. At the South Pole, CO varies between approximately 30 ppbv in summer and 60 ppbv in winter [*IPCC*, 2007].

#### 1.2.2 Methane

Methane is third most abundant greenhouse gas in the troposphere after water vapor and CO<sub>2</sub>. Oxidation of methane by OH in the troposphere leads to the formation of formaldehyde, CO and ozone. The lifetime of methane is about 8 to 10 years in the atmosphere [*Watson et al.*, 1992]. The average atmospheric mixing ratios of CH<sub>4</sub> remained constant at about 715  $\pm$  4 ppbv from year 1700 to 1800.

*Dlugokencky et al.* [1994] have reported an average mixing ratio of 1740 ppbv in the northern hemisphere and 1620 ppbv in the southern hemisphere during 1984 to 1993. The global atmospheric methane concentrations were increasing at a rate of 1.3% per year in the late 1970s and early 1980s [*Blake and Rowland,* 1988] and approached close to zero towards the end of 1990s [*Dlugokencky et al.,* 1998; *Simpson et al.,* 2002].

The current global estimates of methane show dominance of anthropogenic emissions. The major anthropogenic sources are fossil fuel related release (27% of the total anthropogenic source), waste management (24%), enteric fermentation of cattle (23%), biomass burning (11%), and rice paddies (15%). Natural sources of methane are dominated by wetland emissions, particularly in the tropics. The decomposition of organic matter under oxygen-deficient conditions leads to the production of methane. The dominant loss process for methane in the atmosphere is via reaction with the hydroxyl radical, OH ( $k_{298} = 6 \times 10^{-15} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>: *DeMore et al.*, 1997), with minor contributions from stratospheric removal and consumption of methane in soils.

#### 1.2.3 Non-Methane Hydrocarbons

Non-methane hydrocarbons (NMHCs) are emitted into the atmosphere by both natural and anthropogenic sources. The major processes producing anthropogenic NMHCs are fossil fuel combustion, biomass burning, natural gas emissions and industrial processing of chemicals. The major natural sources of these gases include vegetation emissions followed by oceanic emissions.

The dominant mechanism for removal of NMHCs from the atmosphere is their reactions with hydroxyl radicals. Oxidation of NMHCs can lead to a significant production of ozone under favorable conditions like higher solar flux and sufficient amount of NO [*Crutzen*, 1974; *Logan et al.*, 1981; *Collins et al.*, 2002; *Jenkin et al.*, 2002; *Derwent et al.*, 2003]. The oxidation of several NMHCs is known to produce secondary organic aerosols that could affect the visibility, human health and significantly contribute to earth's energy balance [*Kanakidou et al.*, 2005]. Table 1.2 provides detailed information about the various NMHCs, annual budget, major sources, lifetime and reaction rate coefficients with OH radical.

Table 1.2: Various NMHCs, their emission, major sources, lifetime and reaction rate coefficients with OH radical. [Atkinson and Aschmann, 1994; Atkinson et al., 1997; Singh and Zimmerman, 1992; Guenther et al., 1995].

Species	Emission (TgC/yr)	Major Sources	Lifetime	K <sub>OH</sub> 10 <sup>-12</sup> cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup>
Ethane C <sub>2</sub> H <sub>6</sub>	10-15	Natural gas emissions, biomass burning, oceans, vegetation	45 days	0.254
Ethene C <sub>2</sub> H <sub>4</sub>	20-45	Fuel combustion, biomass burning, terrestrial ecosystem	1.4 days	8.52
Acetylene C <sub>2</sub> H <sub>2</sub>	3-6	Fuel combustion, biomass burning	14 days	0.82
<b>Propane</b> C <sub>3</sub> H <sub>8</sub>	15-20	Natural gas emissions, biomass burning, oceans, vegetation	10 days	1.12
<b>Propene</b> C <sub>3</sub> H <sub>6</sub>	7-12	Fuel combustion, biomass burning, oceans	5.3 hrs	26.3
<b>n-Butane</b> C <sub>4</sub> H <sub>10</sub>	1-2	Fuel combustion, Natural gas emissions, biomass burning, oceans	4.7 days	2.44
<b>i-Butane</b> C <sub>4</sub> H <sub>10</sub>	1-2	Fuel combustion, Natural gas emissions, biomass burning, oceans	4.7 days	2.34
<b>n-Pentane</b> C <sub>5</sub> H <sub>12</sub>	1-2	Fuel combustion, Natural gas emissions, biomass burning,	2.9 days	4.0
<b>i-Pentane</b> C <sub>5</sub> H <sub>12</sub>	2-3	Fuel combustion, Natural gas emissions, biomass burning,	3.1 days	3.9

These NMHCs provide important information about the history of an air parcel [*Parrish et al.*, 1992]. Ratios of different pairs of NMHCs emitted from common sources and having different lifetimes with respect to OH can provide an estimate of photochemical processing and age of the air parcel [*Smyth et al.*, 1996]. The life time of acetylene (14 days) is shorter than CO (60 days) and both of them have common loss process by reactions with OH radical. Thus, in an air parcel, the level of acetylene decreases faster than that of CO resulting in lower  $C_2H_2/CO$  ratio with ageing of air-mass.  $C_2H_2/CO$  ratio is greater than 1 pptv/ppbv indicates the influence of recent emission and less than 1 pptv/ppbv indicates that air mass has gone through extensive oxidation and dilution. Ethane (lifetime of 45 days) and acetylene are frequently used for the calculation of age of air-mass.

The age ( $\Delta t$ ) of the pollution in an air-mass is estimated from the following relation.

$$\Delta t = \frac{1}{[OH](k_A - k_B)} \times [\ln([A]_0/[B]_0) - \ln([A]_t/[B]_t)]$$

The  $[A]_t$  and  $[B]_t$  are the mixing ratios of two NMHCs at the measurement location whereas  $[A]_o/[B]_o$  is the assumed measured ratio of these species at the time of emission from the source [*Parrish et al.*, 1992]. The  $k_A$  and  $k_B$  are the reaction rates of species A and B respectively with OH radicals. The [OH] is the mean concentration of hydroxyl radical.

These ratios of NMHCs can also be used as indicators of their emission sources when the effect of dilution is not very significant. Ethene is a main hydrocarbon emitted from biomass burning followed by ethane, acetylene, etc. The ratio of ethene to ethane in biomass burning plumes show values greater than 1.0 [*Blake et al.*, 1994]. The air-mass affected by LPG leakage, oil refining and petrochemical industries show higher propane/ethane ratios in the range of 1.0-2.15 ppbv/ppbv [*Derwent et al.*, 2000]. Petroleum refineries and LPG leakage are major sources of i-butane and n-butane in the atmosphere [*Rudd*, 1995]. For both CO and acetylene, combustion processes particularly in automobiles are the primary sources of emission.

#### **1.3 Atmospheric dynamics in the troposphere**

The dynamical processes control the redistribution of physical and chemical properties in the atmosphere. The size and time scale of the atmospheric motions are regulated mainly by the gravitational force, pressure gradient force and coriolis force. The largest is global or planetary scale circulations that have sizes comparable to the circumference of the earth. Slightly smaller than planetary scale are synoptic scale processes with a scale of about 1000 km like cyclones, anticyclones and waves in the jet streams. Medium size mesoscale processes refer to phenomenon with a scale of tens to hundreds kilometers which include frontal zones, rain bands, the larger thunderstorms and various terrain modulated flows. The small scale processes range from the scale of an individual cloud or plume to the molecular levels (less than about 2 km). The planetary scale circulation dominates mainly in the stratosphere whereas small scale and mesoscale processes in the free troposphere.

The small scale processes particularly play major role within the atmospheric boundary layer (~ 2-3 km altitude from the surface). This region is directly influenced by biogenic and anthropogenic emissions. The day and night variation in temperature governs the dynamics of the atmospheric boundary layer. The day time convective boundary layer and night time inversion layer formation controls the dilution and accumulation of pollutants near the surface. The mesoscale processes like sea breeze circulation can transport the polluted atmospheric boundary layer air mass over the pristine marine environments. Further, the synoptic scale processes like long range transport, dominant in the free troposphere, can blow the pollutants over long distances even across continents.

#### **1.3.1 Atmospheric Boundary Layer**

The atmospheric boundary layer (ABL) is the lowest part of the troposphere. This layer is defined as "the part of the troposphere that is directly influenced by the presence of Earth's surface, and responds to surface forcing with a timescale of about an hour or less" [*Stull*, 1988]. The typical boundary layer height varies from 100 m to 3000 m altitude. The day time atmospheric boundary layer is characterized by strong convection and known as convective boundary layer. The surface friction on the wind flow causes shearing forces and diurnal variation of temperature creates a buoyancy force due to which atmospheric boundary layer boundary layer becomes turbulent during day time. Turbulence is the main cause

of effective transport as well as dilution of emitted pollutants. Extensive mixing of pollutants in day time developed boundary layer can dilute the pollutant concentrations. The layer (entrainment zone) present at the top of the boundary



**Figure 1.4:** *The diurnal evolution of the atmospheric boundary layer over land [Stull, 1988].* 

layer is resistant to vertical motions. It isolates the boundary layer from the free troposphere and slows the transport of pollutants from the boundary layer into the free troposphere. The rapid mixing time within the boundary layer, coupled with the slow exchange time between the boundary layer and the free troposphere, implies that chemical species emitted near the surface are often trapped within the boundary layer.

The radiative cooling after sunset results in the formation of inversion layer near the surface, known as nocturnal boundary layer (NBL). Above this layer, a non-turbulent residual layer forms with the same concentrations and variables as the day time mixed layer. The pollutants emitted during nighttime, can remain trapped within the NBL resulting in large pollution events. After sunrise, the heating of earth surface results in mixing of accumulated pollutants of nocturnal boundary layer with the residual layer air mass. Such meteorological phenomenon can have significant impacts on accumulation, dilution and redistribution of pollutant species and thus the local atmospheric chemistry.

#### 1.3.2 Land-Sea breeze circulation

The different heat capacity of land and ocean results in sea breeze temperature difference causing land-sea horizontal pressure gradients that drive shallow, diurnally varying daytime sea breeze and nighttime land breeze circulations. A sea breeze is a cool shallow wind that blows from ocean towards



**Figure 1.5:** Conceptual depiction of the interaction between the coastal sea breeze circulation and the land plume over the marine region during day time.

land during daytime. It occurs under generally clear sky and is caused by a 5°C or greater temperature contrast between the land and the ocean. The sea-breeze circulation dissipates at evening and a weaker, reverse circulation called the *land-breeze* forms in response to the nighttime cooling of the land surface relative to the sea [*Miller et al.*, 2003].

The coastal air-mass lofted by the sea breeze into the region above the MBL is known as the "land plume" or simply "elevated layer" [*Raman et al.*,

2002]. The formation mechanism of the land plume is sketched in the Figure 1.5. During the various campaigns (DYCOMS, FIRE, CITE 3, NARE 1992, NARE 1993, INDOEX and ICARB) conducted over different oceanic regions (Pacific Ocean, Atlantic Ocean, Arabian Sea, Bay of Bengal and Indian Ocean), the elevated pollution layers were observed varying in their form and degree of pollution [Paluch et al., 1992; Anderson et al., 1993; Berkowitz et al., 1995; Knapp et al., 1998a,b; Lelieveld et al., 2001; Simpson and Raman, 2003]. During different campaigns (INDOEX and ICARB) conducted over ocean surrounding Indian peninsula, the elevated pollution layers were observed through aerosol and trace gas measurements from several platforms. It quickly became clear that the majority of the pollutant outflow occurs in this elevated layer, rather than directly in the MBL [e.g., Manghnani et al., 2000; Lelieveld et al., 2001; Ramanathan et al., 2001; Leon et al., 2001, Reiner et al., 2001; Müller et al., 2001a,b; Franke et al., 2003; Raj et al., 2008; Satheesh et al., 2009; Srivastava et al., unpublished *manuscript*]. The pollution transport regime over Bay of Bengal has received little attention and could be associated with pollutant outflow in elevated layers from highly polluted Indo Gangetic Plain, an issue which deserves more research.

#### **1.3.3 Long range transport**

The large scale advection can transport the pollutants to great distances far away from their local source locations. Several studies have documented the continental outflow [*Calvert*, 1983; *Browell et al.*, 1996; *Blake et al.*, 1999] and intercontinental transport [*Wenig et al.*, 2003; *Forster et al.*, 2001] of air pollution all over the globe. The transport times are typically 5-10 days between continents [*Wild and Akimoto*, 2001]. Recently, the intercontinental transport of pollutants having oxidizing capacity of atmosphere like ozone and its precursors has acquired great concern in the scientific community [*Evans et al.*, 2000; *Trickl et al.*, 2003; *Stohl and Trickl*, 1999; *Stohl et al.*, 2003a,b; *Schmitt and Volz-Thomas*, 1997; *Cooper et al.*, 2010]. Ozone lifted to levels above the boundary layer can be transported over very long (intercontinental) distances due to its longer lifetime in the free troposphere (in day to months) and can contribute to the uncontrolled
background at the downwind region. This is because the major loss processes, scavenging by nitric oxide and dry deposition, occur at or very close to the surface of the earth. It has been shown [*Fiore et al.*, 2002, 2003; *Jaffe et al.*, 2003] that western North America receives a background ozone contribution from Asia and Europe, while *Auvray and Bey* [2005] have demonstrated that Europe receives ozone transported from both North America and Asia. In a recent study, *Cooper et al.* [2010] show a strong increase in free tropospheric ozone during spring time over western North America attributed to transport of Asian pollution.



Figure 1.6: Long range transport over Ahmedabad, India.

From the Asian perspective, 40% of the tropospheric ozone over East Asia may be influenced by European sources [*Newell and Evans*, 2000]. The model studies suggest that European emission may contribute about 4 ppbv of ozone over Central Asia in spring season [*Wild et al.*, 2004]. The trajectory based analysis made over Nainital, a high altitude site in northern India, shows the contribution of long range transport in surface ozone from Africa/Europe region is greatest in January-March at about 8-11 ppbv [*Kumar et al.*, 2010]. However, the contribution of transport of European emissions to the free tropospheric background ozone over Indian region has not been investigated in detail.

#### 1.4 Study of trace gases over the Indian subcontinent

Emissions of various gaseous pollutants have been projected to increase over the Indian subcontinent due to its rapid industrial development and economic growth. However, the observations of trace gases are limited over a few Indian locations. The first measurements of surface ozone is available for mid 1950s during pre-International Geophysical Year (IGY) which was made using Ehmert instrument [Ramanathan, 1956; Dave, 1957]. During 1960-70s, Indian Meteorological Department (IMD) started regular measurements of surface ozone at Delhi, Srinagar, Pune, Nagpur, Trivandrum and Kodaikanal [Sreedharan and Tiwari, 1971]. Later, measurements of surface ozone were started by groups at Jawaharlal Nehru University (JNU) in New Delhi and Indian Institute of Tropical Meteorology (IITM) in Pune [Varshney and Aggarawal, 1992; Khemani et al., 1995]. The first systematic measurements of surface ozone and its precursor gases were started in 1992 over urban (Ahmedabad), rural (Gadanki) and mountain (Mt. Abu) locations by Physical Research Laboratory (PRL), Ahmedabad [Subbaraya et al., 1995; Naja 1997; Lal et al., 2000; Naja and Lal, 2002; Naja et al., 2003a]. Several land campaigns like LC-1, LC-2, MOLEX etc [Lal et al., 2008 a,b] and ship campaigns like INDOEX, BOBEX, BOBPS etc [Naja, 1997; Lal et al., 2006; Chand et al., 2003; Sahu and Lal, 2006c; Sahu et al., 2006; Lal et al., 2007] were conducted over the Indian subcontinent and its surrounding marine regions to understand the spatial and temporal heterogeneity in the distributions of surface ozone and its precursors over this region. However, these studies were limited to surface based observations only.

The measurements of vertical distribution of ozone were initiated at Pune in 1966 followed by the measurements at Delhi and Trivandrum in 1969 by Indian Meteorological Department (IMD), However, concerns have been raised about the quality of the data [*Saraf and Beig*, 2004]. The vertical profiles of ozone are also available since late 1990s with good quality for some Indian cities (Delhi, Mumbai and Chennai) as a part of Measurement of OZone by AIrbus in-service airCraft (MOZAIC) program. However, these measurements are irregular and available up to a ceiling altitude of 300 mb only.

Measurements of vertical distributions of ozone and meteorological parameter, using ozonesonde and radiosonde were made from April 2003 to July 2007 over Ahmedabad to ceiling altitudes of 32-35 km. Later similar experiments were also conducted from Kanpur in the Indo-Gangetic Plain (December, 2004) [Gupta et al., 2007], Bay of Bengal and Arabian Sea (March to May, 2006) in campaign mode [Shilpy, 2008]. Aircraft observations of ozone and its precursors were also made from several land marine interfaces during January 2009. Most of the cited research work shows the general features of ozone in the surface and vertical distributions of ozone over land and marine regions. There are large uncertainty in identifying the sources of ozone and quantifying their contributions to the ozone distribution in the lower troposphere. The origin and budget of the free tropospheric ozone is poorly understood and have the highest priority among the research topics related to tropospheric ozone [Cooper et al., 2010 and references therein]. The budget and distribution of lower tropospheric ozone involves a large number of research problems such as background levels of ozone, regional contribution to its photochemical production; effect of boundary layer processes, boundary layer-free tropospheric exchange and long range transport on its distribution. In the present work, the distribution of ozone is discussed within the boundary layer and in the lower free troposphere (lower 4 km), over inland Indian location Ahmedabad, marine region surrounding the Indian peninsula and various land marine interfaces. In this work, we have attempted to identify the source regions and quantify their contributions in the ozone distribution by using backward trajectory, Potential Source Contribution Function (PSCF), Residence Time Analysis etc.

#### 1.5 Objectives and Chapter details of the thesis

This thesis is focused on the study of various atmospheric processes affecting the distributions of ozone and its precursors in the lower troposphere over the Indian subcontinent and the surrounding marine regions. The following objectives are particularly addressed in the present work:

(1) To characterise the seasonal variation of ozone within the boundary layer and in the lower free troposphere over a tropical urban location Ahmedabad, and estimate the contributions of regional pollution and long-range transport.

(2) To investigate the role of continental transport on the distributions of lower tropospheric ozone and it's precursors over the pristine marine environments surrounding the Indian subcontinent.

(3) To study the chemical and dynamical processes affecting the distributions of ozone and its precursors over different land marine interfaces.

The thesis contains six chapters including the present **Chapter 1** which gives the introduction of the basic works done in this field of research.

**Chapter 2** gives a brief description of various instruments used during this work. The chapter gives information about the operating principles along with technical and calibration details of ozone analyzers, ozonesonde and radiosonde. The basic elements of gas chromatography (used for the measurements of CO, CH<sub>4</sub> and NMHCs) along with instrumental details are summarized. A brief description of satellite instruments, MOPITT (Measurements Of Pollution In The Troposphere), OMI (Ozone Monitoring Instrument) and AATSR (Advanced Along-Track Scanning Radiometer) is presented.

**Chapter 3** discusses the effects of various atmospheric processes like boundary layer dynamics, regional pollution and long range transport on the distribution of ozone within the lower troposphere (below 4 km) over Ahmedabad, an urban city of India. The seasonal variation of mixed layer height, and its effects on the dilution of locally emitted pollutants is presented. Further, the background levels of ozone are estimated within the boundary layer and in the lower free

troposphere. The ozone build up in regionally polluted air masses are quantified. The levels of ozone in air-masses originated from regions of Africa/Europe are estimated in different seasons to find out the contribution of long range transport. These estimates provide useful information about the dominant processes affecting the distribution of ozone during different seasons in the lower troposphere.

**Chapter 4** is focused on the study of vertical distributions of ozone and meteorological parameters in the lower troposphere (lower 4 km) along with surface distributions of ozone and its precursors over Bay of Bengal and Arabian Sea. The vertical distribution of ozone is investigated in polluted and pristine marine regions. The continental source of high levels of ozone in polluted marine region is identified over northern BoB by using PSCF analysis. The contribution of identified source region is estimated using residence time analysis to the levels of ozone. The latitudinal variation and inter correlation studies of surface trace species are made to extract further information about the pollution plume.

**Chapter 5** is based on the aircraft observations of ozone, CO,  $CH_4$  and NMHCs over different land marine interfaces during a campaign in the month of January 2009. The vertical, latitudinal and longitudinal variations of these gases are discussed in detail. The inter correlations of these gases are used to identify the chemical processes and age of air mass. Back trajectories are analysed to identify the dynamical processes affecting the distributions of these gases over different regions during this period.

**Chapter 6** summarizes the major results as well as the limitations of the present work. This chapter also discusses about the future scope of present study in this field of research.

# **Chapter 2**

### **Experimental techniques**

The sensitive and accurate instrumentation form a basis to record the composition of the atmosphere. There have been phenomenal improvements in the measurement techniques of trace gases in the last decade. The short lived reactive trace species like ozone and oxides of nitrogen are measured by in-situ analyzers whereas gas chromatography is widely used method for the measurements of long lived species like CH<sub>4</sub> and NMHCs. The various techniques used for the measurement of ozone and its precursors are discussed here in detail.

#### 2.1 Techniques for ozone measurements

The interest in atmospheric ozone measurement dated from the very beginning of Schönbian's discovery of ozone [*Schönbian*, 1840]. He promulgated a simple method using iodized starch paper to qualitatively assess the ozone amount but this method was vulnerable to humidity and oxidants [*Bojkov*, 1986]. Chemiluminescent method is developed for the ozone measurement in the last century. The oxidation of olefins, rhodamin B dye and luminol by ozone exhibits chemiluminescence, but these substances may get affected by the light and moisture. Ultra-Violet (UV) radiation technique was first carried out in 1912 by

*Fonrobert* [1916] which is well accepted for the surface measurements of ozone now a days. In 1930s, the total columnar ozone observations were made by Godard Dobson [*Dobson*, 1931]. Later, the method was further developed to provide the vertical profiling of ozone known as "Unkehr method" [*Hahn et al.*, 1995]. The rocket borne UV optical sensors were also developed to get the vertical profile of ozone, but below 20 km, data were subject to large source of error due to both instrument as well as atmospheric scattering [*Lal*, 1981].

The total column ozone has been derived for the first time from space by Total Ozone Monitoring Spectrometer (TOMS) since 1979 from ultraviolet measurements of scattered sunlight [McPeters et al., 1998]. SAGE I/II (Stratospheric Aerosol and Gas Experiment) provided the information of ozone distribution in the stratosphere and upper troposphere since 1979, but with poor spatial resolution and coverage. The Global Ozone Monitoring Experiment (GOME), a nadir viewing spectrometer, has been operated since 1995 and provides the vertical profile of ozone in the troposphere and lower stratosphere with a vertical resolution of 5 km [Burrows et al., 1999]. Another satellite borne system Ozone Monitoring Instrument (OMI; launched in 2002) provides the tropospheric columnar ozone. Tropospheric Emission Spectrometer (TES) is operational since 2002, with limb and nadir viewing modes, capable of providing ozone profiles with an altitude resolution of 2.3 km from 0 to 34 km [Beer et al., 2006]. Thus, the satellite based ozone measurements have global coverage area but poor vertical resolution and their validation with in-situ measurements are still a major concern.

The active remote sensing techniques like DIfferential Absorption Lidar (DIAL) can provide the information of ozone distribution with good vertical resolution but its use is often limited by the sensitivity, complexity of the instrumentation, data reduction procedure and the cost. The balloon borne ozonesonde is the only in-situ measurement technique of the ozone observations from surface to lower stratosphere (~ 35 km) with a good vertical resolution and accuracy. This technique is rather simple and inexpensive. The photometric

technique and electrochemical techniques for in-situ measurements of ozone are discussed here in detail.

#### 2.1.1 Photometric technique for ozone measurement

A measurement of ozone using UV radiation technique was based on the absorption of UV radiation at 253.7 nm wavelength by ozone molecules [*Fonrobert*, 1916]. It is well established and frequently used for the measurement of surface ozone. The surface and aircraft study of ozone is made using ozone analyzers (2B Tech. Model 205, ESA model O<sub>3</sub>41M, Thermo model 49i) based on this technique. The operational principle of these instruments is given by Beer Lambert law as follows.

Intensity of the radiation I, passing through normal ambient air is given by

$$I(\lambda) = I_o(\lambda) \exp\left[-\int_0^1 (\sigma_{O_3}(\lambda)n_{O_3} + \sigma_r(\lambda)n_{air} + \sum \sigma'_i(\lambda)n_i)dl\right]$$

Intensity of the radiation passing through O3 scrubbed ambient air

$$I'(\lambda) = I_o(\lambda) \exp\left[-\int_0^t (\sigma_r(\lambda)n_{air} + \sum \sigma'_i(\lambda)n_i')dl\right]$$

Where

 $I(\lambda)$  = Attenuated intensity of radiation due to all species

 $I_o(\lambda)$  = Unattenuated intensity

 $I'(\lambda)$  = Attenuated intensity of radiation due to species other than O<sub>3</sub>

 $\sigma_{o_3}(\lambda)$  = Absorption cross section of ozone at wavelength  $\lambda$ 

 $\sigma_{air}(\lambda)$  = Rayleigh scattering cross section at wavelength  $\lambda$ 

 $\sigma'_i(\lambda)$  = Absorption cross section of other species at wavelength  $\lambda$ 

 $n_{O_1}$  = Number density of ozone

 $n_{air}$  = Number density of air

 $n_i' =$  Number density of other species

The ratio of the two signals gives

$$\frac{I}{I'} = \exp[-\int_{0}^{l} (\sigma_{O_{3}} n_{O_{3}} dl)]$$

The ratio of the intensities of two signals is a function of number density of the ozone. This principle is implemented in the analyzers to measure the ozone mixing ratio in the ambient air. In the analyzer, the ambient air is sucked inside the optical chamber via two different paths alternatively with the help of a pump. The first path consists of ozone scrubber (Copper screens coated with manganese dioxide (MnO<sub>2</sub>)), which converts the ozone present in the sample air to oxygen. The second path is the normal path which samples the ambient air. The air is sampled via two paths for the same time duration (1 sec for 2B, 5 sec for ESA and 10 sec for thermo). The optical bench is illuminated by UV lamp placed at one



**Figure 2.1:** Absorption spectrum of ozone (solid curve), and response of UV detector Cesium Telluride (dashed curve). Emission lines of mercury UV lamp are shown by straight vertical lines. Dotted vertical lines are emission lines eliminated by Vycor filter.

end of the cell, and intensity of the transmitted light through the  $O_3$  scrubbed air and sample air is measured alternatively by a UV photometer placed at other end of the cell. The ratio of intensities measured for ambient air (*I*) and ozone scrubbed air (I') gives the number density. The corrections due to temperature and pressure variations are also compensated in the absorption cells.

The UV lamp used in analyzer is a low pressure, cold cathode mercury vapor lamp with main emission line at 253.7 nm (Figure 2.1). The absorption coefficient of ozone peaks at the same wavelength as shown in the Figure 2.1. The Vycor filter is used to eliminate the emissions lower than 200 nm. The filtered radiation is detected by solar blind "Cesium Telluride" vacuum photodiode having built in interference filters centered around 253.7 nm.



Figure 2.2: Schematic diagram of a single beam ozone analyzer.



Figure 2.3: Schematic diagram of a dual beam ozone analyzer.

The two types of analyzers are available for the measurements of ozone, single beam and double beam, depending on presence of single and double optical bench respectively. In the single beam analyzer, the ozone-scrubbed and unscrubbed ambient air passes through the single absorption cell each for 5 seconds (ESA Model  $O_341M$ ), thus measuring *I* and *I*' alternatively (Figure 2.2).

Ozone Monitor	2B Tech Model 205	ESA Model O <sub>3</sub> 41M	Thermo Model 49i
Optical Bench	Dual Beam	Single Beam	Dual Beam
Range	0 – 200 ppmv	0 – 10 ppmv	0 – 200 ppmv
LDL	< 2 ppbv	1 ppbv	1.0 ppbv
Zero Drift	< 1 ppbv/ hour	< 1 ppbv/7 days	< 1 ppbv/24 hour
	< 2 ppbv/7 days		< 2 ppbv/7 days
Span Drift	<1% per 7 days	< 1% per 7 days	< 1% per month
Response Time	2 s	10-90 s	20 s
Sample flow rate	1.2 LPM	1.6 LPM	1 LPM
Weight	2.3 kg	20 kg	18 kg
Power	5 W	70 W	150 W
Operating	0°C to 35°C	+15°C to 35°C	+20°C to 30°C
Temperature			

Table 2.1: The specifications of various ozone analyzers used in the present study

In the dual beam ozone analyzer, there are two absorption cells with two UV detectors (Figure 2.3). A pair of solenoid valve switch to send ozone-scrubbed air and ambient air through the two absorption cells, thus measuring I and I' simultaneously (2B Tech Model 205 and Thermo Model 49i). The dual beam analyzer has superiority over single beam analyzers in the perspective of lower response time. The specifications of these analyzers are listed in Table 2.1.

The multipoint calibration of these analyzers is done regularly with the help of ozone calibrator (Sonimix 6000 C2) periodically. The calibration plot for ESA analyzer and 2B tech analyzer are shown in Figure 2.4. A good linearity was



Figure 2.4: Calibration curves of surface ozone for ESA analyzer and 2B Tech analyzer.

found in the range of 0 to 300 ppbv with  $r^2 \sim 0.99$  for both the instruments.

#### 2.1.2 Electrochemical technique for ozone measurement

The application of electrochemical technique to ozone measurements led to the Brewer Mast (BM) sonde [*Brewer and Malford*, 1960]. The BM sonde consists of a single electrochemical cell having silver wire anode and platinum gauze cathode immerged in an alkaline potassium iodide (KI) solution. A motor pumps ambient air through a Teflon tube into the reaction chamber. The further details of this type of sonde are given by *Claude et al.* [1987]. The "KC sonde", developed by *Kobayashi and Toyama* [1966], is another galvanic cell having platinum gauze cathode and carbon anode immerged in neutral KI solution. The most successful is Electrochemical Concentration Cell (ECC) ozonesonde developed by *Komhyr* [1969, 1971], which is used in the present work (Figure 2.5).

ECC ozonesonde is a lightweight, balloon-borne instrument that is mated to a conventional meteorological radiosonde. As the balloon carrying the instrument package ascends through the atmosphere, it transmits the information on ozone and standard meteorological quantities such as pressure, temperature and humidity to the ground station. The air segment of this experiment consists of ozonesonde (ECC sensor, Teflon pump, V2C (voltage to current) interface card), meteorological radiosonde and GPS. The ground segment consists of radio receiver, modem and a computer for the data acquisition. The various parts of the balloon sounding systems are discussed here in detail.

#### 2.1.2.1 Electrochemical Concentration Cell (ECC) sensor

The ECC-sensor consists of two half cells made of up polytetrafluoroethylene (Teflon TFE resin) which serves as cathode and anode chamber. Both cells contain bright platinum mesh, serving as electrodes and are immersed in KI solutions of different concentrations. The two chambers are linked together by an ion bridge in order to provide an ion-pathway and to prevent mixing of the cathode and anode electrolytes, thereby preserving their concentration. The Platinum electrodes are chemically inert and they do not take part in chemical reactions. The driving electromotive force (0.13 V) is because of the difference in the concentrations of cathode and anode electrolytes. The ambient air containing O<sub>3</sub> molecules is bubbled through the cathode solution and the following reaction occurs:

#### $2 \text{ KI} + \text{O}_3 + \text{H}_2\text{O} \quad \rightarrow \quad 2 \text{ KOH} + \text{I}_2 + \text{O}_2 \quad (\text{R2.1})$

Iodine,  $I_2$ , is formed and the  $I_2$  concentration of the solution starts to increase. If the external circuit is closed, reaction R2.1 is followed by reactions R2.2 and R2.3.

In the cathode chamber

3 I <sup>-</sup>	$\rightarrow$	$I_3^- + 2 e^-$	(R2.2)
In the anode chamber			
$I_2 + 2 e^-$	$\rightarrow$	2 I <sup>-</sup>	(R2.3)
These chemical reactions result			
<b>3</b> $I^{-} + I_{2}$	$\rightarrow$	$I_3^- + 2 I^-$	(R2.4)

The emf (E) can be calculated approximately from the Nernst equation

$$E \approx -\frac{0.0591}{2} \times \log K$$

Where E is the emf produced within the cell (approximately 0.13 V at 25°C).

$$K = \frac{(a_1)_{I_3^-}}{(a_4)_{I_2}} \times \frac{(a_3)^2 I^-}{(a_2)^3 I^-}$$

Where  $a_1$ ,  $a_2$  are the activities of the tri-iodide and iodine within the anode chamber and  $a_3$ ,  $a_4$  are the activities of the iodide and iodine within the cathode chamber. The activities are approximately equal to concentrations. K  $\approx 1$  at equilibrium.

The partial pressure of ozone is a measure for local ozone concentration. It is given by the following expression

$$P_3 = 4.307 \times 10^{-4} (I - I_{BG}) \times T_p \times t \times C_{ef}$$

Where,

 $P_3$  = partial pressure of ozone (mPa)

I = measured ozone current ( $\mu A$ )

 $I_{BG}$  = current caused by other oxidants like  $O_2$  ( $\mu A$ )

 $T_p$  = measured air flow temperature from pump base (K)

t = pumping time for 100ml air (sec)

C<sub>ef</sub>=correction due to reduced ambient pressure for pump



Figure 2.5: Schematic of the ECC ozonesonde.

#### 2.1.2.2 Radiosonde

The radiosonde measures the meteorological parameters and transmits the data to the ground based receiving and processing system (Figure 2.6). It is an electronic unit that comprises three major sections: a suite of sophisticated meteorological sensors, signal processing electronics and a radio transmitter to relay the measurements to the ground based receiver. In this study, we have used Vaisala RS 80-15 radiosonde, Finland which uses capacitance based temperature, pressure and relative humidity sensors to measure meteorological quantities [*Vaisala*, 1989]. The specifications of all the meteorological sensors including their resolution and accuracy are given here.



Figure 2.6: The Vaisala RS80 radiosonde and the Garmin GPS.

BAROCAP Capacitive aneroid
1060 hPa to 3 hPa (mb)
0.1 hPa
0.5 hPa
0.5 hPa
THERMOCAP Capacitive bead
+60°C to -90°C
0.1°C
0.2°C up to 0.5 hPa, 0.3°C for 50-15 hPa, 0.4°C above 15 hPa level
0.2°C

Humidity	
Sensor type	HUMICAP Thin film capacitor
Measuring range	0 to 100% RH
Resolution	1% RH
Accuracy:	
Reproducibility	< 3% RH
Repeatability	2% RH

#### 2.1.2.3 Global Positioning System (GPS)

Global positioning system (GPS 25-LVC; Garmin) (Figure 2.6) onboard the balloonsonde payload calculates its location accurately by receiving the microwave signals from the GPS satellites. The GPS consists of 24 satellites with orbital period of 12 hours, distributed in 6 orbital planes equally spaced in angle. Each satellite carries an atomic clock which transmits its location in coded signal. The receiver system requires minimum four satellites signals to calculate its location in space and time. The horizontal and vertical accuracy of the GPS receiver is  $\pm 2$  m and  $\pm 10$  m respectively.

#### 2.1.2.4 V2C Interface

The innovative system designs V2C interface electronics is an important part of digital data acquisition. The analog data of ECC ozonesonde, meteorological data of radiosonde and GPS information are sent to V2C interface (Figure 2.7). The GPS data is communicated to V2C interface at every 5 s interval. The data are then compiled into a binary packet along with CRC (Cyclic Redundancy Check) and sent for frequency shift keying (FSK) modulation. The signal is finally frequency modulated at a frequency between 400 to 406 MHz, before transmission. The FM modulated data packets are transmitted at every 1.2s.

#### 2.1.2.5 Ground based receiver system

The ground segment consists of a front end Yagi antenna with a preamplifier, a radio receiver, a Modem (300 baud) and a computer to receive and store the transmitted data. The dedicated data acquisition software acquires and logs the data in binary format with a real time display of balloon sounding parameters. The post processing software extracts the information of sounding altitude, temperature, RH, pressure, wind speed, wind direction and ozone.



Figure 2.7: The balloonsonde data coding, transmission and receiving system overview.

#### 2.1.2.6 Preparation and launch of Ozonesonde

The preparation and checking of ozonesondes carried out by standard method [*Komhyr*, 1986]. The ozonesonde performance (pump efficiency, sensor response etc) is checked, and ECC anode and cathode sensors are conditioned with KI sensing solution before 3 days to one week prior to the flight. The sensors are recharged with electrolytes on the flight day before the launch. The prepared



Figure 2.8: Balloon with ozonesonde payload during ascent.

ozonesonde is kept in a styrofoam box and launched with the help of a 1200 gram rubber balloon filled with helium gas. The payload is kept about 30 m away from the balloon with the help of a pulley to avoid the sample contamination by balloon (Figure 2.8). The balloon ascends to an altitude of about 35 km ( $\sim$  4 hPa) before it bursts. A parachute is used to limit the decent velocity of the payload after balloon burst. The ECC sensor can be recovered after flight and reused after standard cleaning and checking procedure.

#### 2.2 GC technique for CO and CH<sub>4</sub> measurements

The chromatography is a technique which separates the components of a mixture through their differential partitioning between the stationary and mobile phases. In gas chromatography, the analyte in gaseous mobile phase passes through the liquid or solid stationary phase. The difference in partition coefficients of the components of the analyte results into different retention time on the stationary phase. The different rates of migration as the analyte moves over the adsorptive stationary phase provide separation. This separation process takes place within a chromatographic column containing the stationary phase. The repeated adsorption and desorption of the components of the mixture determines the rate of migration through the column.



Figure 2.9: The schematic of gas chromatograph for CO and CH<sub>4</sub>.

The GC Varian Vista 6000, USA with Flame Ionization Detector (FID) is used for the measurement of CO and CH<sub>4</sub>. The column is a 5 m long packed SS tube with a stationary phase of molecular sieves 13X. The carrier gas is the high purity helium gas (99.9999%) with a flow of 30 ml/min. Hydrogen and zero air are the flame gases with their respective flows of 30 ml and 300 ml.

The GC with its peripherals schematic is shown in Figure 2.9. The column is kept in isothermal condition at 70°C during sample processing and baked at 150°C to remove the column impurities. The air samples are collected in preevacuated glass bottles (300-800 ml volume) and injected into the GC with the help of six port switching valve (VICI, USA). The CO cannot be directly identified by the flame ionization detector. It is converted to  $CH_4$  by methanizer containing Nickel catalyst at 325°C by following reaction.

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

The chromatogram of CO and  $CH_4$  is shown in figure 2.10. The calibration of CO and  $CH_4$  is performed with the help of calibration gases supplied by LINDE.



Figure 2.10: A typical GC chromatograph for CO and CH<sub>4</sub>.

### 2.3 GC technique for NMHCs measurements

The GC Hewlett Packard 5890 series II equipped with Flame Ionization detector is used to measure the NMHCs in the air samples. The column is the porous layer open tubular (PLOT) capillary column of 50 m length and 0.32 mm diameter having stationary phase of KCl/Al<sub>2</sub>O<sub>3</sub>.

Helium gas is used as the carrier gas with a flow rate of 8 ml/m, and hydrogen and zero air are used as the flame gases with the flow rates of 30 ml/m and 300 ml/m respectively. The hydrogen generator (Whatman, model 7532) and zero air generator (Whatman, model UK 76-883) are used to produce the high purity hydrogen and zero air respectively. The pre-concentration unit is used to

trap the sufficient amount of NMHCs in the sample line due to their trace amounts (pptv to few ppbv range) in the atmosphere. The trapping is done, using 1/8" stainless steel loop filled with 75-100 micron size glass beads and immerged into the liquid nitrogen (Figure 2.11). The sample passes through this cryo trapping system and NMHCs are effectively trapped within this loop. The sample trapped in loop is heated to 100°C with the help of boiling water and carried with helium gas into the GC. The sample loading, isolation and injection processes are controlled by six port and eight port actuated valves (Valco Instruments limited) in the transfer line shown in the Figure 2.11. To separate the C2 to C5 hydrocarbons with wide range of boiling points effectively, the GC temperature was programmed as follows:

-1°C (3 min) ----- 4°C/min ----- 40°C (4 min) ----- 3.5°C/min ----- 110°C (0 min) ----- 35°C/min ----- 200°C (10 min).



**Figure 2.11:** The schematic of GC and sample injection system for the analysis of NMHCs.



Figure 2.12: A typical NMHC GC chromatograph.

Analytical data are processed by the Hewlett Packard integrator (model HP3395). The gases are identified according to their retention times. A typical chromatogram of NMHCs is shown in the Figure 2.12. The system was calibrated with the standard reference gas supplied by Intergas, UK.

### 2.4 Satellite based measurements of CO, NO2 and fire

Measurement of atmospheric composition from space has revolutionized our understanding of three dimensional distributions of trace gases in the atmosphere. The satellites have enabled the direct observations of transport of anthropogenic species and global observations of regulatory species over a period of years. The fire activities are also being captured by the satellite based instruments. Here we will discuss the satellite observations of CO, NO<sub>2</sub> and fire used in the present study.

# 2.4.1 CO observations by Measurement Of Pollution In The Troposphere (MOPITT)

The MOPPIT instrument is a nadir viewing IR correlation radiometer, launched in 1999 aboard the NASA Terra satellite. This satellite is in a polar, sunsynchronous orbit at 705 km altitude with an exact 16 days repeat cycle and a 1030 (LT) northward and southward cross over time of equator. The instrument field of view is 22 x 22 km<sup>2</sup> with across track swath of 640 km which provides global coverage in every 3 days. The MOPITT is a cross-track scanner which senses upwelling terrestrial infrared radiation (4.7 µm) and reflected solar radiation (2.2-2.4 µm) by gas correlation spectroscopy to get the profile of carbon monoxide and columnar amount of carbon monoxide and methane respectively. In gas correlation spectroscopy, a cell of the gas to be measured is used as an optical filter in the infrared to measure the signal from the same gas in the atmosphere. The CO profile is reported at seven pressure levels (1000 mb, 850 mb, 700 mb, 500 mb, 350 mb, 250 mb, and 150 mb levels) in the troposphere [Deeter et al., 2004]. The MOPITT version 3 retrievals, used in the present study, have been validated using in-situ aircraft measurements and results show a good agreement with the average bias less than 20 ppb at all levels [Emmons et al., 2004]. Kar et al. [2008] have shown that daytime MOPITT retrieval can provide the useful information on the surface sources of atmospheric CO over the Indian subcontinent.

## 2.4.2 NO<sub>2</sub> observations by Ozone Monitoring Instrument (OMI)

OMI is a wide angle, non-scanning, nadir viewing near UV/Visible Charge Coupled Devise (CCD) spectrometer onboard NASA's Earth Observing System (EOS) Aura satellite (launched in July 2004). The AURA satellite orbits at 705 km in a sun-synchronous polar orbit with an exact 16 days repeat cycle and a 1345 local equator crossing time. OMI measurements cover a spectral region of 264– 504 nm (spectral resolution 0.42 nm to 0.63 nm) and a nominal ground footprint of 13 x 24 km<sup>2</sup> at nadir. This instrument measures the solar backscattered irradiance in a swath of 2600 km with a telescope Field of View (FOV) of 115° in across-track dimension, and provides the information of ozone (columnar and profile), clouds, aerosols, surface UV irradiance and columnar amount of several trace gases like NO<sub>2</sub>, SO<sub>2</sub>, HCHO, BrO and OClO. The total column and tropospheric column NO<sub>2</sub> is measured in the spectral range of 405-465 nm. The estimated accuracy of vertical column NO<sub>2</sub> under clear sky condition is ~ 5% (~  $0.2 \times 10^{15} \text{ molec/cm}^2$ ) in unpolluted case and 20% (~  $0.8 \times 10^{15} \text{ molec/cm}^2$ ) in polluted case. The vertical column error can be further larger (about 50%) in the presence of pollution and cloud. The relative errors in the tropospheric column NO<sub>2</sub> are ~ 30% and ~ 60% under clear and cloudy conditions respectively [*Boersma et al.*, 2002].

OMI's spatial resolution exceeds Global Ozone Monitoring Experiment (GOME)'s 320 x 40 km<sup>2</sup> resolution by a factor between 5 and 40 and SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY)'s by a factor up to 5.7 [*Wenig et al.*, 2008]. Its daily global coverage is an improvement over GOME and SCIAMACHY, which provide the global coverage in 3 and 6 days respectively.

## 2.4.3 Fire detection by Advanced Along-Track Scanning Radiometer (AATSR)

AATSR is the imaging multi-spectral radiometers (Vis/IR) & multiple direction/polarisation radiometers on board the European Space Agency (ESA) satellite ENVISAT. It is the most recent in a series of instruments designed primarily to measure Sea Surface Temperature (SST), following on from ATSR-1 and ATSR-2 on board ERS-1 and ERS-2. AATSR data have a resolution of 1 km at nadir, and are derived from measurements of reflected and emitted radiation taken at the wavelengths 0.55  $\mu$ m, 0.66  $\mu$ m, 0.87  $\mu$ m, 1.6  $\mu$ m, 3.7  $\mu$ m, 11  $\mu$ m and 12  $\mu$ m.

The fire counts are obtained from the AATSR using data from algorithm 1 in the present study, which identifies a hot spot if the temperature is greater than 312 K in the 3.7 micron band. Other space borne systems that provide information about fires are the Advanced Very High Resolution Radiometer (AVHRR) and Moderate Resolution Imaging Spectro-radiometer (MODIS). Data from AVHRR and MODIS suffer from over estimation of fire due to interferences by solar radiation during daytime [*Kaufman et al.*, 1998]. AATSR senses the fire during nighttime only thus minimizing the interferences caused by solar reflectance.

# Chapter 3

# Distribution of ozone in the lower troposphere over Ahmedabad

The Asian continent has been recognized for higher ozone production due to rapid industrialization and urbanization [*Andreae and Crutzen*, 1997]. This region is a major source of free tropospheric ozone over western America in upwind condition [*Cooper et al.*, 2010]. The Chemistry Transport Model (CTM) estimation [*Berntsen et al.*, 1996] indicates that ozone production efficiency is maximum over India, followed by Japan and China, under the enhancement to precursors over these regions. Thus, the investigation of lower tropospheric ozone is extremely important particularly over the Indian region.

Distribution of ozone in the lower troposphere is governed by various processes. The in-situ photochemical production and loss of ozone play major role within the boundary layer whereas transport is the main factor altering its distribution in the lower free troposphere. There is a need to quantify the relative contributions of ozone produced due to regional emissions of precursors and transport from distant upwind locations. The back-trajectories are found to be an important tool to interpret the ozone levels in relation to transport from source regions in several studies [*Lewis et al., 2007; Jiang et al., 2003; Taubman et al., 2006; Suthawaree et al., 2007; Delcloo and De Backer, 2008; Devis et al., 2009*].

A refined trajectory based method has been introduced by *Pochanart et al.* [2001] in which surface ozone data are tagged with the residence time of air-mass to interpret the contributions of long range transport and regional production of ozone over Europe. This approach was used for the first time in analyzing ozonesonde data over Europe [*Naja et al.*, 2003b] and Japan [*Naja and Akimoto*, 2004]. Such trajectory assisted analysis of ozone sounding data is not made over the Indian region.

The studies of surface ozone and its precursors over India within the boundary layer [Khemani et al., 1995; Lal et al., 2000; Naja et al., 2002; Pulikesi et al., 2006; Debaje et al., 2003; Reddy et al., 2008] and at high altitude sites [Naja et al., 2003; Kumar et al., 2010] show distinct seasonal variations. The mixing ratios of surface ozone are reported to be maximum during late autumn, winter and early spring in western India. Such elevated levels are explained on the basis of accumulation of pollutants in the shallow boundary layer and availability of sufficient solar flux for this period. The lower mixing ratio of ozone in summer is associated with the onset of Indian monsoon resulting in low level precursors of ozone, cloudy conditions and rainfall. The ozone observations at two high altitude sites, Mt Abu (1680 m amsl) and Nainital (1958 m amsl), situated in western and northern parts of India respectively, also exhibit different seasonal cycles. The seasonal pattern of ozone at Mt. Abu is similar to Ahmedabad, while that at Nainital shows prominently higher mixing ratio of ozone during the spring [Kumar et al., 2010]. This feature indicates that there is distinguishable role of regional emissions of precursors and local meteorology in seasonal variations of ozone over two different high altitude locations.

To delineate the contributions of various processes like boundary layer dynamics, local photochemistry, regional emissions of precursors, onset of monsoon, long range transport etc. in the distribution of ozone within the boundary layer and in the lower free troposphere, the simultaneous investigation of ozone in these atmospheric regions is needed. This chapter presents simultaneous seasonal variations of ozone in the boundary layer and in the lower

#### 3.1 Site description and meteorology

The observational location, Physical Research Laboratory (PRL), is situated in the western part of Ahmedabad (23.03°N, 72.54°E, 49 m amsl). The location of Ahmedabad is shown in Figure 3.1. This is an urban city having several industries and a power plant. The observation site is situated about 10-15 km away from the industrial area. The balloon flight experiment was conducted from the roof of the main campus of PRL from April 2003 to July 2007. The ECC ozonesondes and radiosondes were launched fortnightly in the time window of 0900 to 1000 hrs (LT) in coordination with local Air Traffic Controller (ATC). A total of 82 payloads were launched during the study period. The details of the balloon payload have been given in Chapter 2.



**Figure 3.1:** Location of observational site Ahmedabad (23.03°N, 72.54°E; 49 m above the mean sea level).



**Figure 3.2:** Average seasonal wind fields at 925 mbar over India and surrounding regions (Ahmedabad is marked in the map) during 2003–07. The wind field data are obtained from NCEP/NCAR reanalysis.

Figure 3.2 shows average winds over the Indian region during 2003-2007. The wind obtained NCEP/NCAR data are from reanalysis (http://www.cdc.noaa.gov/data/reanalysis/reanalysis.shtml). This figure consists of four panels, showing the average wind fields for five years from 2003 to 2007 at 925 mbar for different seasons. These plots represent the general transport patterns during different seasons over the Indian subcontinent. During the summer-monsoon (also known as south-west monsoon) period, from June to August, the south-westerly winds blowing from marine region bring the moist air resulting into heavy rainfall. The relative humidity is observed to be very high up to 70-80% during this period. On the other hand, the sub-continent experiences drier northerly and north-easterly winds (relative humidity about 20-30%) during the winter season from December to February. Spring (March to May) and autumn (September to November) seasons are referred as the transition periods, when the sub-continent undergoes a wind reversal from north-easterly to south-westerly and vice versa. The difference between summer and winter temperatures is observed to be around 13°C.

# 3.2 Surface ozone and mixed layer height over Ahmedabad3.2.1 Distribution of surface ozone over Ahmedabad

The average annual distribution of ozone has been studied in detail over Ahmedabad since 1991 [*Lal et al.*, 2000]. Generally, ozone levels are found to be higher during late autumn and winter months. The lowest ozone mixing ratios are observed during summer season. This seasonal variation of ozone is caused by several factors. One of the major factors is the seasonality in the mixing ratios of precursors of ozone (CO, NO<sub>x</sub>, CH<sub>4</sub> and NMHCs) and solar radiation flux.

Low levels of ozone during late spring and summer are due to the low levels of precursors related to onset of southwesterly monsoon which brings pristine marine air. The wind circulation changes from southwesterly to northeasterly in the late autumn and persists during winter. The northeasterly wind brings polluted air, rich in precursors of ozone, from northern Indian regions particularly Indo-Gangetic Plain. Effects of these processes on ozone and its precursors have been studied in detail over this study region [*Naja*, 1997].

Another key parameter which affects the distribution of these gases is "atmospheric boundary layer" which limits the extent of their vertical mixing. Atmospheric boundary layer (ABL) dynamics and its effects on the distribution of trace gases have not been studied in detail over this region. In the forthcoming sections, we will discuss about the seasonal variation of mixed layer and its impacts on the distributions of trace gases.

#### 3.2.2 Seasonal variation of mixed layer height over Ahmedabad

Knowledge of mixed layer height (MLH) is one of the crucial parameters for the treatment of ABL processes and its impact on trace gas distributions. The strength of pollutant dispersion and hence the distributions of trace gases within the ABL are governed mainly by the magnitude of MLH (h), thereby providing a direct and strong justification on the accuracy of h in observational and modeling studies.



**Figure 3.3:** Typical virtual potential temperature and specific humidity profiles observed over Ahmedabad for two days of different years. Solid line represents the VPT profile and dash dot line shows the specific humidity profile. Horizontal dash line shows the top of the mixed layer.

The radiosonde data obtained from balloon ascents are used to extract the MLH information. A linear interpolation technique is adapted to regrid the raw meteorological data to 10 m regular interval for bringing uniformity to all the ascents and makes the comparison convenient among different ascents. These

regridded data are used for the calculation of virtual potential temperature ( $\theta_v$ ) and specific humidity (q), the key parameters used for the determination of MLH top, using following equations:

$$\theta_v = \theta (1+0.61 \text{ r})$$
  
q = 0.623 e/ (p-0.377 e)

Where  $\theta$  is the potential temperature (K), r is the mixing ratio (g/kg) of water vapor, p is the ambient pressure (mb) and e is the vapor pressure (mb) of air parcel. Due to extensive turbulent mixing, the values of virtual potential temperature and specific humidity remain almost constant in the mixed layer. In most of the vertical profiles of these parameters, a sharp increase in  $\theta_v$  is noticed with a concurrent decrease in specific humidity just above the top of the mixed layer. In the present investigation, we have identified the top of the mixed layer as the height at which the first significant inversion of virtual potential temperature and specific humidity profiles is evident [Subrahamanyam et al., 2003]. To be more precise, the term 'significant' indicates a VPT gradient of 2 K/km or more [Parasnis and Morwal, 1991]. The accuracy of the identification of MLH depends on the vertical resolution of the VPT. The gradient method generates a maximum uncertainty of  $\pm$  50 m in the identification of MLH. Demonstration of top of the mixed layer in typical plots of  $\theta_v$  and q observed on two different days in different years are shown in Figure 3.3. The top of the mixed layer is marked with horizontal dashed lines in both the profiles. It was not possible to determine the top of the mixed layer in all the profiles, and about fourteen ambiguous profiles were discarded from the analysis in which a clear-cut identification of the mixed layer was not evident as per above mentioned criteria.

The variation of mixed layer height can significantly affect the dilution and accumulation of anthropogenically emitted precursors of ozone and thus play an important role in the distribution of ozone in the lower troposphere. The seasonal variation of mixed layer height over the study location is examined. Figure 3.4 consists of four panels representing the variation of mixed layer top in the four seasons respectively. In order to accommodate January and February months along with the December (winter season) in the same plot, the day numbers of January and February are biased by 365. Figure 3.4a represents the MLH variation for spring season (MAM). The mixed layer height varies within a range of about 200 m to 1120 m during these months. Though a clear-cut trend is not seen, the first half of this season (March to mid of April) experiences lower heights of mixed layer as against higher heights seen in the later half of the season. Barring a low height of about 250 m in May 2004, the second half of the season consistently experiences the mixed layer height above 700 m.

Figure 3.4b depicts the variation of mixed layer for summer monsoon season (JJA) which happens to have enormous moisture within the atmosphere and the experimental site experiences associated rainfall. Depending on the convective conditions of the atmosphere, the study domain undergoes active and break phases of the monsoon during these months. On a given convective day, if the strong solar heating supports the upward mixing, the mixed layer height can be very high and on the other hand a sudden rainfall can bring down the mixed layer height.

Signatures of active and break phases of monsoon are quite clearly seen in the variation of mixed layer height in the summer-monsoon. The mixed layer height, in general, is seen to be higher (> 700 m) in the beginning of the season, which gets dropped to low values with the advancement of summer-monsoon. In a broad sense, the variability in mixed layer height is very large in this season and can be attributed to strong convective activities associated with heavy rainfall in this region.

A decreasing trend in the mixed layer height is seen to be emerging in the post monsoon season (Figure 3.4c), where the magnitude of mixed layer drops to low values below 250 m. These variations can be attributed to weakening of convective activities in this season. This is also the season that happens to be a transition period from the wet south-westerly wind to the drier north-easterly wind



**Figure 3.4:** *Mixed layer top variation for different seasons observed over Ahmedabad. The winter season (DJF) panel contains the January and February days biased by 365.* 

(Figure 3.2). In the beginning of this season, mixed layer heights are found to be in a range from 400 m to 700 m which decrease to a range of about 150 m to 350 m at the end of the season [*Srivastava et al.*, 2010].

Figure 3.4d shows the MLH variation for winter season. During winter months, the mixed layer height does not show a large variability. Winds come from drier northerly region so the moisture content is minimum in the atmosphere during these months (Figure 3.2). In this season, the solar heating of the earth's surface is too weak to enhance the MLH higher in the atmosphere. The MLH magnitudes are confined to be in the range of about 150 m to 400 m.

Variation in monthly mean air temperatures observed at 100 m altitude from these balloon ascents is shown with the monthly mean of mixed layer heights for the individual months in Figure 3.5. The temperatures at 100 m were obtained from each flight and averaged on monthly basis. The 100 m altitude is chosen to avoid the effect of heating due to building reflectance on the surface temperature. The maximum temperature of  $31.6 \pm 2.1$ °C is observed in May and minimum of  $20.1 \pm 2.3$ °C is observed in December, which is quite similar to MLH variation. This reveals that temperature of earth's surface directly influences the depth of mixed layer in the atmosphere. It is known that warmer earth's surface forces the turbulent mixing higher in the atmosphere resulting in higher mixed layer. Similar variation can be observed in the average mixed layer height and air temperature except for the summer-monsoon when, higher MLHs were observed on clear sunny days and lower on cloudy/rainfall days.



**Figure 3.5:** Average monthly variation of temperature at 100 m (obtained from radiosonde temperature sensor) and ABL over Ahmedabad during 2003–07. The vertical bars represent  $\pm 1\sigma$  variation.

Distributions of trace gases are highly influenced by dynamics of MLH near the earth's surface. Ventilation Coefficient (VC) is a parameter which quantifies the effects of MLH variation and wind speed on local air pollution [*Krishnan and Kunhikrishnan*, 2004]. This represents the rate by which pollutants within the mixed layer will be blown off from its location. It is given by the

following equation.

$$VC(m^2/s) = h \times \frac{\sum_{i=1}^{n} v_i}{n}$$

Where h is the mixed layer height and  $v_i$  is the wind velocity at different heights (i) within the MLH. High values of VC reflect the strong dispersion so that it is a representative of good air quality, whereas low VC shows poor ventilation and it corresponds to accumulation of locally emitted pollutants. The VC has highest value (~ 5640 m<sup>2</sup>/s) during June and lowest (~ 1140 m<sup>2</sup>/s) during December period. It remains high for summer/monsoon and decreases during post-monsoon and attains its minimum during winter. This trend is quite similar to MLH, which reflects the dominance of boundary layer processes on this parameter.

The surface ozone is measured at this site by using UV based analyser during 2002. We have used CO data at 1000mb from MOPITT (Measurement of Pollutants in the Troposphere), which is onboard NASA's Earth Observing System's (EOS) Terra satellite. High ozone (~ 40-60 ppbv) is observed during late autumn and winter, whereas its concentration was observed to be low (< 25 ppbv) for the entire summer/monsoon season. The surface CO concentrations are around 200 ppbv during post monsoon and winter months, start decreasing from April onwards and attain its minimum (~ 60 ppbv) in July month. The CO data are not available for August possibly due to cloudy days in this month. Average monthly concentrations of surface ozone and CO along with ventilation coefficient are shown in Figure 3.6. It shows the reverse trend in ozone and CO variation with VC. To investigate the impact of VC on the distribution of these gases, the correlation of monthly variation of ozone and CO are examined with VC. The exponential fit is used to demonstrate the dependence of pollution concentration on MLH dynamics as discussed by the Schäfer et al. [2006]. The square of correlation coefficients of VC with ozone and CO are found to be 0.87 and 0.40 respectively. Ozone is photo chemically produced by CO, methane and non-methane hydrocarbons in the presence of NO<sub>x</sub> and sunlight whereas major sources of CO are the anthropogenic emissions, mainly the vehicular emission and
biomass burning. Apart from that, the only chemical source of CO is formaldehyde (HCHO) but its contribution is negligible in comparison to direct emission over this location [*Lal et al., 2000*]. Thus, it is better to study the effects of VC on CO rather than ozone as it will give a clear picture of dispersion of locally emitted pollutant. The mixed layer height defines the upper limit of vertical mixing of trace gases. When the mixed layer is shallow (low VC), the anthropogenically emitted CO will get trapped within it. The accumulation of CO within lower volume will enhance its mixing ratio. This is the prime cause of high



**Figure 3.6:** Average monthly variation of ozone and CO along with ventilation coefficient over Ahmedabad. The vertical bars represent one sigma value.

CO mixing ratios during autumn and winter. On the contrary, mixed layer height remains high during summer season resulting in high VC, and CO mixes within a larger volume. This results in the dilution of CO within the mixed layer. The photochemical ozone production is highly dependent on CO concentration, thus it also follows the similar seasonal trend. However, it is difficult to separate out the contributions of MLH dynamics and pollutant transport effects on the distributions of these gases.

# **3.3** Vertical distributions of ozone, temperature and relative humidity

The ozonesonde and radiosonde profile data provide good opportunity to investigate the vertical distributions of ozone and meteorological parameters over Ahmedabad. Figure 3.7 shows the average vertical distributions of ozone during winter (DJF), spring (MAM), summer-monsoon (JJA) and autumn (SON) up to 8 km. This figure also shows the individual day ozone profiles for every season. Ozone levels are higher during winter below 2.5 km while these are higher during spring and autumn in the altitude range of 2.5 to 4 km. These seasons are drier seasons with average relative humidity below 40% (Figure 3.9). At higher altitudes (above 6 km) ozone mixing ratios are maximum during summer. An elevated layer of enhanced ozone levels is observed in the 500-2000 m altitude range during winter which is absent in the ozone profiles of other seasons. The ozone mixing ratios are found to be minimum within the boundary layer (< 40 ppbv below 2 km and  $\sim$  20 ppbv below 1 km) in summer. The relative humidity is found to be highest (> 60%) accompanied with higher temperature in this season particularly within 4 km (Figure 3.8 and 3.9). This is due to the rainy season with the availability of higher solar flux over the study location. The vertical distributions of ozone are found quite similar in spring and autumn with in the lower 2 km. In contrast to the lower part, minimum ozone values are seen in winter and maximum in summer-monsoon season in altitude regions above boundary layer (2-3 km). Therefore, it appears that different meteorological processes play important roles in the ozone distributions within boundary layer and lower troposphere. In view of this, ozone distribution in the lower 4 km is further analyzed using back air trajectories utilizing spatial and temporal classification of air-masses and is discussed in the next section.



**Figure 3.7:** Seasonal variation of vertical distribution of average ozone up to 8 km in different seasons namely Winter (DJF), Spring (MAM), Summer-Monsoon (JJA) and Autumn (SON). The horizontal bars are  $\pm 1\sigma$  variation. Individual profiles used for the averaging are also shown.



Figure 3.8: Average annual variation of relative humidity over Ahmedabad.



Figure 3.9: Average annual variation of temperature over Ahmedabad.

# 3.4 Back-trajectories and geographical sectors

The distribution of ozone in the lower troposphere is largely influenced by the photochemistry and transport. The back-trajectories can provide important information about the type of air-mass arriving at the observation location and its effects on the distribution of ozone. The trajectories simulation has been done by



**Figure 3.10:** The seven days back trajectories arriving at Ahmedabad at 1 km altitude at 4 GMT (0930 hrs IST) during different months of year 2005.

using the METeorological data EXplorer (METEX) developed at Centre for Global Environmental Research (CGER) [*Zeng et al.*, 2008]. The METEX uses the NCEP (National Centers for Environmental Prediction) reanalysis data having spatial resolution of 2.5°x 2.5° at vertical resolution of 17 pressure levels archived at every six hours. This trajectory model is different from other models as this separates modeling from data input so it can be used with various meteorological data like NCEP, ECMWF etc. The general meteorology at Ahmedabad is studied using seven days back-air trajectories for each month of year 2005 and their



**Figure 3.11:** Altitude variation of seven days back trajectories arriving at Ahmedabad at 1 km altitude at 4 GMT (0930 hrs IST) during different months of year 2005.

spatial and altitude distributions are examined at 1 km and 3 km regions. Figures 3.10 and 3.12 shows the distributions of air-masses which arrived at observation site at 1 km and 3 km respectively in each month. Altitude distributions of air-masses are also shown in Figures 3.11 and 3.13. Most of the trajectories originated from South-West Asia, Northern Africa and Southern Europe during



**Figure 3.12:** Seven days back trajectories arriving at Ahmedabad at 3 km altitude at 4 GMT (0930 hrs IST) during different months of year 2005.



**Figure 3.13:** Altitude variation of seven days back trajectories arriving at Ahmedabad at 3 km altitude at 4 GMT (0930 hrs IST) during different months of year 2005.

January to May. In summer season, air masses arriving at 1 km are basically originated from marine region particularly from Arabian Sea and Indian Ocean. The altitudes of these trajectories are also found to be rather lower during this season. The effect of marine air-mass is more prominent at 1 km than 3 km altitude. The wind reversal starts from late September and afterwards most of the air trajectories are found to be originating within the Indian subcontinent in October, November and December at 1 km. The trajectories at 3 km are found to be more influenced by transport from Africa and Europe regions during this period. The spatial coverage of trajectories at 3 km is larger than that of 1 km due



**Figure 3.14:** The spatial coverage of 10 days back trajectories originated from (1) West Indian (WI) region, (2) marine region, and (3) Africa/Europe region. The vertical bars represent  $\pm 1\sigma$  variation.

to higher wind speed at high altitudes. These observations are used to classify preliminary sectors which might be affecting the observations over Ahmedabad. The air masses of three different regions influence the site during different months (Figure 3.14). These regions are defined to classify the trajectories:

(1) The region from 18°N to 30°N and from 65°E to 80°E is designated as West Indian (WI) region.

(2) The Arabian Sea, Bay of Bengal and Indian Ocean are designated as the marine regions.

(3) The region west of 65°E and excluding marine region is defined as Africa/Europe region.

WI region is the region of large anthropogenic emissions including vehicular and industrial emissions. The air-mass circulates over this region during late autumn and early winter in lower altitudes. The air masses reach at observation site from marine region during late spring, entire summer-monsoon and early autumn. The third sector mainly covers the air masses originating mostly from northern Africa and southern Europe. Figure 3.14 includes the average back-air trajectories originating from three defined sectors. There are very few trajectories (< 1%) from East Asian region and are not classified explicitly.

#### 3.5 Residence time of air-masses

The ten days back-air, five particle trajectories, one at observational location and four at the corners of the grid made surrounding the observations site at 0.5 degrees displacement in latitude and longitude are simulated at 0930 IST (4 GMT). All the five trajectories are checked for the coherency [Naja et al., 2003b] before using them for further analysis. The trajectories are calculated at seven altitudes (1 km, 1.5 km, 2 km, 2.5 km, 3 km, 3.5 km and 4 km) in the lower troposphere for each balloon flight day. The average residence time is calculated for each balloon flight and seven predefined altitudes over three defined sectors i.e. WI region, marine region and Africa/Europe region. The residence time is assigned to 1 day if air-mass has spent less than 1.5 days, 2 days if air parcel has spent between 1.5 days to 2.5 days and so on for the other days. The residence time corresponding to the 1km altitude region is tagged with average ozone mixing ratio between 0.75 km and 1.25 km. Similarly, residence time of air-mass at 1.5 km is tagged with average ozone between 1.25 km and 1.75 km. This procedure is followed for 2.0 km, 2.5 km, 3.0 km, 3.5 km and 4.0 km. The ozone values below 0.75 km region are not considered in the present analysis to avoid the effects of immediate local emission of precursors of ozone, dry deposition and variation in balloon launch times during entire study period. Further, the analysis

is performed in the two regions i.e. boundary layer (BL) (up to 2 km) and the lower troposphere (LT) (2 km to 4 km).

### 3.5.1 Seasonal and frequency distribution of residence time

Figure 3.15 depicts the seasonal variation of average residence days in the boundary layer and in the lower troposphere for air masses of WI, marine and Africa/Europe regions. The average residence days in the boundary layer show



**Figure 3.15:** The seasonal variation of residence days of trajectories in boundary layer and lower troposphere over Western India, marine and Africa/Europe regions.

prominent maximum during late autumn and winter for WI air masses. However, secondary winter maximum is not seen in the lower troposphere. The effect of

marine air mass dominates from late spring to early autumn with 2-3 days of average residence time for boundary layer. The average residence days over marine region for lower tropospheric air masses are found to be less than 1 day thus discarding the possibility of significant impact of marine air over lower troposphere at study location. For the Africa/Europe region, the average residence days are found in the range of 4 to 8 days during spring and summer-monsoon, 3-4 days during winter and less than 3 days during autumn in the boundary layer.



**Figure 3.16:** Variations in percentage of trajectories having different residence days in boundary layer and lower troposphere over Western India, marine and Africa/Europe regions.

Whereas, in the lower troposphere, the average residence days in the Africa/Europe region are found to be maximum during winter and spring. Therefore, regionally polluted air-mass dominates during September and October both within the boundary layer and in the lower troposphere, while marine air-mass during summer/monsoon and Africa/Europe during winter/spring.

Figure 3.16 shows the frequency distribution of residence days for all the three sectors in the boundary layer and lower troposphere. The maximum fraction of trajectories in the WI region is in the 2 days (1.5 to 2.5 days) for the boundary layer (28.7%) and lower troposphere (26.2%). For the marine region, the maximum numbers of trajectories are found to have residence time less than 1 day for boundary layer (23.4%) and lower troposphere (58.6%). Similarly the maximum percentages of trajectories for Africa/Europe region have residence time of 4 days in the boundary layer (16.5%) and 8 days in the lower troposphere (19.1%).

#### **3.5.2** Seasonal variation of mean altitude of trajectories

The annual variations of monthly mean altitude of trajectories in both BL and LT for all the three sectors are shown in Figure 3.17. Interestingly, seasonal variation in average altitudes of air-masses is minimal for WI region, when compared with other two sectors. A slight decreasing tendency (100-200 m) in average altitude is observed with the advancement of the spring season. The mean altitudes in marine air-masses are found in the range of 1-2 km with a maximum in the summer monsoon for the boundary layer. For the lower troposphere, average altitude varies from 2 to 3.5 km. The average altitudes are found to be highest in Africa/Europe region among all the three sectors. The mean altitude is found maximum over this region during late autumn, winter and early spring for both the boundary layer (3.5-4 km) and the lower troposphere (4-5 km). The decreasing tendency in mean altitude is evident with the advancement of spring, and minimum altitudes are found during August and September for the boundary





layer ( $\sim 1.5$  km) and the lower troposphere ( $\sim 2$  km). This indicates that during the months of May to September the boundary layer air masses of Africa/Europe region are transported to study location.

#### 3.6 Dependence of ozone on residence time over Western India

In order to understand the seasonal variations of ozone in the boundary layer and lower troposphere, based on influences of different air masses having varying residence times over different geographical regions, tagged analysis of ozone with air-mass residence time is performed. The average ozone mixing ratio in the boundary layer and lower troposphere from each ozonesonde flight are tagged with corresponding residence time over defined WI region. Data of cloudy days and events of long range transport are not considered in the analysis. Figure 3.18 shows the dependence of ozone mixing ratios on the residence time over this region in the boundary layer and in the lower troposphere for different seasons. The ozone values increases with increasing residence days for 3 to 6 days mainly in spring and up to some extent in summer and autumn. The mixing ratios of ozone increases with a rate of 4.5 ppbv/day and 3.4 ppbv/day during spring in the boundary layer and lower troposphere, respectively. During summer/monsoon, the boundary layer air mass has significant contributions from marine region therefore tagged data are not available for more than 4 days residence time (Figure 3.18c). The mixing ratios of ozone shows tendency of build-up with the rate of 2.5 and 3.1 ppbv /day in the boundary layer and lower troposphere respectively during this season. This observed growth in ozone with increasing residence time of airmasses is due to the accumulation of ozone and its precursors over this region during the residence period. The availability of sufficient solar radiation induces ozone formation through the photo-oxidation of the accumulated precursors. Solar radiation is highest in spring over this region (Figure 3.19).

A slight increase rate is observed during winter in the ozone mixing ratio (about 0.75 ppbv/day), but a clear systematic increase in ozone mixing ratio with residence time is absent during this season. The accumulation of local pollution is very high due to shallow boundary layer accompanied with sufficient solar flux during this season, thus the average ozone values are already high (~ 50 ppbv). NO concentrations are also reported to be maximum during this season at this site



[*Lal et al.*, 2000]. The simultaneous photochemical production and NO titration may be the possible causes for the absence of ozone build up in winter.

**Figure 3.18:** Variation of ozone mixing ratios with residence days in boundary layer and lower troposphere during winter (DJF), spring (MAM), summer/monsoon (JJA) and autumn (SON) different seasons over regionally polluted sector. The vertical bars show  $\pm 1\sigma$  variation in ozone mixing ratio and horizontal bars show  $\pm 1\sigma$  variation in residence time of corresponding air masses used in the averaging.

Generally, it is observed that the ozone mixing ratio achieves its saturation levels after about 6 days during spring and autumn seasons within the boundary layer. Its mixing ratio remains almost constant or some time decreases with increasing residence days further. Similar feature has been reported by *Pochanart et al.* [2001] for the surface ozone data at Swiss Alpine site Arosa, and *Naja and Akimoto* [2003] for the ozonesonde data at two European sites, Hohenpeissenberg and Payerne. This decreasing feature after 6 days may arise due to unfavourable weather conditions (like clouds and rain, lesser amount of solar radiation etc) for the photochemical production of ozone over the WI region. The other possible limiting phenomenon for further enhancement in ozone levels in air parcel may



**Figure 3.19:** The daily and monthly variations of solar radiation over Ahmedabad at 1400-1500 hrs (IST) during the year 2009. Vertical bars show  $\pm 1\sigma$  variation.

be the titration of ozone by high level of NO over WI region. Therefore, it is observed that generally air-masses those have spent 3-6 days over this region are found to be sufficiently photoxidised and can be taken as the representative of polluted air of this region.

In order to estimate the ozone value before the air enters the WI region; its values from six to one day are linearly extrapolated back-ward to zero day condition as in the study of *Naja et al.*, [2003]. These estimated ozone values of zero day residence time would be described here as background ozone. The ozone values corresponding to zero day will be equivalent to background ozone levels in the air-masses those are just entering the boundaries of WI sector. We feel that estimated "background" ozone in the boundary layer may be affected by local photochemistry, however in the lower troposphere it should be more representative of regional background levels.

The annual background mixing ratio of ozone is estimated using this procedure and found as about 28 ppbv for boundary layer and about 42 ppbv for lower troposphere. The background mixing ratios of ozone is also calculated for different seasons. The background ozone (~ 26 ppbv) obtained for JJA within the boundary layer represents the ozone level for the cleaner air from Arabian Sea. The background ozone and rate of increase of ozone with residence days within the boundary layer and in the lower troposphere during different seasons are given in Table 3.1.

Table 3.1: The background mixing ratios of ozone and increase rates of ozone in the boundary layer and lower troposphere are provided here for different seasons. The six days regression line is fitted for first six days and extrapolated to zero day to get the background levels of ozone.

	Boundary layer		Lower troposphere	
Season	Background O <sub>3</sub> (with six days regression) (ppbv)	Rate of increase of O <sub>3</sub> with residence days (ppbv/day)	Background O <sub>3</sub> (with six days regression) (ppbv)	Rate of increase of O <sub>3</sub> with residence days (ppbv/day)
Winter	47.6	0.70	43.1	0.80
Spring	33.3	4.50	39.9	3.44
Summer	26.1	2.59	33.7	3.19
Autumn	40.0	2.42	45.1	1.66

#### **3.7 Contributions of different air-masses**

### **3.7.1 Regionally polluted air-mass**

The air-mass is considered as the regionally polluted boundary layer air mass if it has spent 3 to 6 days in the WI sector and its mean altitude remains lower than 3 km over this region. Air-mass within 3 km will restrict the contribution from higher height. The monthly variations of the average boundary layer and lower tropospheric ozone in regionally polluted air masses are shown in Figure 3.20. The average mixing ratio of ozone obtained from all data show a minimum during summer-monsoon with levels of about 30 ppbv in the boundary

layer. This is largely due to wind reversal from north westerly to south westerly which brings the pristine maritime air-mass to the observation site. A comparison of ozone in regionally polluted air-mass and average ozone clearly show that ozone levels in the regionally polluted air-mass are higher than average ozone by 21% during spring and 40% during summer in the boundary layer. The average distribution of ozone in the lower troposphere is different compared to the variations in the boundary layer. Unlike the boundary layer, the two peaks are identified during May and October months in average ozone variation. Due to the higher heights region, air-masses are defined as regionally polluted in the lower troposphere if the air-masses spent 3 to 6 days over regionally polluted region and



**Figure 3.20:** The monthly distribution of average ozone with variation of ozone in regionally polluted air in the boundary layer and lower troposphere. Vertical bars show  $\pm 1\sigma$  variation.

less than 5 days over long range transport region with its mean altitude over WI region less than 4.5 km. The mixing ratios of ozone in these air masses are found to be significantly higher (8-11%) than average ozone during spring and summer. The second peak identified during October month also seems to be contributed from regionally polluted air-mass as ozone levels remain 5-7 ppbv higher than average ozone during this month.



**Figure 3.21:** The seasonal variation of regionally polluted and background levels of ozone. Vertical bars show  $\pm 1\sigma$  variation. The circles show the build up of ozone contributed from regional pollution.

The difference between regionally polluted ozone and background ozone gives the estimate of photochemical build up of ozone contributed from local pollutants (Figure 3.21). The build up is maximum (~ 21 ppbv) during spring season in the boundary layer due to availability of intense solar flux and high levels of regional pollutants accumulated during winter seasons in shallow boundary layer. Low levels of background ozone are observed due to marine air mass arrived during late spring. The build up is significant during spring and summer in the lower troposphere.

### 3.7.2 Marine air-mass and influence of long range transport

During April to August period, the marine originated air-masses dominate particularly in boundary layer region as shown in Figure 3.22a. The air-masses are categorised as the marine air-mass if they have spent more than 3 days over marine region and less than 2 days over regionally polluted sector. The mixing ratios of ozone are found to be 2.5 to16 ppbv lower than the average ozone mixing ratios showing that this air mass are playing a major role in dilution of ozone during these months. There were very few trajectories in the lower troposphere from the marine region and their residence times were also not sufficient to identify the contribution in the LT region. Average mixing ratios of ozone in the

boundary layer during this period in the marine air-mass is 28.8 ppbv, which is nearly comparable to the background level of ozone in regionally polluted air.



Figure 3.22: The seasonal distribution of (a) average ozone with seasonal variation of marine ozone in boundary layer and (b) average ozone with seasonal variation of LRT ozone in the lower troposphere. Vertical bars show  $\pm 1\sigma$  variation.

Influence of long range transport (LRT) is expected not to be very significant in the boundary layer and this analysis was limited to the lower tropospheric region. In the lower tropospheric region, the long range transport type of air-masses is classified on the basis of three factors. They should have spent minimum 3 days over Africa/Europe region and less than 1.5 days over marine sector with their average altitude over WI region greater than 3 km. Altitude criteria will restrict the contribution from regionally polluted region. These air-masses show high ozone level during the month of May-July with 9-20 ppbv (32%) higher mixing ratio than average ozone of all data (Figure 3.22b). It appears both regionally polluted air mass and long range transport are playing major role in variations of the lower tropospheric ozone

## 3.8 Surface ozone at Ahmedabad

Surface level ozone data over Ahmedabad are also used in association with back-air trajectory to perform the residence time analysis. The backward

trajectories are calculated at 500 m over Ahmedabad, and tagged with the corresponding ozone mixing ratio for further analysis similar to that of ozone sounding data. Figure 3.23 shows the dependence of ozone on residence time over the regionally polluted sector and the corresponding ozone mixing ratios over Ahmedabad during daytime (1400-1500 hrs) and night time (0200-0300 hrs).



**Figure 3.23:** The variation in surface ozone mixing ratios with residence days over WI region in daytime (1400-1500 hrs) and night time (0200-0300 hrs) during winter (DJF), spring (MAM), summer/monsoon (JJA) and autumn (SON). The vertical and horizontal bars show  $\pm 1\sigma$  variation in ozone mixing ratio and residence time respectively.

The surface mixing ratios of ozone are found to increase over Ahmedabad during day time until the air-masses have spent four to six days over WI region. This increase is attributed to the accumulation of locally emitted pollutants. The solar flux is higher during spring and autumn over Ahmedabad whereas the winter season also experiences sufficient amount of solar radiation, necessary for photo chemical production of ozone. The daytime production of ozone ceases after 5-6 residence days, which is also observed in the boundary layer ozone (ozonesonde data). The ozone increases with residence time with a rate of 4.1 ppbv/day during winter. Growth rate is observed to be 5.6 ppbv/day during spring and 6.4 ppbv/day during autumn. As mentioned earlier, air-mass is largely from marine

region during summer/monsoon period therefore very few trajectories are observed over WI during this season. This is leading to fewer classified ozone data during summer/monsoon period.

It is important to note that classified ozone data in night time (0200-0300 hrs) do not show any significant growth with increasing residence time during any season. The background levels of ozone are estimated by extrapolation method as well as by the night time average ozone levels. The night time ozone levels are lower by 2 to 8 ppbv than the background levels of ozone calculated by extrapolation method. Good agreement is found during spring season when the difference between them is observed about 2 ppbv. The background and night time levels with rate of increase of ozone (ppbv/day) are given in Table 3.2.

Table 3.2: Background surface ozone, night time surface ozone and rate of increase of surface ozone during four seasons at Ahmedabad are given.

Season	Background O <sub>3</sub> (with six days regression) (ppbv)	Nighttime O <sub>3</sub> (ppbv)	Rate of increase of O <sub>3</sub> with residence time (ppbv/day)
Winter	26.2	$17.6 \pm 3.0$	4.1
Spring	18.5	$16.9 \pm 3.7$	5.6
Summer	20.4	$12.5 \pm 2.8$	-
Autumn	19.9	$15.6 \pm 2.4$	6.4

The comparison shows that the ozone production rate is maximum during spring (4.5 ppbv/day) in the boundary layer (ozonesonde data) and during autumn in the surface ozone (6.4 ppbv/day). This is to be noted that boundary layer data from ozonesonde are regional representative whereas the surface ozone might have more contribution of local pollution over Ahmedabad. The lower altitude regions are more influenced by marine air-mass during early autumn resulting into lower background levels of ozone during autumn near the surface (20 ppbv) than boundary layer (40 ppbv). The cleaner air-masses are adapting the local pollution very fast resulting into higher production rate of surface ozone.



**Figure 3.24:** The seasonal variation of regionally polluted ozone, marine ozone and background ozone over Ahmedabad. Vertical Bars show  $\pm 1\sigma$  variation.

The mixing ratios of ozone in the regionally polluted and marine air-mass with the background levels are shown in Figure 3.24. Ozone in regionally polluted and marine air-masses shows greater differences during spring and autumn. Regionally polluted ozone is about 18 ppbv to 20 ppbv greater than the background and marine air-masses during the spring. Background ozone and ozone in regionally polluted and marine air-masses are nearly similar during summer season. This is due to the wash out of pollutants and cloudy weather during this season.

#### **3.9** Comparison with other sites

Analysis of ozonesonde data at Ahmedabad show higher regionally polluted ozone levels during winter to early spring and during late autumn in the boundary layer. While, in the lower troposphere, a clear maxima is seen in May and October. Background levels of ozone is estimated by technique introduced by *Pochanart et al.* [2001] for both in the boundary layer and lower troposphere. Over the two European sites, Hohenpeissenberg and Payerne, the background levels of ozone shows a broad maximum during spring-summer and minimum during autumn-winter for both bounadry layer and lower troposphere [*Naja et al.*, 2003]. Simlar variations are reported for several surface ozone sites over Europe [*Bronnimann et al.*, 2000; *Schuepbach et al.*, 2001]. This observation is completely opposite from present results having minimum background levels during spring and summer. This is due to the effect of marine air-mass over this location during these seasons. Few surface ozone European sites like Arosa and Mace Head also show summer minimum in background ozone mixing ratios [*Dervent et al.*, 1998; *Pochanart et al.*, 2001], similar to those at Ahmedabad, but these are attributed to dry deposition of ozone near the surface.

The boundary layer and lower tropospheric regionally polluted ozone also show spring and summer maximum over both the ozonesonde sites in Europe. The regionally polluted ozone shows a distinct maximum during spring followed by autumn and summer in the lower troposphere over Ahmedabad. The levels of ozone mixing ratios are found to be 20 ppbv higher in the air-mass arriving over this location from European region during summer (LRT), but this effect got diluted due to arrival of cleaner air-mass in the boundary layer which also affects the ozone levels in the lower troposphere. The levels of ozone in long range transported lower tropospheric air mass over Ahmedabad and European photochemially aged air-mass are almost comparable with 60-70 ppbv ozone levels in summer. During this season, the mean altitude of back-trajectories are found lower in Africa/Europe region.

The annual monthly average variations of ozone within the boundary layer and in the lower troposphere are compared with the surface ozone distribution over high altitude sites Mt. Abu (24.6°N, 72.7°E, 1680 m amsl) and Nainital (29.37°N, 79.45°E, 1958 m amsl) in India. The seasonal variation of ozone within the boundary layer is similar to seasonal variation of ozone over Mt.Abu. The ozone mixing ratios start declining after March onwards and attains their minimum in June [Lal et al., 2000] which is quite similar to boundary layer ozone variation in the present study. Mt Abu is nearer to Ahmedabad and well within the boundary layer range taken in the present investigation (1 to 2 km). Thus the similarity in ozone distribution is expected. The ozone distribution over Nainital shows a systematic increasing tendency in ozone from January to May and a dramatic decraese after June onwards. This increasing tendency of ozone is similar to ozone distribution in lower troposhere over Ahmedabad. The springtime high ozone over Nainital is explained on the basis of influences of biomass burning and regional pollution of northern India [Kumar et al., 2010]. Spring time high ozone is also reported at Mt Fuji (35.35°N, 138.73°E, 3776 m amsl) and Mauna Loa (19.5°N, 155.6°W, 3397 m amsl) [Oltmans and Levy, 1994; Tsutsumi et al., 1994]. These variations are explained on the basis of downward motion of air over high altitude site. The present investigation indicates that lower tropospheric ozone mixing ratios are getting enhanced in spring time due to long range transport. The downward motion of ozone rich air is not investigated in the present study.

# **Chapter 4**

# Ozone and its precursors over Bay of Bengal & Arabian Sea

The transport of air pollution from the source to remote regions is an important issue in global climate change studies. The developing regions of Asia are known to contribute large emissions of ozone precursors due to increasing urban and industrial growth. In India, burning of biofuels like wood, agricultural waste and ruminant dung is the major source of air pollution [*Yevich and Logan,* 2003]. The Bay of Bengal (BoB) and the Arabian Sea (AS), the two marine regions surrounding India, are often influenced by the outflow of these pollutants [*Rasch et al.,* 2001; *de Gouw et al.,* 2001; *Sahu et al.,* 2006].

Field campaigns were conducted over BoB during the last decade; e.g., the Bay Of Bengal EXperiments (BOBEX) and Bay Of Bengal Process Studies (BOBPS) to study the trace gas distributions over this region [*Sahu and Lal*, 2006c; *Sahu et al.*, 2006; *Lal et al.*, 2007]. During these campaigns, continuous surface measurements of ozone were carried out along with the precursors like CO, CH<sub>4</sub>, and non-methane hydrocarbons (NMHCs). These studies reveal that the major pollution originated from Indo-Gangetic Plain (IGP) significantly influences the northern part of BoB. Prior to the BoB experiments, surface as well as vertical distributions of ozone and other gases were investigated during INDian Ocean EXperiment (INDOEX) in the years of 1997, 1998, and 1999 over large area of the Indian Ocean including southern parts of the Arabian Sea and Bay of Bengal [*Ramanathan et al. 2001*; *Zachariasse et al.*, 2001; *Chand et al.*, 2003]. The presence of pollution plumes (rich in ozone, CO, SO<sub>2</sub>, CH<sub>3</sub>CN etc.) above the marine boundary layer (MBL) in the range of 1-3 km over the Northern Indian Ocean and Southern AS have been reported [*Lelieveld et al.*, 2001; *Reiner et al.*, 2001]. This layer is attributed to the advection of residual layer air-mass of continental origin as a consequence of land-sea-breeze circulation [*Raman et al.*, 2003].

The continental originated air masses from Asian sources are transported to the northern Indian Ocean via two different pathways during INDOEX 1999 [*Lelieveld et al.*, 2001]. During the month of February, the air originating from the Indian subcontinent (mainly from the Indo Gangetic Plain) reached to the observation location Kaashidoo Climate Observatory (4.97°N, 73.47°E) after passing through northern BoB. In the month of March, the air mostly originating from South West Asia passed over the AS before arriving at observation location. The pollution levels were found to be higher in cases of transport from the Indian land region via BoB. However, these measurements were limited to Arabian Sea and Indian Ocean except a small part in the southern BOB. Due to the lack of studies of vertical distribution of ozone over Bay of Bengal and Arabian Sea regions, the understanding of influence of air-mass transported from the Indian subcontinent to the surrounding marine region remains poor.

The oceanic segment of an extensive, multi-institutional, multi-instrument and multi-platform field campaign, namely, the "Integrated Campaign for Aerosols, gases and Radiation Budget (ICARB)" was conducted over adjoining marine regions of Indian subcontinent during March to May, 2006 as a part of Indian Space Research Organization's Geosphere Biosphere Program (ISRO-GBP) [*Moorthy et al.*, 2008]. The major objectives of the campaign were:

- Study of spatial-temporal heterogeneity of the distribution of aerosols and trace gases.
- 2) Investigation of various sources of aerosols and gases over marine regions.
- Study of elevated layers in the vertical distribution of aerosols and trace gases in polluted coastal and pristine oceanic regions.
- Investigation of long range transport, regional meteorology and mesoscale processes like sea breeze circulation on the spatial and vertical distribution of aerosols and trace gases.

In order to achieve these objectives from the perspective of atmospheric chemistry, the surface measurements of precursors of ozone like CO,  $CH_4$  and NMHCs were made during the campaign. In addition to that, the vertical distributions of ozone and meteorological parameters were also measured. These valuable data sets, collected over the coastal to open ocean, provided an excellent opportunity to study the transport of pollutants from land to the pristine marine environment.

#### 4.1 Cruise track and meteorological conditions

The measurements were made onboard the oceanographic research vessel (ORV) Sagar Kanya (SK) during its cruises 223A over the BoB and 223B over the AS. Figure 4.1 shows the cruise track of ICARB-2006 with grab sampling locations and the balloon launching locations, marked with the dates of observations. This experiment was planned to cover broad areas of the Bay of Bengal and the Arabian Sea. The ship sailed off from Chennai (13.1°N, 78.3°E) on 18 March 2006 and covered an extensive oceanic region over BoB stretching from 5.5°N to 20.6°N and 76°E to 93°E during its first phase. The ship halted at Kochi (10.0°N, 76.2°E) on 12 April. In the second phase of the campaign, the ship sailed off from Kochi on 18 April and covered the latitudinal span of 9°N to 22°N and longitudinal span of 58°E to 76°E over AS before ending at Goa (15.4°N, 73.8°E) on 11 May.



**Figure 4.1:** Cruise track during ICARB. Overlaid circles on cruise track depict the locations of balloon flights with date of month and triangles show the grab sampling locations. 'Mr' denotes March, 'Ap' denotes April and 'My' denotes May. Major ports of Indian mainland near the cruise track are also shown.

Ozonesondes and radiosondes were launched every alternate day during the entire campaign. The details about the payload were given in Chapter 2. Twenty nine balloon flights were conducted mostly between 0930 and 1030 IST (Indian Standard Time, IST = UT + 5.5 hrs) during the entire campaign. The balloon payload on 19 March contained only radiosonde. The meteorological parameters suggest the effect of strong convective activity on 30 March. The vertical distribution of ozone was strongly affected by this event and the profile was distinct from other profiles over the marine region. Thus, the measurements made on 19 and 30 March are not included in the present study. In addition to



**Figure 4.2:** *Time series variations of various daily averaged meteorological parameters with the location of the cruise during entire campaign.* 

these measurements, the surface level precursors of ozone were also observed. Air samples were collected in glass bottles (300 - 800 ml) everyday at 0800 hrs and 2000 hrs using oil free metal bellow compressor during the campaign. These air samples were later analyzed by gas chromatographic technique for CO,  $CH_4$  and NMHCs. The details of these techniques were given in Chapter 2.

The surface meteorological parameters like temperature, pressure, relative humidity (RH), SST and wind speed measured on board ship at regular intervals. Figure 4.2 shows the time series variations of several meteorological parameters over BoB and AS. Air temperature varied between 27.5°C and 30°C during the entire cruise with an average value of 28.5°C over BoB and 29.1°C over AS. RH also shows considerable variation during campaign as it increased up to 79% on

25 March and recorded a minimum of 53% on 6 April during BoB phase. The minimum and maximum daily averaged RH over Arabian Sea is recorded as 73.5% and 90.5% respectively. Towards the end of the cruise, the RH showed a marginal increase. The average RH was observed to be 71.2% over the BoB and



**Figure 4.3:** Synoptic wind fields over Bay of Bengal and Arabian Sea for the first cruise leg (20 March-12 April, 2006) at (a) 850 mb and (b) 700 mb and for the second leg (18 April-10May, 06) at (c) 850 mb and (d) 700 mb.

79.8% over the AS. The wind speed also shows significant variation during the entire study period. The minimum and maximum wind speed was recorded 2.3 m/s and 13.8 m/s respectively. The horizontal wind speed varied in the range of 2 to 9 m/s during most of the days. The average wind speed was found to be  $6.1 \pm 2.1$  m/s and  $6.6 \pm 2.4$  m/s over the BoB and AS respectively. During the first phase SK-223A, surface winds were northeasterly when ship was traveling

88

parallel to coastal region which later changed to southwesterly and southeasterly. The winds were mainly southwesterly over the AS.

The synoptic scale winds at 850 and 700 mb, obtained from NCEP-NCAR reanalysis, prevailing over the Indian region during the first and the second legs of the cruise are also shown in Figure 4.3. The top two panels (Figures 4.3a and 4.3b) depict the wind fields at 850 and 700 mb during the first cruise leg (18 March to 12 April) when the ship was traversing over BoB. The continental air particularly from IGP was advancing over northern part of BoB, which is evident at both pressure levels and more prominently at 700 mb. The wind pattern was easterly south of 12°N. During the second leg of the campaign, the AS was at the downwind flow of southwest Asia at 850 mb and 700 mb (Figures 4.3c and 4.3d). The wind pattern at 700 mb changed direction in the region south of 12°N and mainly came from southern India over this region. In order to study the influence of winds coming from different origins on the vertical distribution of ozone, both the marine regions are subdivided into northern and southern parts with the 12°N as the line of separation.

# 4.2 Vertical distribution of ozone

The vertical distributions of ozone and meteorological parameters have been studied within the 4 km altitude range over Bay of Bengal (BoB) and Arabian Sea (AS). The objective of this investigation was to delineate the roles of various processes affecting the distribution of ozone in the lower troposphere like long range transport, continental outflow, regional meteorology, sea breeze circulation etc. The findings of the work are discussed here in detail.

## 4.2.1 Structure of marine boundary layer

The vertical distributions of meteorological parameters provide a unique opportunity to explore the various features of the distributions in the marine boundary layer (MBL). The top of the MBL is identified as the height (MLH) at

which the first significant inversion in virtual potential temperature (VPT) and specific humidity profiles is evident [*Subrahamanyam et al.*, 2003]. In most of the vertical profiles of these parameters a sharp increase in VPT is noticed with a concurrent decrease in specific humidity just above the top of the mixed layer.



**Figure 4.4:** Typical vertical profiles of virtual potential temperature and specific humidity over (a) Northern Bay of Bengal, (b) Southern Bay of Bengal, (c) Northern Arabian Sea and (d) Southern Arabian Sea. The horizontal dashed lines show the top of the mixed layer.

Figure 4.4 represents typical vertical variations of VPT and specific humidity over northern BoB (N-BoB), southern BoB (S-BoB), northern AS (N-AS) and southern AS (S-AS) up to 4 km. The convective marine boundary layer is

observed well within the altitude range of 400-1000 m from the surface over all the marine segments. This layer was capped by strong temperature inversion. The mixed layer heights were observed to be higher over the southern regions than the northern parts of both BoB as well as AS. Interestingly, the existence of double mixed layer structure is evident over N-BoB (Figure 4.4a).

The second mixed layer is observed to be sandwiched between the MBL and the free troposphere (1-3 km range) having lower humidity and warmer VPT than in the MBL. A sharp increase in VPT and sudden fall in specific humidity have been observed just above this layer. This feature of double mixed layer is evident in almost all the profiles over N-BoB. The variations of meteorological parameters over N-AS are found somewhat similar to over N-BoB. Though the second mixed layer structure is evident, the sharp inversion observed at the top of the second mixed layer in N-BoB profiles is absent over this region (Figure 4.4c). As seen in Figures 4.4b and 4.4d, the double mixed layer structure is completely absent over S-BoB and S-AS. VPT increases and specific humidity decreases above the mixed layer top, without any abrupt change showing the absence of any layer of different thermal characteristics over both the southern regions. The MBL top is slightly higher (~ 150 m) over the southern parts than the northern parts over both the marine regions. The profiles shown in Figure 4.4 are representative of each oceanic region and fairly depict the general variation of upper air meteorological parameters.

# 4.2.2 Vertical distributions of ozone over Bay of Bengal & Arabian Sea

The vertical distributions of ozone are investigated separately over northern and southern regions of both BoB and AS. The two regions are separated on the basis of different wind regimes prevailing over these regions (discussed in Section 4.1). Seven balloon flights were conducted over N-BoB, four flights over S-BoB, eleven fights over N-AS and five over S-AS. Figures 4.5 a,b,c,d shows the average vertical distributions of ozone with  $\pm 1\sigma$  variation over N-BoB, S-BoB, N-AS and S-AS, respectively. The average mixed layer ozone was found to be 40.6  $\pm$  15.5 ppbv over N-BoB. Ozone levels in the mixed layer are observed between 50 and 58 ppbv at the observation locations near northern coastal region. The levels are seen much lower (18-30 ppbv) in the mixed layer over southern part of N-BoB. This leads to a large variability (~ 15 ppbv) in the mixed layer



**Figure 4.5:** Vertical profiles of average ozone (circle) and its variability (horizontal bars of  $\pm 1\sigma$ ) over Northern Bay of Bengal, Southern Bay of Bengal, Northern Arabian Sea and Southern Arabian Sea.
ozone over N-BoB. A well mixed layer of very high ozone mixing ratio (60-80 ppbv) persists in the range of 1 to 3 km altitude above marine boundary layer. This ozone rich layer is present in the altitude range of second mixed layer. The layer structure disappears above 3 km as shown in Figure 4.5. Vertical ozone distributions over S-BoB do not show any layer above MBL. Ozone in mixed layer is observed about 20 ppbv with small variability ( $\leq \pm 5$  ppbv). A gradual increase in ozone, with a rate of about 15 ppbv/km, is observed up to about 3 km and reaches average mixing ratio of about 60 ppbv at 3.5-4 km range. The ozone values of about 55-60 ppbv characterize the lower free tropospheric mixing ratio over the continental locations in India during pre-monsoon [*Shilpy*, 2008; *Sahu et al.*, 2009].

The ozone-mixing ratios over N-AS, remain nearly constant around 20-30 ppbv within the MBL. Its levels increase above MBL, attain 50-60 ppbv around 2 km and remain fairly constant up to 4 km. The maximum variability ( $\sigma \sim \pm 10$  ppbv) was observed in the range of 0.5-1.5 km and 3.1-4 km (Figure 4.5 b). Over S-AS, nearly constant mixing ratio of ozone (20-28 ppbv) is evident up to 1 km and above that it increases slowly with altitude up to 3.2 km and attains an average range of 50-55 ppbv at 4 km. The vertical distributions of ozone over S-BoB and S-AS are fairly similar to each other. The profiles of ozone over these regions show the vertical structure of ozone over pristine marine environment in the absence of any influence of continental outflow. The mixing ratio of ozone is found to be significantly low within the marine boundary layer in all the four marine segments except for a few flights conducted over the northern part of N-BoB.

The low MBL ozone may be attributed to:

- (a) Absence of sufficient photochemical production due to lower levels of precursors of ozone.
- (b) Photochemical loss in low NO environment. Major loss of ozone takes place due to its reaction with OH and HO<sub>2</sub> radicals in pristine marine environment ([NO] ppbv<[O<sub>3</sub>]ppbv/4000) during day time.

- (c) Loss of ozone due to halogen chemistry over marine region.
- (d) Dry deposition of ozone on oceanic surface.

Ozone increases above MBL in the absence of significant loss due to these mechanisms. The average mixing ratios of ozone at every one km interval over the four marine regions are listed in Table 4.1. The table clearly shows significantly higher levels of average ozone over N-BoB below 3 km. However, the ozone levels over N-AS is also moderately high with respect to S-BoB and S-AS. Above 3 km, the levels of ozone are comparable for all parts of the AS and BoB.

Table 4.1: Average ozone (ppbv) with  $\pm 1\sigma$  value observed over different altitude ranges and different marine segments during the campaign conducted in March-May 2006.

Marine region	0-1 km O <sub>3</sub> (ppbv)	1-2 km O <sub>3</sub> (ppbv)	2-3 km O <sub>3</sub> (ppbv)	<b>3-4</b> km O <sub>3</sub> (ppbv)
N-BoB	$46.4 \pm 6.3$	$67.4 \pm 2.0$	$68.7 \pm 0.9$	$58.6 \pm 4.3$
S-BoB	23.4 ± 1.0	34.0 ± 5.5	49.4 ± 3.5	55.6 ± 0.8
N-AS	29.1 ± 6.1	47.7 ± 4.6	55.4 ± 0.7	56.4 ± 1.3
S-AS	26.1 ± 0.5	$36.3 \pm 4.4$	47.4 ± 1.6	55.1 ± 1.9

The vertical distributions of ozone over northern and southern marine regions are quite different as discussed in previous sections. The northern regions are characterized by high ozone above the marine boundary layer, particularly within 1-3 km altitude range. In order to study the level of pollution over northern region as compared to the southern marine region, differences in the average levels of ozone and meteorological parameters over the two regions are examined.

Figure 4.6(a) shows the difference between the average profiles of ozone, specific humidity and temperature over N-BoB and S-BoB. It is explicit that ozone-mixing ratios are quite higher over N-BoB than over S-BoB. The values are

nearly 17-19 ppbv higher in N-BoB than S-BoB up to 500 m. The highest difference of 40 ppbv occurs around 1.2 km altitude. There is almost no difference above 3 km height, which seems to be a background free tropospheric level of ozone. The higher levels of ozone are particularly evident in the altitude range of 0.5 to 3 km over N-BoB. The pronounced differences in the average profiles of



**Figure 4.6:** Differences in average profiles of ozone, specific humidity and temperature between northern and southern (a) Bay of Bengal and (b) Arabian Sea.

specific humidity and temperature show that the drier and warmer air is present over N-BoB in this altitude range. There are also some small differences above 3 km in the temperature and humidity but these can be due to natural variability. The vertical distribution of ozone difference is found to be well correlated with temperature difference and anti-correlated with specific humidity difference with  $r^2$  values of 0.91 and 0.94 respectively within 500 m to 2.3 km showing the air mass sustained the specific signature of a particular plume. The drier and warmer air-mass present above the MBL over N-BoB than S-BoB indicates the advection of residual layer air-mass of continental origin over N-BoB. The high level of ozone in this air mass shows strong signature of polluted air mass, rich in either ozone or precursors of ozone. Similar differences are observed between the average profiles of meteorological parameters over N-AS and S-AS (Figure 4.6 b). The meteorological parameters show the drier and warmer air over N-AS also in the same altitude range. Ozone difference is observed positive between 500m and 3 km over N-AS by  $\sim$  10-15 ppbv, which is comparatively lower with respect to BoB. The correlation  $(r^2)$  between ozone and temperature was found to be 0.8 but there was poor correlation between ozone and specific humidity indicating mixing of transported air with the local marine air up to some extent over this region. These profiles show significant influence of transported polluted air from landmasses with very high level of pollution, 40 ppbv more than mixed layer ozone over N-BoB, while it also suggest that N-AS is experiencing the less polluted air during the March-April months.

# 4.2.3 Identification of source regions: Potential Source Contribution Function

The identification of source locations for the high ozone plumes are performed using Potential Source Contribution Function (PSCF). The PSCF receptor model was developed by *Ashbhaug et al.* [1985] and *Malm et al.* [1986] and has been used in several studies for quantitative apportionment of sources of aerosols [*Cheng and Hopke,* 1993; *Polissar et al.,* 2001; *Raman and Hopke,* 2007] and gas phase organic constituents [*Hsu et al.,* 2003; *Hoh and Hites,* 2004]. The

reliability of the method has been cross checked with respect to known source regions [*Begum et al.*, 2005].

The calculation of PSCF depends on the observed levels of pollutants at the receptor site and back trajectories associated with the receptor location at the sampling time. High levels of pollutants at source locations are assumed to be mixed with the air parcel and transported to receptor locations. Thus air parcel back trajectories are related to the observed levels of pollutants by matching the trajectory arrival time with the time of observation at the receptor location.

The PSCF is calculated for a particular grid cell by counting the number of trajectory end points terminating in that cell. The end points of trajectories are the pair of latitude and longitude, showing the location of air parcel back in time. Suppose the total number of endpoints falling in a cell is  $(n_{ij})$ . A subset of these back trajectory endpoints  $(m_{ij})$  exists, having arrival time at receptor location corresponding to higher pollutant levels than a given criteria (50<sup>th</sup> percentile in present study [*Cherian et al.*, 2008]). Then the PSCF for ij<sup>th</sup> cell will be

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$$

This function provides a conditional probability estimate of geographical locations responsible for the high concentration samples. The PSCF calculation can be made collectively for a well mixed layer, assuming that trajectories at different altitudes within this layer are contributing for its pollution level. If back-trajectories at different altitudes are also taken into consideration the PSCF is called total PSCF (TPSCF) [*Cheng et al.*, 1993] which is calculated using individual probabilities over each altitude.

$$TPSCF_{ij} = \frac{\sum_{k} (m_{ij})_{k}}{\sum_{k} (n_{ij})_{k}}$$

Where k denotes different altitudes.

The probability depends on the distributions of end points and a sufficient number of back trajectories can depict a correct picture of probable source locations. The smaller number of  $n_{ij}$  may generate the large error in the probability estimation. Hence, a weighting function, originally proposed by *Zeng and Hopke* [1989], is applied to the PSCF. The function is given as



**Figure 4.7:** Total Potential Source Contribution Function (TPSCF) map over (a) Northern Bay of Bengal, (b) Southern Bay of Bengal, (c) Northern Arabian Sea and (d) Southern Arabian Sea.

Entire geographical area covered by back-air trajectories is subdivided into 1°x1° grid cells. The seven days kinematic back-air trajectories are calculated for each flight location by using the METEX trajectory model [*Zeng et al.*, 2008].

The effectiveness of PSCF calculation largely depends on the number of sufficient back trajectory end points. In order to improve the performance of the method, a square grid cell of  $0.5^{\circ} \ge 0.5^{\circ}$  is made around the flight locations and back-trajectories are also calculated at its four corners [*Naja et al.*, 2003]. The process is repeated at every 250 m starting from 750 m to 3250 m (ozone plume range). These trajectories are tagged with the corresponding ozone mixing ratios at respective altitudes for the estimation of TPSCF.

The TPSCF map is displayed over the area covered by air parcels before reaching to the observational locations in four different marine regions (Figure 4.7). The plot for N-BoB highlights south west Asia and Indian land region particularly Indo Gangetic plain as the potential source regions for high ozone plume over N-BoB (Figure 4.7a). The high TPSCF values (0.6-1) are found to be confined within these regions.

The TPSCF map shown in Figure 4.7b represents the potential source regions over S-BoB. The high TPSCF values (> 0.5) are found to be spread over the IGP, N-BoB, S-BoB and some parts of Indian Ocean. This map is mainly confined within the oceanic area influenced by pristine marine air and supports the absence of polluted plume of enhanced ozone mixing ratio. Thus, the effect of transport from Indian subcontinent is found to be confined over N-BoB and air over the S-BoB is found relatively cleaner, representing the dominance of pristine marine air.

The TPSCF map over N-AS is shown in Figure 4.7c. The map reveals that high TPSCF values (> 0.5) over N-AS are spread mainly over the South-West Asia, and North Africa with the influence of Central-West India. The South-West Asian region and North Africa are mainly deserts, and the pollution source is natural gas emission over this region. TPSCF map over S-AS is depicted in Figure 4.7d. The TPSCF values were found in the range of 0.5-1 over the N-AS, S-AS, few coastal regions of south and west India and few locations over BoB. But the major TPSCF spread region with high values (> 0.6) was confined within marine region of AS. Thus, the similarity observed in vertical ozone over S-BoB and S-AS is supported by TPSCF maps, which reveal the dominance of clean marine air over both the regions.

#### 4.2.4 Residence time analysis

The residence time analysis is performed in the plume region over BoB and AS to separately quantify the ozone contribution from different regions. The spatial coverage of PSCF distribution is used to allocate the preliminary sectors affecting the BoB and AS. Three regions are defined for trajectory classification:



**Figure 4.8:** The spatial coverage of three regions designated as Northern Indian region, marine region and Africa/South-West Asia/South Europe.

(1) the region from 18°N to 32°N and from 68°E to 88°E is designated as Northern Indian Region (NIR); (2) the Arabian Sea, Bay of Bengal and Indian ocean are designated as the marine region and (3) the region west to the 68°E and excluding marine region is considered as Africa/South-West Asia/South Europe (Figure 4.8). The southern and north-east regions of India are unclassified as very few trajectories originated from these regions. The air masses of different origins



**Figure 4.9:** The vertical distributions of average ozone with  $\pm 1\sigma$  variation over Bay of Bengal and Arabian Sea in the plume range. The ozone levels are also depicted in NIR, marine and LRT air masses.

are studied in detail for BoB and AS. An air mass is considered as the regionally polluted if it has spent more than 3 days over NIR and less than 3 days over marine region. These air masses will be sufficiently influenced by regional pollution with lesser effect from other regions. An air mass is categorized as the long range transport air mass if it has spent more than 3 days over Africa/southwest Asia/south Europe sector. The marine air mass is identified on the basis of residence time greater than 3 days over marine region. The difference in ozone levels are examined in different air-masses with respect to average ozone over BoB and AS (Figure 4.9). The ozone levels are found to be 25.5% higher in NIR air-mass than average ozone levels over BoB in the altitude range of 0.75-2.5 km. In this region, the ozone mixing ratios are lower by 19% in the marine air-mass than the average levels. The influence of LRT is evident at higher altitudes above 2.5 km. The marine air mass is affecting the distribution of ozone in the whole altitude range. In the altitude range 2.5 to 3.25 km, the ozone levels are found 8.2% lower in marine air-mass and 16.4% higher in LRT air-mass over BoB. The NIR pollution is not playing major role at higher altitudes (> 3 km), indicating the pollution plume is mainly affected by northern Indian region. On the contrary, there is no distinct contribution (< 6%) of any region over Arabian Sea as evident from Fig. 4.9 (right panel).

#### 4.2.5 Satellite derived CO and NO<sub>2</sub>

The TPSCF can only identify most probable source regions, which are linked to the observed high ozone layers. However, it cannot indicate whether ozone or its precursors were transported to the locations of observations. In this section we attempt to add information on spatial distribution of CO and NO<sub>2</sub>, the two main precursors of ozone [*Seinfeld and Pandis*, 2006], around the observation region. The CO and NO<sub>2</sub> distribution maps are obtained from MOPITT (Measurements Of Pollution In The Troposphere) [*Warner et al.*, 2001; *Deeter et al.*, 2004] and OMI (Ozone Monitoring Instruments) [*Boersma et al.*, 2002] instruments, respectively. The CO data correspond to 850 mb with a spatial resolution of 1°x1°. The daily data have a poor spatial coverage and time averaging for study period will not depict the correct spatial distribution of CO over the study region. Thus, the monthly averaged gridded CO data (level 3) are used for a better statistical representation. These data are averaged for March and April 2006 for the first leg when the ship was traversing over BoB region and April and May 2006 for the second leg, when observations were made over AS (Figure 4.10). However, available column integrated daily tropospheric NO<sub>2</sub> values (clear-sky condition, 0-30% clouds) with spatial resolution of  $0.25^{\circ} \times 0.25^{\circ}$  are used for this study. Though, the data are column integrated, these represent NO<sub>2</sub> content in the lower 4 km of the troposphere, in the absence of a significant



**Figure 4.10:** *MOPITT derived average CO distributions for (a) March and April for the first phase of the cruise and (b) April and May showing the same for the second phase.* 

source in the upper troposphere such as lightening and aircraft exhaust. These data are averaged from 18 March to 12 April for BoB and from 18 April to 10 May for AS segment (Figure 4.11). These maps are inter-compared with TPSCF maps to locate the source regions of high ozone plumes.

Distribution of CO at 850 mb shows that its concentrations are higher (~ 200 ppbv) over the locations wherein the TPSCF are also higher like IGP, Pakistan etc. The column integrated NO<sub>2</sub> values are also found to be significantly high (>  $5x10^{15}$  mol/cm<sup>2</sup>) over IGP and both these data together support the evidence of favorable conditions for ozone formation. The CO and column NO<sub>2</sub> concentrations were found to be comparatively low (CO < 140 ppbv and NO<sub>2</sub> <  $1x10^{15}$  mol/cm<sup>2</sup>) over S-BoB, S-AS and central N-AS regions. However, the

coastal locations of N-AS are the regions of higher CO ( $\sim$  140-180 ppbv) as well as higher column NO<sub>2</sub> (1-9 x10<sup>15</sup> mol/cm<sup>2</sup>) than over N-AS.



**Figure 4.11:** The OMI derived average  $NO_2$  column distributions  $(10^{15} \text{ mol/cm}^2)$  for (a) 18 March to 12 April for the first phase of the cruise and (b) 18 April to 10 May showing the same for the second phase.

#### 4.2.6 Comparison with MOZART model

The Model for OZone And Related Tracers (MOZART) is a global chemical transport model which simulates the chemistry and transport processes

in the atmosphere. The model is based on the detailed atmospheric chemistry of 63 chemical species with 133 gas phase, 2 heterogeneous and 33 photolytic reactions. The POET (Precursors of Ozone and their Effect on the Troposphere) emission inventory is used as input in the model and meteorological input data are obtained from NCEP. There are 28 sigma levels from surface to 40 km with horizontal resolution of 2.8° x 2.8° [*Sheel et al.*, 2010]. The vertical profiles of ozone compared with the MOZART Model results.

Figure 4.12 shows the vertical distributions of ozone observed by ozonesonde and simulated by MOZART at different observational locations. The model reproduces the major features present in the profiles however it is unable to capture the small scale variations. The model overestimates the mixed layer ozone



**Figure 4.12:** Comparison of ozone profiles obtained from ozonesonde and MOZART model for different balloon flights days.

in some profiles. This may be due to higher emission estimated by POET inventory or due to shortcoming of model with respect to additional loss process (like halogen chemistry) of ozone in the MBL. This highlights the need of further modification of emission inventory, and model with possible chemical and physical mechanisms, to reproduce the low ozone levels in the MBL.

#### 4.2.7 Comparison with other measurements

The average profiles of ozone over four marine regions are compared with the average vertical profiles of ozone over Delhi and Chennai, obtained from MOZAIC (Measurement of OZone and water vapour in AIrbus in-service airCraft) for spring season. The MOZAIC program was initiated in 1993 to collect the ozone and humidity data in long range commercial airlines. The ozone and humidity sensors were installed in the five European aircrafts for the measurements during takeoff and landing of the flights. The mean vertical profiles of ozone over these two locations are calculated by averaging all flights data available for March to May months during 1996 to 2001. The MOZAIC data is not available during the study period.

The measurements of vertical distributions of ozone by Indian Meteorological Department (IMD) are made during the study period, using Brewer Mast ozonesonde, every fortnightly from Delhi, Pune and Trivandrum. It would have been useful to use these data for observing the levels of ozone over these regions. But the quality of this data is a major concern. Thus we have used the MOZAIC data averaged for the pre-monsoon season.

The average level of ozone is found to be 10 to 20 ppbv higher over Delhi in comparison to Chennai within 500 to 1500 m range (Figure 4.13). The difference decreases with the increasing altitude and persists up to 3 km. This is to be noted that the difference in ozone profiles over different oceanic segment is also evident up to this altitude only. The ozone levels are higher over the N-BoB

than over Delhi. Delhi is one of the highly polluted cities situated in IGP, which is the most probable source region identified in source apportionment analysis.

The lower levels of ozone have been reported over the source locations in comparison to downwind locations in several studies [*Fowler et al.*, 1999; *Chand*, 2002]. This feature is also observed during MObile Lab Experiment [MOLEX] over Gujarat during January 2002. The day time peak ozone levels were found about 55 ppbv over urban city Ahmedabad whereas its levels were found about 78-86 ppbv over rural areas of Bagodra, Bhavnagar, Mahua, Gadada and Khambhat, downwind to Ahmedabad [*Chand*, 2002]. The ozone titration takes place over the urban locations due to excess emission of fresh NO [*Fowler et al.*, 1999]. This may be a probable reason of lower levels of ozone over Delhi than



**Figure 4.13:** The average vertical distribution of ozone over N-BoB, S-BoB, N-AS, S-AS, Chennai and Delhi in the lower 4 km during spring season.

N-BoB. Also, intra-annual variability in ozone levels over Delhi may also be another cause of this difference. Chennai is a coastal area situated near the line of separation of N-BoB and S-BoB. The level of ozone at this station is found to be higher than S-BoB and less than N-BoB. The ozone levels over Chennai are almost similar to the ozone levels over N-AS above 0.5 km.

The elevated layers rich in pollutants have been observed above marine boundary layer over different oceanic regions all over the world. Based on aircraft observations during Dynamics and Chemistry of Marine Stratocumulus (DYCOMS) Experiment and the First ISCCP (International Satellite Cloud Climatology Project) Regional Experiment (FIRE), Paluch et al. [1992] have reported intrusion of layers having ozone concentrations greater than 70 ppbv above mixed layer inversion attributed to baroclinic flow from the coastal regions over the Eastern Pacific during summer. During the NASA Global Tropospheric Experiment (GTE) Chemical Instrumentation Test and Evaluation (CITE 3) expedition, the aircraft measurements of vertical ozone off the U.S. east coast during August-September 1989 shows that mixed layer ozone concentrations were higher by a factor of 3 within the air-masses of continental origin (~ 60 ppbv) with respect to clean marine background air (~ 20 ppbv) [Anderson et al., 1993]. Their study reveals that continental contribution towards high ozone dominates up to 2.4 km altitude. The vertical measurements of ozone in series of aircraft flights during North Atlantic Regional Experiment (NARE, August-September, 1992) shows the ozone mixing ratios above the mixed layer were 50-70 ppbv twice that of ozone within the mixed layer having typical concentration of 20-30 ppbv over the western North Atlantic [Berkowitz et al., 1995]. Knapp et al. [1998] reported advection of polluted continental air rich in ozone up to 90-130 ppbv above mixed layer having ozone concentration of 20-40 ppbv over the Maritime Provinces of Canada during NARE, 1993.

Similar layers of enhanced ozone have been observed over AS and Indian Ocean during the INDOEX conducted in February-March, 1999 [*Lelieveld et al.*, 2001; *Simpson and Raman*, 2003]. The levels of ozone over N-BoB during

ICARB is comparable to those observed over AS and IO during INDOEX. The INDOEX was conducted during February March period when the levels of pollution is higher due to accumulation in shallower boundary layer. Ozone levels could be further higher over N-BoB during this period due to advection of higher levels of pollutants over ocean. The present results show very clear evidence for transport of continental pollution over the marine regions surrounding India especially over the N-BoB from IGP. It is to be noted here that N-BoB is on the downwind of the IGP during most of the year.

#### 4.3 Surface measurements of trace gases during ICARB

The elevated layer of ozone over N-BoB is attributed to advection from IGP. But we are unable to answer precisely whether ozone itself got transported or photo chemically formed over the ocean by the transported pollutants like CO,  $CH_4$  and NMHCs. It was not possible to get the vertical profiles of these species simultaneously with ozone and meteorological parameters due to technical limitations. To partially fulfill this gap, we made measurements of these species twice in a day during the cruise. It is assumed that, surface distribution of these species will sustain the chemical composition of the plume air due to boundary layer-free troposphere interactive exchange. The assumption is also supported by higher level of surface ozone over N-BoB with respect to other oceanic regions. The results of the surface measurements are discussed below.

#### 4.3.1 Spatio-temporal variations of O<sub>3</sub>, CH<sub>4</sub>, CO and NMHCs

The spatio-temporal variations of surface ozone, CO, CH<sub>4</sub> and NMHCs are shown along with the cruise track data (latitude and longitude) during the campaign in Figure 4.14. The first panel of the figure shows the variation of surface ozone. The number of data points is less as these are based on 20 minute surface measurements of ozonesonde on balloon flight days. The mixing ratios of ozone decreased from 48-54 ppbv to 15-25 ppbv from N-BoB to S-BoB. The lowest levels of O<sub>3</sub> (~ 15 ppbv) were observed on 30 March when the sky was cloudy. The distribution of ozone showed almost constant levels of 20-28 ppbv



**Figure 4.14:** Variations of surface ozone and its precursor gases over BoB and AS during ICARB, 06.

over the Arabian Sea except on 27 April (day of year 117) when ozone attained its minimum of 10 ppbv.

The CH<sub>4</sub> variation is shown in the second panel of the figure. Its level increased from 1.8 ppmv to 1.91 ppmv when the ship moved from Chennai to north coast of BoB. Its level started declining while moving towards S-BoB and it was 1.75-1.79 ppmv at the end of this phase of the cruise (SK 223A). During the

AS phase, the CH<sub>4</sub> levels decreased from 1.79-1.81 ppmv to 1.71-1.73 ppmv from south to north. This is a reverse trend than that observed over the BOB. The CO distribution shows relatively large variation over BoB with respect to AS. Its values increased from 161 ppbv to 234 ppbv while moving from Chennai to northern coastal areas of BoB. Its levels decreased when the ship moved towards S-BoB and attained its minimum (~ 88 ppbv) in the southeast part of BoB. During AS phase, its levels decreased by 22% from S-AS to N-AS. The minimum-mixing ratio of 52 ppbv is recorded in the middle of AS on 30 April.

The distributions of ethane and n-butane showed similar variations to CO. Their mixing ratios showed higher levels (1269 pptv and 637 pptv respectively) over N-BoB. Their mixing ratios decreased in the range of 300-400 pptv and 50-100 pptv at the end of SK 223A. A significant variation is absent in their distribution over AS and their levels varied between 200-650 pptv and 20-108 pptv.

The time series variations of alkenes and acetylene show very different variations from other trace species. These species showed large variability during the entire cruise period. Sharp peaks in the mixing ratios of ethene, propene and acetylene were observed on 21 March with values of 497, 372 and 236 pptv. Their levels remained low in the ranges of 47-119 pptv, 10-73 pptv and 6-40 pptv over the central BoB during 24 to 30 March. Their mixing ratios increased significantly with ranges of 156-424 pptv, 45-367 pptv and 49-271 pptv respectively over S-BoB. Their higher levels persisted over S-AS also with large variations, and decreased to lower values at the end of the SK 223B. All these gases also show lower values over the N-AS.

The seven days back-trajectories are examined over sampling locations at 0.5 km to delineate the various processes affecting the distributions of observed trace species. The back-trajectories have been subdivided in six different groups based on the origin of trajectories. These regions are northern, mid and southern, BoB and AS. The trajectories are shown in Figure 4.15. For the measurements



**Figure 4.15:** Seven days back-trajectories during the campaign over northern, mid and southern parts of BoB and AS at 500 m amsl.

over northern part of BoB, the trajectories originated over the polluted IGP. Consequently, the levels of  $O_3$ ,  $CH_4$ , CO, ethane and n-butane were highest in these air-masses. Over the central region of BoB, few trajectories originated from Andhra Pradesh and others originated from marine region. Thus, the levels of pollutants were diluted due to the mixing of pristine marine air masses. The mixing ratios of anthropogenic species are found to be lower in this air masses. The observations over S-BoB are influenced mainly by the air masses arriving from the Indian Ocean. This is the cleanest part of BoB as we observed lower levels of pollutants over this region. The last three panels of the figure show the back trajectories over AS. The maximum number of trajectories is found to be originating over AS itself in all the three groups. The transport of continental pollution is absent in this region. Thus the levels of species found lower over the AS.



**Figure 4.16:** Interspecies correlations of ozone, CO,  $CH_4$  and few NMHCs over BoB and AS. The straight lines are best linear fits.

Figure 4.16 shows the correlations between various pairs of trace species over BoB and AS. A strong correlation ( $r^2=0.90$ ) between ozone and CO over BoB indicates the photochemical formation of ozone in the polluted air mass. On

the other hand, the correlation was very poor ( $r^2=0.08$ ) over AS with lower levels of both the species. This indicates their background levels over pristine marine regions of AS. The correlations of CO with ethane and n-butane are also found to be very strong with  $r^2$  values of 0.77 and 0.78 respectively over BoB indicating their transport from common and collocated sources over this region. The mixing ratios of ethane and n-butane show a very good correlation with  $r^2$  value of 0.89. These correlation are rather poor ( $r^2$  values 0.36 and 0.13 respectively) among these species over AS.

A poor correlation of CO with acetylene as well as ethane with acetylene discards the possibility of combustion related sources over the continent over BoB and AS. Moderate to good correlations with  $r^2$  values of 0.63 and 0.59 are observed in ethene and propene over BoB and AS. These are the only species, which show a significant correlation over AS also. This suggests their biological emissions from oceanic regions.

#### 4.3.2 Latitudinal variations of trace gases

Figure 4.17 shows the latitudinal dependences of ozone and its few precursors having anthropogenic sources over N-BoB (latitude <  $12^{\circ}$ N). The wind regime over this region is mostly northwesterly. The back-trajectories show that the pollutants were mainly transported from the IGP. The north to south gradient, in such case, provides information on the combined effects of chemical transformation and dispersion of these gases over the remote regions by the prevailing wind. The latitudinal gradient of ozone is 5.2 ppbv/deg, CH<sub>4</sub> is 5.3 ppbv/deg, CO is 9.9 ppbv/deg, ethane is 93.2 pptv/deg and n-butane is 59.7 pptv/deg.

Two points are clearly discernable from the figure:

1) The mixing ratios of ozone, CO, ethane and n-butane sharply decrease from north to south.

 The gradients of gases (other than methane, which has much longer lifetime than all other gases discussed here) are steeper in ICARB compared to INDOEX and BOBPS (Table 4.2).



**Figure 4.17:** *Latitudinal variations of O*<sub>3</sub>*, CO, ethane and n-butane over N-BoB during ICARB 2006. The straight lines are best linear fits.* 

The sharp decrease in the mixing ratios of species (other than methane) are expected, as their chemical loss process combined with dilution in the absence of local sources leads to continuously decreasing mixing ratios while moving farther south over the ocean. The north south gradients are sharper due to injection of highly polluted air mass in the MBL from the northern coast of BoB and the absence of arrival of any other polluted air-mass in between. The highest level of ozone observed during entire BOBPS was 35 ppbv, which is far less than the level of ozone (~ 54 ppbv) over N-BoB during ICARB. Also, the back-trajectories have swept the pollution from middle and south India over the BoB during BOBPS affecting the north south gradient during that period. This may be the probable cause of the lower decrease rate of pollutants during BOBPS.

marine regions surrounding Indian subcontinent [Chand et al., 2001; Muhle et al., 2002; Sahu et al., 2006c].

Table 4.2: The latitudinal gradients of few trace gases during different campaigns over

Latitudinal gradient	INDOEX 1999 (AS) (FebMar.)	BOBPS 2002 (BoB) (SepOct.)	ICARB 2006 (BoB) (MarApr.)
Ozone (ppbv/deg)	1.7	1.37	5.2
CH <sub>4</sub> (ppbv/deg)	2.3/1.7	10.65	5.3
CO (ppbv/deg)	4	3.86	9.9
Ethane (pptv/deg)	-	29	93.2
n-Butane (pptv/deg)	-	5	59.7

However, the latitudinal gradient of methane is two times higher during BOBPS than ICARB. This may be due to the continental sources of methane during BOBPS. This campaign was conducted in September-October month. *Mukhopadhyay et al.* [2002] have reported that emission of methane from Sundarban coastal mangrove forest ecosystem is maximum during this period of year. Its emission is also enhanced by paddy fields over land areas formed as a consequence of heavy rains during July August.

The alkenes and acetylene do not show any significant north south gradient during ICARB. These species are mostly emitted by vehicular emission, which probably is not playing a major role towards the production of pollutants.

#### 4.3.4 Comparison with other measurements

Measurements of ozone and other related trace gases were made over the BoB and the AS during the INDOEX 1999 [*Muhle et al.*, 2002], BOBEX 2001 [*Lal et al.*, 2006], BOBEX 2003 [*Sahu et al.*, 2006], and BOBPS 2002 [*Lal et al.*, 2007]. INDOEX and BOBEX campaigns were conducted in the month of February and March whereas; the BOBPS was conducted during September and October. The intra-seasonal, intra-annual and spatial variability is imbedded in the distributions of these gases during different campaigns. Their averages with  $\pm 1\sigma$  variations are given in Table 4.3 for all the campaigns conducted over the study region.

Table 4.3: Comparison of mixing ratios of ozone and its various precursor gases over BoB and AS during different cruise campaigns.

Species	INDOEX 1999, (AS)	INDOEX 1999, (BoB)	BOBPS 2002, (BoB)	BOBEX II 2003, (BoB)	ICARB 2006, (BoB)	ICARB 2006, (AS)
O <sub>3</sub> (ppbv)	$43.9\pm8.0$	$42.2 \pm 12.0$	$27 \pm 6$	$34 \pm 6.4$	$31.9 \pm 15.2$	$22.7\pm4.4$
CO (ppbv)	$217\pm42.0$	$217 \pm 31$	$143 \pm 23$	$193 \pm 40$	$145 \pm 38$	86.7 ± 14.1
CH <sub>4</sub> (ppmv)	$1.73\pm0.05$	$1.92\pm0.05$	$1.75\pm0.05$	$1.72 \pm 0.04$	$1.81\pm0.03$	$1.74\pm0.02$
C <sub>2</sub> H <sub>6</sub> (pptv)	544 ± 86.6	-	561 ± 130	$1181 \pm 362$	$589 \pm 280$	338 ± 125
C <sub>2</sub> H <sub>4</sub> (pptv)	-	-	$299 \pm 170$	$198 \pm 60$	$194 \pm 154$	$165 \pm 106$
C <sub>3</sub> H <sub>6</sub> (pptv)	-	-	$129 \pm 50$	$106 \pm 50$	$112 \pm 92$	$132 \pm 88$
$n-C_4H_{10}$	-	-	$145 \pm 50$	98 ± 123	$187 \pm 157$	$49 \pm 23$
(pptv)						
C <sub>2</sub> H <sub>2</sub> (pptv)	$141 \pm 21$	-	$128 \pm 80$	$471 \pm 276$	$100 \pm 75$	$85 \pm 77$

Extensive measurements of all  $C_2$ - $C_5$  NMHCs were not made during INDOEX. The levels of ozone, CO and various NMHCs are found to be lower than BOBEX II but higher than BOBPS during present campaign over BoB, while CH<sub>4</sub> level is lower than BOBEX I and higher than other measurements. This difference may be due to prevailing wind regimes from different directions over the study region. During February-March, the northeasterly and westerly winds

dominate over the BoB region carrying higher level of pollutants. The higher degree of pollution also depends on the dynamics of continental boundary layer and the level of anthropogenic emission particularly fossil fuel and biomass burning. Accumulation of pollutants takes place in the shallow boundary layer resulting in higher level of pollution. The atmospheric boundary layer remains shallow during February-March (BOBEXs) with respect to late March and April months (ICARB period over BoB) and prevailing winds transport them over the ocean. Acetylene is lower during ICARB than during BOBEX and BOBPS indicating the lower effect of vehicular emission during ICARB. IGP is identified as the source region for higher levels of pollutant gases over N-BoB. Thus, the levels of measured gases over N-BoB are compared with their levels in Hissar (25°5'N, 74°47'E), a semi-urban site situated in the North West region of IGP. The trace gas measurements were made over Hissar during December 2004 [*Lal et al.*, 2008]. The average levels of ozone and its precursors over Hissar and N-BoB during the respective study periods are shown in Table 4.4.

Species	Hissar	Northern BoB
O <sub>3</sub> (ppbv)	33.4 ± 9.6	$35 \pm 16$
CO (ppbv)	553.5 ± 292	$162 \pm 37$
Ethane (pptv)	$8600\pm3800$	$696 \pm 292$
Ethene (pptv)	$9300 \pm 11400$	$145 \pm 127$
Propene (pptv)	$2800\pm2600$	$84 \pm 79$
n-Butane (pptv)	$2120 \pm 1890$	$240 \pm 167$
Acetylene (pptv)	$3100\pm3300$	$103 \pm 68$

Table 4.4: Comparison of ozone and its various precursors over Northern Bay of Bengal and Hissar.

The ozone levels are found lower at Hissar than over N-BoB. This is due to the inclusion of night time ozone levels, which are much lower due to the absence of photochemical production and loss of ozone over polluted land areas like NO titration and dry deposition. The CO levels are found to be higher by three times over Hissar. The anthropogenically emitted NMHCs are found to be more than ten to thirty times higher over this location with respect to N-BoB. Similarly, measurements of these gases at Ahmedabad, an urban location in the central west of India, also show much higher levels as compared to these marine regions. The inter-correlation and ratio of various non-methane hydrocarbons indicated the influence by intense local biomass burning at Hissar during the study period. In addition to that, the measurements over Hissar were made during December, 2004. This is the winter season over Indian subcontinent, which gets affected by frequent temperature inversions leading to accumulation of pollutants in the lower volume.

## **Chapter 5**

### Distributions of ozone and its precursors over land & marine interface

The marine regions surrounding the peninsular India is being polluted from the outflow of pollutants from many south Asian countries [*Lelieveld et al.*, 2001; *Ramnathan et al.*, 2001; *Satheesh et al.*, 2006; *Moorthy et al.*, 2008; *Murugavel et al.*, 2008]. Most of these countries are highly populated, accompanied by rapid industrialization and agricultural growth and thus are major sources of anthropogenically emitted pollutants. Emissions from south Asia are strongly influenced by inefficient combustion processes, especially biofuel burning in cook stoves, widespread uses of two stroke engines etc. This region contributes a disproportionally large part in total global CO and NMHCs emissions, approximately 1.5 times larger than its relative contribution to CO<sub>2</sub> and NO<sub>x</sub> [*Lawrence and Lelieveld*, submitted to ACP 2010]. These gases are major precursors of ozone in the troposphere. The study of their vertical distributions is equally important as ozone over India and surrounding marine regions to understand their roles in chemistry of the tropical troposphere and global climate change.

As discussed in Chapter 4, the layers of very high mixing ratios of  $O_3$  were observed in the altitude range of 1-3 km over northern BoB region (> 12°N)

during ICARB, 2006 (See Chapter 4). The detailed investigation of air parcel back trajectories showed plumes with high ozone originated over continental regions of India. However, the vertical measurements of its precursors like CO, CH<sub>4</sub> and NMHCs were not made during this campaign.

Simultaneous measurements of ozone, CO, methane and light NMHCs were made in the lower troposphere along the air segments of Winter ICARB (WICARB) campaign during 1-20 January 2009. This period was chosen because the boundary layer remains shallow over the continent and pollutants are advected over BoB from the various upwind regions. The major objectives of the campaign were to (1) characterize the continental outflow of pollutants, (2) spatio-temporal variations of trace gases and aerosols over marine regions, (3) study their vertical profiles in the lower troposphere, and (4) study the changes in chemical compositions during the transport from coastal to cleaner oceanic regions. In this chapter, we will present the results related to ozone and its precursors obtained from the different air-segments of WICARB.

#### 5.1 Experimental details and meteorological conditions

The air-segment of WICARB was conducted using Beechcraft Super King Air B-200 (VT-EBB) of National Remote Sensing Centre (NRSC), Hyderabad, India during the month of January 2009. The aircraft was operated in unpressurised mode with a ceiling altitude of 3 km. A total of 10 air sorties were conducted from one inland site Hyderabad (17.45°N, 78.45°E); two east coastal sites of Vishakhapatnam (17.72°N, 83.22°E) and Chennai (12.99°N, 80.17°E); one remote island Port Blair (11.64°N, 92.73°E); and one western coastal site of Mangalore (12.96°N, 74.88°E).

Two different types of flights were made during the campaign.

- 1) Multi-level sorties
- 2) Bi-level sorties



**Figure 5.1:** The flight path of air sorties from five different experimental locations. The dashed lines show the bi-level sorties and solid lines show multi-level sorties.

The multi-level sorties were performed in step and staircase mode (back and forth) at six different altitude levels (500 m, 1000 m, 1500 m, 2000 m, 2500 m and 3000 m) to investigate the vertical variations of various gases over the respective locations. The bi-level sorties were made at two altitude levels (750 m and 1500 m) in order to study the gradients in the mixing ratios of these species from coast towards the open ocean. The spatial coverage of each sortie with label is shown in Figure 5.1 and further details are given in Table 5.1. Typical multilevel and a bi-level sortie path profiles are shown in Figure 5.2.

The ambient air was aspirated via SS inlet lines fitted under the nose of the aircraft. The in-situ measurement of ozone was made with a time resolution of 10 seconds using UV absorption based Dual Beam 2B ozone analyzer (Model 205). The air samples were also collected using an oil free compressor (Metal Bellow, USA) in the glass bottles volumes of 300-800 ml. These samples were analyzed



**Figure 5.2:** *Typical altitude variation of aircraft paths for multi-level and bi-level sorties during WICARB (Paths shown for Vishakhapatnam). The sampling locations are also shown over the paths.* 

using two gas chromatographs, Varian Vista, 6000 and Hewlett Packard 5890 II to get the concentrations of CO,  $CH_4$  and NMHCs ( $C_2$ - $C_5$ ) respectively. The detailed descriptions of these systems and calibration procedures have been already discussed in Chapter 2.

Figure 5.3 shows the wind fields representing the flow patterns over India and surrounding marine regions prevailed during the campaign. The wind field data are obtained from the NCEP (National Center for Environmental Prediction). The four panels of this figure show the average wind vectors at four different pressure levels of 1000 mb, 925 mb, 850 mb and 700 mb. The wind was calm over central India at 1000 mb, 925 mb and 850 mb whereas westerly wind

prevailed at 700 mb. On the other hand, the strong winds from northeast influenced the marine regions of BoB and Arabian Sea. The wind vectors at 850 and 700 mb indicate the transport of continental air mass over northern BoB. The winds were mainly easterly over southern BoB, southern AS and Indian Ocean (south of  $12^{\circ}$ N) at 850 mb and 700 mb.

S.N.	Locations	Date	<i>Type of Sorties</i>	Flight Take off time (am, IST)	Total flight duration (hours)	Name of Sortie
1	Hyderabad	02-01-09	Multi-level, East-West	10:39	3.12	H1ML
2	Visakhapatnam	04-01-09	Multi-level, East-West	09:57	3.52	V1ML
3	Visakhapatnam	05-01-09	Bi-level, East- West	10:15	2.13	V2EW
4	Port Blair	09-01-09	Bi-level, East- North-South- West	06:35	2.68	P1EN
5	Port Blair	09-01-09	Bi-level, North-South	10:56	1.66	P2NS
6	Port Blair	12-01-09	Multi-level, East-West	06:27	2.94	P3ML
7	Port Blair	13-01-09	Bi-level, West- East	06:10	2.41	P4WE
8	Port Blair	14-01-09	Bi-level, South- North	06:20	2.32	P5SN
9	Chennai	16-01-09	Bi-level, East- West	10:19	2.40	C1EW
10	Mangalore	19-01-09	Multi-level, South-West	09:13	3.11	M1ML

#### Table 5.1: Details of air sorties conducted during W-ICARB.



**Figure 5.3:** The synoptic wind fields (*m*/*s*) at four different pressure levels averaged for 1-20 Jan, 09 over the Indian subcontinent.

### 5.2 Longitudinal variations of ozone and its precursors 5.2.1 Longitudinal variation over Vishakhapatnam

The mixing ratios of ozone measured during V2EW sortie over Vishakhapatnam are shown in Figure 5.4. The ozone values are averaged for every 0.1° longitude and are shown with  $\pm 1\sigma$  variation. The starting longitude 83.2°E is a costal location and aircraft moved away from coastline on a constant latitude path. The average mixing ratios of ozone were found in the range of 50  $\pm$  5 ppbv near the coast at 750 m level which increased with a rate of 2.0 ppbv/deg



**Figure 5.4:** The longitudinal distributions of  $O_3$  (with  $\pm 1\sigma$  variability), CO, CH<sub>4</sub>, ethane and n-butane over ocean away from coastal area (Vishakhapatnam) to open ocean at 750 m and 1.5 km.

longitude and attained the maximum ozone level ( $60 \pm 2$  ppbv) at 86.7°E. The reverse trend is observed at 1.5 km altitude, where ozone decreased with longitude with a rate of 1.5 ppbv/deg and reached its minimum mixing ratio at 86.7°E (43 ±

4 ppbv). This is to be noted that up to 85.8°E, the ozone levels at both the altitudes were more or less same, whereas this longitude onwards the ozone values started changing.

Similar trends can be seen in the distributions of CO, CH<sub>4</sub>, ethane and nbutane at both the height levels. The average concentrations of these species were found to be higher at 750 m than 1500 m and increases with increasing longitude. Their mixing ratio decreases with increasing longitudes at 1500 m level. The difference in the mixing ratios of these gases between 750 m and 1500 m (in the samples of same longitude) are examined. The average difference of CO, CH<sub>4</sub>, ethane and n-butane between 750 m and 1500 m levels were found 41 ± 24 ppbv,  $0.017 \pm 0.01$  ppm,  $198 \pm 215$  ppbv and  $312 \pm 83$  ppbv respectively in the samples collected before 86°E (towards west) and  $133 \pm 12$  ppbv,  $0.09 \pm 0.01$  ppm,  $931 \pm$ 284 ppbv and 713 ± 250 ppbv in the samples collected on and after 86°E (towards east). This shows that these gases have large difference (2-5 times higher with respect to samples collected near coastal area) between two altitudes collected over open ocean. This again suggests that aircraft encountered two air-masses of different chemical compositions at two different altitudes on and after 86°E and vertical mixing is absent between them.



**Figure 5.5:** The vertical distributions of potential temperature (K) and relative humidity (%) over different marine locations. These figures are placed in the increasing order of distance from land (DFL). The arrows indicate the top of marine boundary layer.

To investigate the cause of different air-masses encountered over open ocean, we examined the vertical distributions of meteorological parameters over the ocean (Figure 5.5). The radiosondes were launched from the ocean during ship cruise segment of W-ICARB. The four flights are examined which were launched from marine locations 13.09°N-80.29°E (distance from land ~ 12 km), 13.86°N- $80.94^{\circ}$ E (distance from land ~ 92 km),  $14.84^{\circ}$ N- $81.47^{\circ}$ E (distance from land ~ 151 km) and 15.11°N-83.01°E (distance from land ~ 320 km) during 26-28 December 2008. Figure 5.5 shows the vertical distributions of potential temperature and relative humidity at these locations in the increasing order of longitudinal distance from nearest land. These profiles show the presence of mixed layer top at 400 m, 500 m, 600 m and 1100 m when the ship was away from the coastal areas by 12 km, 92 km, 151 km and 320 km respectively. Simpson and Raman [2006] have also reported higher mixed layer altitudes over ocean with increasing distance from land. Near the coast, the marine mixed layer height was shallow (~ 400 m) which increased with distance from the coast and achieved  $\sim 1$  km over the open ocean.



**Figure 5.6:** Schematic depiction of path of aircraft during bi-level sortie over east of Vishakhapatnam (Solid blue line). Variation of atmospheric boundary layer and marine boundary layer from coast to open ocean is shown by dashed blue line.
It is quite possible that 85.8°E onwards off the coast of Vishakhapatnam, the aircraft entered into the marine mixed layer at 750 m level which is detached from the free tropospheric air due to MBL inversion exist between 750 m to 1.5 km. The temperature inversion at the top of the marine boundary layer will restrict the mixing of marine boundary layer air-mass to the lower free tropospheric air-mass. Thus, the two different types of air-masses were encountered at two different altitudes after this longitude. A schematic diagram of this event is shown in Figure 5.6.

### 5.2.2 Longitudinal variation between Chennai and Port Blair

The longitudinal variation of ozone and its precursors are examined by simultaneous study of bi-level sorties C1EW and P3WE at Chennai and Port Blair respectively (Figure 5.7). The longitudinal variation from 80°E to 90.7°E between the two stations has been explored. Ozone, CO, CH<sub>4</sub> and alkanes show a clear increase from Chennai to Port Blair at 750 m. Assuming a linear trend; ozone, CO, ethane, propane and n-butane show a longitudinal increase of 0.58 ppbv/deg, 7.3 ppbv/deg, 62.3 pptv/deg, propane 11.2 ppbv/deg and 32.3 pptv/deg respectively. The significant increase is absent in the distribution of CH<sub>4</sub> due to its relatively homogeneous mixing in the atmosphere (long lifetime  $\sim 12$  years). Also, the ethene and propene do not show a significant longitudinal gradient in the marine boundary layer. This may be due to their local oceanic emissions. The gradients in the distributions of these species are quite weak at 1500 m altitude. Aerosol total scattering coefficient at 550 nm also shows a clear increase from Chennai to Port Blair with a gradient of  $\sim 3$  M/m per degree longitude at 750 m while this gradient is quite weak at 1500 m [Sreekanth et al., 2010]. These results show that the region around Port Blair is more polluted than Chennai and easterly wind blows the polluted plume from Port Blair towards Chennai. The gradient in gases is stronger at 750 m due to limited vertical mixing of pollutant gases within the MBL. The dilution of gases is taking place by mixing during the advection of the plume. In the lower free troposphere, the large dilution and mixing takes place in the atmosphere leading to poor longitudinal gradient.



**Figure 5.7:** The longitudinal variations of ozone, CO, ethane, propane and n-butane at 750 m observed between Chennai and Port Blair.

## 5.3 Spatial distributions of ozone and its precursors over BoB

Figure 5.8 shows the spatial distributions of ozone, CH<sub>4</sub>, CO and various NMHCs over BoB at 750 m during W-ICARB. These distributions are obtained by interpolation of mixing ratios observed during V2EW, P2NS, P4WE, P5SN and C1EW sorties from Visakhapatnam, Chennai and Port Blair. The objective of the interpolation was to depict the spatial heterogeneity of these gases and compare their levels over different regions. The maximum ozone mixing ratio (~ 55 ppbv), observed over east of Vishakhapatnam, is 10 ppbv higher than south of Port-Blair and 20 ppbv higher than east of Chennai. The spatial variations of methane, CO and ethane show higher mixing ratios over east of Vishakhapatnam



**Figure 5.8:** The spatial distributions of ozone, CO,  $CH_4$  and various NMHCs over Bay of Bengal at 750 m during WICARB.

and south of Port Blair. The average mixing ratios of these gases are 1.90 ppmv, 256 ppbv and 2210 pptv over east of Vishakhapatnam and 1.88 ppmv, 256 ppbv and 2578 pptv over south of Port Blair, respectively. The propane, ethene and acetylene are found highest over south of Port Blair, whereas n-butane shows its highest mixing ratio over east of Vishakhapatnam. The levels of all these gases

are found significantly low over Chennai. Similar spatial distributions with lower mixing ratios are also found at 1500 m level, which are not shown here. These observations indicate advection of pollutants over east of Vishakhapatnam and south of Port Blair. The heterogeneity in the spatial distribution of relatively short lived species like n-butane, ethene, propane and acetylene (lifetime less than 15 days) suggests the distinct sources of pollutants over these two regions. The measurements of surface ozone and CO are also made during ship segment of WICARB over BoB [*Asatar et al.*, 2010]. The surface ozone also show highest levels (> 60 ppbv) over north BoB followed by south east BoB (40-60 ppbv). However, CO mixing ratio shows 290 ppbv over north BoB and 379 ppbv over south east BoB. The lowest CO values of 167 ppbv were measured over southwest BoB. These variations are similar to the present study.

The key features in the distributions of trace gases are examined using backward trajectories obtained using METEX trajectory model. The seven days back-trajectories are calculated at observation locations at the time of flights with 0.1° spatial resolution for all bi-level sorties (for 750 m and 1500 m both). The spatial and altitude variation of trajectories arriving at 750 m over observation locations of eastward sortie of Visakhapatnam and southward sortie of Port Blair are shown in Figure 5.9. The trajectories ending at the observation locations over East of Vishakhapatnam originated from Pakistan and central north Indian region. These trajectories passed over the states of Delhi, Uttar Pradesh, Bihar and West Bengal, also known as Indo Gangetic Plain, before arriving at observation points. This region is highly populated and hence sources of many anthropogenic pollutants [Beig and Ali, 2006]. The atmospheric boundary layer altitude remains shallow over these areas during January which leads to the accumulation of pollutants near the surface. The altitudes of back-trajectories are within lower 3 km in past 120 hours when they were traversing over this region. Thus, these air masses bring the pollutants, accumulated within the boundary layer over IGP, leading to high mixing ratios of these gases over east of Vishakhapatnam. The other group of back-trajectories reaching south of Port Blair is also shown in the same figure. These trajectories traverse the regions of South East Asia, mainly



**Figure 5.9:** The spatial and altitude variations of seven days back trajectories at 750 m over Vishakhapatnam and Port Blair.

Myanmar and Thailand, before arriving at observation locations. These regions are well known for fire activities round the year. The fire active locations over this region during 1-12 Jan 2009 are shown in Figure 5.10. This shows that air parcels have passed through the fire affected areas before arriving over south of Port Blair. The altitudes of the trajectories are found higher than 2 km before last 72 hours. The air mass descended over fire region, and swept the pollutants with them over the observational location. This may be the possible reason of the high levels of pollutants over south of Port Blair.



**Figure 5.10:** Spatial distribution of fire locations observed by Advanced Along Track Scanning Radiometer (AATSR) during 1-12 Jan 2009.

The percentage abundances of different NMHCs are compared in IGP plume and SEA plume at 750 m and shown in pie diagram (Figure 5.11). The abundance of ethane is found highest (53-55%) in both the air masses due to its longer lifetime of 45 days. The second highest abundant gas is n-butane despite its lower life time (4.7 days) indicating its large emission with respect to other gases at source locations, particularly over IGP. Propane shows dominance in the SEA plume with a relative abundance higher by a factor of 2 than IGP plume. Other NMHC species also show comparatively higher abundances in the SEA plume, as shown in Figure 5.11.

The surface measurements of these NMHCs were made over Ahmedabad and Mt Abu during year 2002 [*Sahu and Lal*, 2006a, 2006b]. The relative percentage contributions of ethane, ethene, propane, propene, i-butane, acetylene and n-butane are 19.7%, 15.5%, 23.4%, 5.5%, 9.8%, 11% and 15% respectively at Ahmedabad. While these contributions at Mt. Abu are 39%, 10.8%, 14.7%, 5.4%, 6.7%, 13% and 10% respectively. At urban location Ahmedabad, local emission play major role resulting into highest contributions of relatively short lived gas, propane. At Mt Abu, east of Vishakhapatnam and south of Port Blair, transport from source locations is a key parameter in their distribution resulting into higher abundances of ethane. The relatively higher percentage of n-butane over present study locations needs further investigations.



**Figure 5.11:** *Pie diagrams showing the percentage abundances of several NMHCs over* (*a*) *east of Vishakhapatnam and (b) south of Port Blair.* 

### 5.3.1 Photochemical processing in IGP and SEA plumes

The major source of atmospheric CO and acetylene is the combustion processes [*Xiao et al.*, 2007]. These gases are removed from the atmosphere by reaction with OH radicals, with mean atmospheric lifetime of two weeks and two months for  $C_2H_2$  and CO respectively. The level of  $C_2H_2$  decreases faster with time in an air parcel after emission, leading to lower  $C_2H_2$ /CO ratio. Thus, this ratio can be used as an indicator of photochemical age of air-mass. The  $C_2H_2$ /CO ratio is particularly useful for diagnosing the age of air-mass at the remote locations because the  $C_2H_2$  lifetime is sufficiently long and its correlation with CO remains strong in aged air mass also. The  $C_2H_2$ /CO ratio greater than 1.0 pptv/ppbv is representative of fresh emission of few days whereas less than 0.5 pptv/ppbv are indicative of aged air mass [*Gregory et al.*, 1996].



**Figure 5.12:** Correlation plots of CO and acetylene over Vishakhapatnam (Sortie V2EW) and Port Blair (Sortie P5SN).

The C<sub>2</sub>H<sub>2</sub>/CO ratios are examined in the air samples collected over east of Vishakhapatnam and south of Port Blair which are shown in Figure 5.12. The value of ratio is 0.40 pptv/ppbv in the Vishakahpatnam, indicating the arrival of sufficiently aged air mass over this region. However, the moderately aged air masses are found in the south of Port Blair with C<sub>2</sub>H<sub>2</sub>/CO ratio of 0.73 pptv/ppbv. The air-masses arriving with stronger wind speed at south of Port Blair, have transported many short lived NMHCs from SEA, inspite of significant dilution during the transport. This ratio is found about 7.8 pptv/ppbv at Hissar, a location in IGP, during winter season attributed to intense local biomass burning over this location [*Lal et al.*, 2008].

### 5.3.2 Age of IGP and SEA plumes

Several studies have estimated the photochemical age of the air mass, on the basis of hydrocarbon ratios. These are commonly known as hydrocarbon clocks [*Robert et al.*, 1984]. This conventional hydrocarbon clock is based on the first order chemical loss of hydrocarbons due to OH radicals as given below.

$$[A]_t = [A]_0 \exp(-kA \times [OH] \times t)$$

 $[A]_t$  is the concentration of hydrocarbon A at the time of emission,  $[A]_t$  is the concentration at time t after the emission and  $k_A$  is the reaction rate coefficient for the reaction of hydrocarbon and OH radical. Using chemical reactions of two hydrocarbons, the photochemical age of the air-mass can be calculated from simultaneous measurements of hydrocarbons A and B, having different reactivities towards OH.

$$t = \frac{1}{[OH](k_A - k_B)} \times [\ln([A]_0/[B]_0) - \ln([A]_t/[B]_t)]$$

This method is based on the assumption that mixing during transport is negligible or proportional to the concentrations within the air parcel. We have used acetylene and ethane for A and B which are widely used for this type of analysis due to their longer lifetimes (14 days and 45 days respectively). The *k* value of acetylene is  $9 \times 10^{-13}$  cm<sup>3</sup>/s and for ethane it is  $2.5 \times 10^{-13}$  cm<sup>3</sup>/s [*Atkinson et al.*, 1997]. The initial hydrocarbon ratio at the time of emission is assumed to be 0.85 and the concentration of OH radical used in the calculation is  $3 \times 10^{6}$  [*de Gouw et al.*, 2001].

The average age of air-masses calculated at 750 m over east of Vishakhapatnam is  $19.1 \pm 1.6$  days and over south of Port Blair is  $16.6 \pm 1.2$  days, much longer than 2-5 days calculated from the back-trajectories for the direct transport from source regions. This result provides the strong experimental evidence of severe effect of dilution to the estimation of age of air mass over a clean receptor location. Probably, the polluted air-masses originated from IGP and SEA, have been subject to extensive mixing with the background oceanic air and contain only small signature of direct emission from source regions. The age of air-mass was also estimated over BoB during BOBEX II using acetylene and

ethane during February 2003 [*Lal et al.*, 2007]. In the absence of significant dilution, the age estimated from the ratio of these hydrocarbons and trajectories matched well during this campaign.

## 5.4 Vertical distributions of ozone and its precursors

Figures 5.13, 5.14 and 5.15 show the vertical distributions of ozone, CO, CH<sub>4</sub> and various NMHCs from surface to 3000 m over Hyderabad, Visakhapatnam, Port Blair and Mangalore. The mixing ratios of ozone vary in the range of 40-55 ppbv in lower 1.5 km and 35-40 ppbv in 2-3 km altitude range over Hyderabad, Visakhapatnam and Port Blair. In contrast, ozone increases over Mangalore from 35-40 ppbv in lower 1.5 km to 45-50 ppbv in 2-3 km altitude range. The CO, CH<sub>4</sub> and most of the NMHCs decrease with increasing altitude at all observation sites. The maximum CO concentrations were observed over Port Blair (~ 280 ppbv) and minimum over Mangalore (~ 147 ppbv) with an average concentration of 220-225 ppbv over Hyderabad and Visakhapatnam at 0.5 km altitude. Though, the CO concentration is minimum over Mangalore at 0.5 km, its concentration is observed to be maximum (85-110 ppbv) at this site in 2.5-3 km altitude range. Ethane and n-butane show very high concentrations (2000-2750 pptv) below 1.5 km over Vishakhapatnam and Port Blair whereas their concentrations are significantly lower (1300-1600 pptv) over Hyderabad and Mangalore. Mixing ratio of propane, is surprisingly very high  $(642 \pm 156 \text{ pptv})$ over Port Blair whereas it's mixing ratios are in the range of 90-115 pptv over other three locations. The propene and acetylene are found below the detection limit of the instrument over Hyderabad. The alkenes and acetylene show small scale variations over different locations. All these gases are found to be lower in mixing ratios and invariant with altitude above 1.5 km showing their background free tropospheric mixing ratios over respective locations.



**Figure 5.13:** Vertical distributions of ozone, CO and  $CH_4$  (with  $\pm 1\sigma$  variation) over *Hyderabad, Vishakhapatnam, Port Blair and Mangalore.* 



**Figure 5.14:** Average vertical distributions of alkanes (ethane, propane and n-butane, with  $\pm 1\sigma$  variation) over Hyderabad, Vishakhapatnam, Port Blair and Mangalore.



**Figure 5.15:** Average vertical distributions of alkenes (ethene and propene) and acetylene with  $\pm 1\sigma$  value over Vishakhapatnam, Port Blair and Mangalore.

Mangalore is the only site where the mixing ratio of ozone increases with altitude. Though the levels of alkanes are low, the mixing ratios of alkenes and acetylene are found maximum above 2 km over this location among all. The propene concentrations start increasing above 1.5 km and show a sharp increase up to 2.5 km. The ozone production efficiency of alkenes is 7-9 times higher with respect to CO, alkanes and acetylene [Finlayson-Pitts and Pitts, 2000]. This may be the possible reason of increasing ozone with altitude over Mangalore.

The radiosondes were launched from Vishakhapatnam and Port Blair on the multi-level sortie days at an interval of few hours due to technical reasons. This experiment was not conducted at Hyderabad and Mangalore. Figure 5.16 shows the vertical profiles of Virtual potential temperature (VPT), relative humidity (RH), wind speed and wind direction up to 3.5 km over Vishakhapatnam and Port Blair respectively. The layers of different thermal characteristics are clearly discernible in both cases. This Figure indicates a sharp decrease in RH with strong inversion in VPT at about 2 km over Vishakhapatnam. The wind speed is moderate below 2 km and decreases sharply in inversion layer. Wind direction is northwesterly and southwesterly below inversion layer which changes to northeasterly in the altitude range of 2-3 km range. The altitude profiles of trace gases show well mixed region up to 1.5 km, above which their mixing ratios dropped off rapidly. This indicates the presence of inversion layer between 1.5 and 2 km altitude range during the multi-level sortie while the radiosonde data is available by couple of hours late.



**Figure 5.16:** Vertical distributions of virtual potential temperature, relative humidity, wind speed and wind direction over Vishakhapatnam and Port Blair on Multi-level sortie days during WICARB [Sreekanth et al., 2010].

The radiosonde profile over Port Blair shows two convective stable and unstable layers. The VPT and RH profiles showed convectively unstable region up to 1 km coinciding with well mixed region of trace gases. The moderate to high wind speed of 8-10 m/s from north east direction is found in this altitude range. A sharp

decrease is noticed above this altitude in RH with a sharp increase in VPT indicating the top of mixed layer. The wind speed dropped to 4 m/s in the inversion layer, while wind direction remained northeasterly. The mixing ratios of trace gases suddenly dropped across mixed layer in the absence of vertical mixing. Another convective region is found sandwiched between two stable layers in the range of 1.3 to 1.9 km range. The high levels of ethene and propene at 1.5 km found closely associated with this elevated mixed layer.

## 5.5 Interspecies correlation of various trace species

The ratio of several pairs of NMHCs provides the information about the major emission sources, but it has certain limitations. The composition of trace gases in an air parcel may change between sampling time and the time of emission not only by photochemical processes but also by the mixing with the background air. *McKeen and Liu* [1993] and *McKeen et al.* [1996] have suggested the modified rate of change reaction for hydrocarbons including the mixing term.

$$\frac{dA}{dt} = -kA[OH][A] - kM([A] - [A]b)$$

Where, the A is a hydrocarbon species,  $k_A$  is the reaction rate coefficient of reaction of A with OH,  $k_M$  is the mixing coefficient which determines the rate of dilution of air rich in hydrocarbon with background air. [A]<sub>b</sub> is the concentration of hydrocarbon A in the background air.

The background levels of short lived species emitted from anthropogenic sources are low and long lived species are high in the atmosphere. The various NMHCs are co-emitted from different emission sources. The ratio at the time of emission will be different from the ratio after significant dilution due to higher dilution rate of short lived species. Thus, the emission ratios inferred from the correlation plots may not be good estimates of actual values. This is the major limitation in the present case where dilution is playing the prime role. We can not



**Figure 5.17:** Correlation plots of CO with methane, ethane and n-butane over Hyderabad, Vishakhapatnam, Port Blair and Mangalore for multi-level sorties.

infer the source information by comparing the observed ratios of gases and ratios obtained from emission inventories. However, the tighter correlations of different gases indicate their common sources. Figure 5.17 shows the correlation of CO with methane, ethane and n-butane over Hyderabad, Vishakhapatnam, Port Blair and Mangalore. All these alkanes show very good correlations with CO. This shows their common anthropogenic emissions over the Indian subcontinent.

## **5.6** Comparison with other measurements

The vertical profiles of ozone, CO and some light NMHCs were measured by the airborne observations during INDOEX campaign [*Lelieveld et al.*, 2001; *De Gouw et al.*, 2001]. The flights were performed with Citation twinset aircraft from Male international airport to study their distributions over Northern Indian Ocean (NIO). The winds were northeasterly from Feb 14 to Mar 4, 1999 and changed to northwesterly during Mar 13 - 21, 1999. The average mixing ratios of trace gases in the 0-3 km altitude range for the present study and those measured during the INDOEX are shown in the Table 5.2. The mixing ratios of ozone in

Table 5.2: The average levels of few trace gases measured between 0-3 km duringINDOEX 1999 and WICARB 2009.

Campain and place	Ozone (ppbv)	CO (ppbv)	Ethane (pptv)	Propane (pptv)	Acetylene (pptv)
INDOEX	$13 \pm 5$	$220\pm40$	$900\pm300$	$60 \pm 40$	$330\pm190$
Feb1999, NIO					
INDOEX	$12 \pm 4$	$150 \pm 30$	$530 \pm 190$	$30 \pm 30$	$120 \pm 80$
Mar1999,NIO					
WICARB	$44 \pm 7$	$132 \pm 69$	$1158\pm400$	81 ± 40	-
Jan 2009					
Hyderabad					
WICARB	44 ± 9	$141 \pm 76$	$1480 \pm 715$	$61 \pm 46$	$40 \pm 12$
Jan 2009					
Vishakhapatnam					
WICARB	$42 \pm 3$	$165 \pm 94$	$1624\pm959$	$383\pm263$	$113 \pm 27$
Jan 2009					
Port Blair					
WICARB	$41 \pm 4$	$128 \pm 31$	$1003 \pm 314$	38 ± 31	$45 \pm 35$
Jan 2009					
Mangalore					

the present study were higher by  $\sim 30$  ppbv compared to those measured during the INDOEX. This is due to rapid development of southern Asia resulting into higher anthropogenic emissions of precursors of ozone in one decade. The levels of ethane are also found higher during WICARB particularly over Vishakhapatnam and Port Blair. These two sites were affected by transport of pollutants from IGP and biomass burning plumes from SEA, respectively. The levels of propane are found comparable during both the campaigns except over Port Blair during WICARB, where it is almost 4 times higher. This may be attributed to effect of biomass burning plume. In contrast to these gases, CO and acetylene show higher levels during INDOEX than WICARB. The levels of these species are higher during February 1999 over NIO than during January 2009 over Port Blair. The air pollution originated from the atmospheric boundary layer over south Asia during INDOEX and advected in elevated layers above marine boundary layer over Indian Ocean [Lelieveld et al., 2001]. These elevated layers are not evident during WICARB. These layers of higher pollution may be contributing to 0-3 km averaged mixing ratios of few pollutants during INDOEX resulting into their higher levels.

# **Chapter 6**

## **Summary and Future Plan**

The thesis is focused on the study of different processes affecting the distributions of ozone and its precursor gases (CO,  $CH_4$  and NMHCs) in continental, marine and coastal environments within the lower troposphere over the Indian region. A brief summary of the thesis work is presented here.

## 6.1 Distribution of ozone in the lower troposphere over Ahmedabad

Various processes affecting the distributions of ozone and other trace gases in the lower troposphere are not well understood over the Indian region. Detailed ozone measurements were limited to surface levels over land and marine regions in the last decade. A program to study vertical distribution of ozone along with meteorological parameters was initiated in 2003 at PRL, Ahmedabad. Measurements of ozone, temperature, pressure, relative humidity and wind were made using balloon borne ozone and radiosondes, launched fortnightly from Ahmedabad. The general trend of tropospheric ozone distribution has been discussed by *Shilpy* [2008] on the basis of these observations. But a detailed study of various processes affecting the distribution of ozone in the boundary layer and in the lower free troposphere has not been done before. The present work is focused to study the distribution of ozone in the boundary layer and in the lower free troposphere and processes affecting its distribution in the lower troposphere.

Ahmedabad is an urban city in the western part of India where there are several industries and a power plant. The balloon measurements were carried out over this location from April 2003 to July 2007 and analyzed for the lower 4 km altitude range. The mixed layer top information is extracted from the derived meteorological parameters like virtual potential temperature and specific humidity profiles. The effect of seasonal variation of mixed layer on the distribution of surface levels of pollutants is investigated. Ozone and its major precursors CO and NO<sub>x</sub> observed to be higher during winter season when the mixed layer height remains shallow due to lower solar intensity leading to their accumulation in a smaller volume. Their levels are found lower during late spring and sunny summer days when the mixed layer height remains high causing their dilution in larger volume.

The role of transport of pollutants is also investigated in this work both in the boundary layer as well as in the lower free troposphere on the basis of ten days backward trajectories. The trajectories are found to be originating from three major regions, namely the local western Indian region; Bay of Bengal, Arabian Sea and Indian Ocean, and Africa/Europe. Thus, the back trajectories are clubbed together based on the residence time (number of hours spent) in different regions represented by 3-dimensional paths and classified into three major groups namely trajectories representing long range transport, from regionally polluted sector and from the clean marine region. The ozone levels at Ahmedabad increase with increasing residence time (at regional sector) till 4-6 days for all seasons except winter. During winter, in-situ ozone production from precursors dominates thereby inhibiting any other effect. By extrapolating the ozone levels to a zero residence time in regional sector, we get an average background ozone mixing ratios of about 28 ppbv in the boundary layer and 42 ppbv in the free troposphere. This background ozone mixing ratio is comparable to average ozone mixing ratio during summer-monsoon season in the boundary layer. The seasonal variation of ozone shows its higher levels during late autumn, winter and early spring (> 50 ppbv) and minimum during summer-monsoon (~ 30 ppbv) in the boundary layer. The higher ozone levels during late autumn, winter and spring seasons are dominated by regionally polluted air mass whereas poor ozone levels during summer-monsoon are influenced by marine air mass. The ozone levels are found to be higher by up to 40% in regionally polluted air mass and lower by up to 38% in marine air mass in comparison to average ozone levels. In the lower free troposphere, the distribution of ozone is found to be affected mainly by the long range transport particularly in late spring and early summer. The ozone levels are found to be 32% higher in the air mass of long range transport with respect to average ozone levels from May to July months.

#### 6.2 Ozone and its precursors over Bay of Bengal & Arabian Sea

As a part of Integrated Campaign for Aerosol, gases and Radiation Budget (ICARB), a cruise campaign was conducted over Bay of Bengal (BoB) and Arabian Sea (AS) during March to May, 2006. Vertical distribution of ozone and meteorological parameters were measured at almost every alternate day during the cruise using ozone and radio sondes. Atmospheric samples, collected everyday at 0800 and 2000 hrs by grab sampling method, were analysed for CO, CH<sub>4</sub> and light non-methane hydrocarbons. As per the wind regimes, the whole study area was subdivided into northern BoB (N-BoB), southern BoB (S-BoB), northern AS (N-AS) and southern AS (S-AS) at 12°N as the line of separation. The wind was northwesterly during the campaign carrying large amount of pollutants particularly from the Indo-Gangetic plain to N-BoB.

The vertical distributions of derived meteorological parameters, specific humidity and virtual potential temperature (VPT), were used to identify the top of the mixed layer. The mixed layer height (MLH) varied from 0.3 km to 1.0 km during the entire campaign. A second mixed layer was observed over N-BoB sandwiched between MLH and free troposphere in the altitude range of 0.5 to 3

km. Ozone levels were found to be significantly high (50-90 ppbv) twice that of mixed layer ozone in this altitude range. This second mixed layer as well as high ozone plumes were absent over S-BoB, N-AS and S-AS. The northern marine regions were drier and warmer in the plume range with respect to southern marine regions indicating the effect of continental air-mass over northern regions. The difference in ozone levels between northern and southern ocean was found to be significant over BoB (up to 40 ppb). The pollution sources were investigated over all the four marine regions using potential source contribution function (PSCF) analysis. This analysis is based on ozone levels over the receptor locations and seven days back-trajectories arriving at those observation locations. This analysis has shown that N-BoB was being polluted from Indo-Gangetic Plain (regional pollution) followed by transport from northern Africa, south west Asia and southern Europe (long range transport - LRT). Other marine regions were mainly fed by local pristine oceanic air. From the residence time analysis over BoB, the ozone levels are found to be 20 to 30 ppbv higher in the regionally polluted airmass up to 2.5 km. The levels of ozone in the LRT air masses were found to be 10-20 ppbv higher than average levels above 2.5 km. Marine air masses were having ozone levels 10-20 ppbv lower than average levels over this region. Over Arabian Sea, significant difference in average ozone and its levels in air-masses of different origins were not found. This suggests that IGP is the main source of pollutants over N-BoB. Major precursors of ozone namely CO (at 850 mb, obtained from MOPITT) and NO<sub>2</sub> (columnar, Obtained from OMI), were also examined for the study period over the source regions. These gases have shown significantly higher levels over the identified source locations and strongly supported the conclusions based on PSCF and residence time analyses. The ozone profiles are compared with MOZART model results and other measurements available over Indian region during spring season.

The mixing ratios of surface ozone, CO, CH<sub>4</sub>, ethane and n-butane are found to be higher over N-BoB with respect to other marine regions. Ozone showed a very good correlation ( $r^2$ =0.9) with CO indicating its photochemical production in polluted air over N-BoB. Good inter-correlations ( $r^2 > 0.75$ ) of CO, ethane and n-butane in this air-mass suggest their common continental sources. These species have also shown a strong latitudinal gradient again supporting their continental sources. Ethene and propene, species having anthropogenic as well as oceanic emission sources, have shown their maximum mixing ratios over S-BoB. These species were found to be fairly correlated with each other over BoB and as well as over AS indicating the dominance of their oceanic emissions.

### 6.3 Ozone and its precursors over land & marine interface

The aircraft segment of Winter Integrated Campaign for Aerosol, gases and Radiation Budget (W-ICARB) was conducted from Hyderabad (17.45°N, 78.45°E), Visakhapatnam (17.72°N, 83.22°E), Chennai (12.99°N, 80.17°E), Port Blair (11.64°N, 92.73°E) and Mangalore (12.96°N, 74.88°E) during January, 2009. The in-situ measurements of ozone were made and grab samplings were performed onboard the aircraft. The air samples were analyzed for CO, CH<sub>4</sub> and light non-methane hydrocarbons using GC techniques at PRL, Ahmedabad. The bi-level sorties were made to study the longitudinal gradients of these species across the land sea interface (750 m and 1500 m). Multilevel sorties were performed at six different altitude levels (500 m to 3000 m) to investigate the vertical distributions of various gases.

Longitudinal variations of all these gases are examined over Visakhapatnam. Their concentration levels are found quite similar at 750 m and 1500 m levels till 85.8°E. The concentrations of these gases increase at 750 m and decrease at 1500m towards open ocean east of 85.8°E. The radiosonde measurements made from ship segment during WICARB show that near the coast, the marine mixed layer height remains shallow (~ 400 m), however its height increases with distance from coast to open ocean. This suggests that the aircraft entered into the marine mixed layer east of 85.8°E at 750 m level which is detached from the free tropospheric air due to MBL inversion present between 750 m to 1500 m. Thus, the two different types of air-masses were encountered at two different altitudes east of this longitude.

The longitudinal variation of trace gases is examined by combining data from Chennai bilevel and Port Blair westward bi-level sorties. The ozone, CO, ethane, propane and n-butane show a longitudinal increase of 0.58 ppbv/deg, 7.3 ppbv/deg, 62.3 pptv/deg, propane 11.2 ppbv/deg and 32.3 pptv/deg respectively from Chennai to Port Blair at 750 m. This indicates that Port Blair is more polluted than Chennai. This systematic trend in trace gases is absent at 1500 m level.

The longitudinal distributions of trace gases and back-trajectories indicate advection of Indo Gangetic pollutants over east of Vishakhapatnam and South East Asian plume over south of Port Blair. The seven days back trajectory analysis indicates that Visakhapatnam is affected by the outflow of IGP (Indo Gangetic Plain). The measurements at Port Blair indicate the effect of emission from the fire active locations of Myanmar and Thailand. The comparative study shows that pollutant levels are higher over south of Port Blair than east of Vishakhapatnam. The age of the air-mass is estimated on the basis of acetylene and ethane mixing ratios [de Gouw et al., 2001]. The average age of air-masses calculated at 750 m over east of Vishakhapatnam is  $19.1 \pm 1.6$  days and over south of Port Blair is  $16.6 \pm 1.2$  days, much higher than 2-5 days calculated from the back-trajectories for the direct transport from source regions. This shows significant dilution of air-mass over the marine region. The tracer of photochemical age of air-mass C<sub>2</sub>H<sub>2</sub>/CO ratios are also investigated over these regions and found to be 0.40 pptv/ppbv in the east of Vishakhapatnam, indicating the presence of significantly aged air mass. However, the moderately aged air mass is found in the south of Port Blair with  $C_2H_2/CO$  ratio of 0.73 pptv/ppbv.

The levels of CO and various non-methane hydrocarbons are also found higher over Visakhapatnam and Port Blair than over Hyderabad and Mangalore in multilevel sorties. Their vertical distribution is explained in the light of radiosonde profiles. A very good correlation is observed between CO, CH<sub>4</sub>, ethane and nbutane at every location showing their common sources over the entire study area during this period.

### 6.4 Future scope

The troposphere is the most important but least investigated atmospheric region for various chemical and physical processes. The tropical Asian region, recognized as a major source of anthropogenic and biogenic emissions, is a data void region of trace gases. The major drawback of the present study is the lack of continuous observations and modeling studies over source and receptor locations. The following suggestions can be considered as an extension of the present work and to improve our understanding of processes affecting the distribution and budget of tropospheric ozone and its impacts on air quality and climate.

- ✓ A comprehensive understanding of ozone budget, distribution and trends in the lower troposphere are needed over the tropical regions. Simultaneous observations of ABL evolution, and vertical distributions of ozone, CO, oxides of nitrogen, sulfur dioxide, hydrocarbons and water vapour by Lidar/DIAL system over the tropical region can provide useful information about the chemistry, transport and mixing in the boundary layer and lower free troposphere. In addition to that, vertical measurements of met parameters like temperature, pressure, humidity and wind will be helpful to study the influences of meteorology and transport in the troposphere.
- ✓ Uncertainty in the budget and distribution of rate limiting ozone precursor  $NO_x$  has significant impacts on ozone budget estimates. Large uncertainties are reported in the contribution of various sources for  $NO_x$  emission. Free tropospheric  $NO_x$  study involves several important research topics like production by lightning, convective transport from boundary layer in to the upper troposphere, recycling of  $NO_x$ , and heterogeneous reactions and scavenging of odd nitrogen species.

Measurements and modeling studies should be planned to understand these effects on its distributions in the upper troposphere.

- ✓ The photochemistry of  $HO_x$  and  $RO_2$  radicals should be experimentally investigated for the reliable evaluation of ozone budget. The role of oxidations of NMHCs and various heterogeneous processes in the budgets of these radicals needs to be studied. Attention should also be paid to the  $HO_x$  photochemistry particularly in the upper troposphere where water vapor concentrations are low.
- ✓ The distributions of ozone and other trace gases depend on meteorological conditions like convective activities, which dominate in the tropical region. The convection can effectively transport halogenated species resulting into ozone depletion in the upper troposphere. The role of wet deposition of reactive species on ozone budget in the upper troposphere is not well understood yet. The time resolved measurements should be planned to understand these effects on its distributions in the upper troposphere.
- ✓ Satellite based instruments can provide vertical distribution of ozone but their sensitivity in the lower troposphere is a major concern particularly in the tropics. The long term ozonesonde data can be used to validate the satellite borne ozone measurements like TES, GOME etc and bias and variability of satellite data can be characterized in the tropical land and oceanic regions.
- ✓ The modeling studies are useful to quantify the budget of various trace species and to simulate their atmospheric transport, chemical transformations and removal from the atmosphere. A 3D chemistry transport model will provide an opportunity to study various atmospheric processes affecting the trace gas distributions in the troposphere. A tagged tracer model will be helpful to quantify the contributions in trace gas

distributions from different sources. Further improvement in models in terms of chemical mechanisms, aerosol effects, dry deposition and photolysis is an important work. Simultaneous in-situ observations (land, ocean and air) together with atmospheric modeling will provide a tool to fine tune these numerical models and enhance our understanding of different features of ozone and its precursors at local, regional and global scales.

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# List of Acronyms and Abbreviations

ABL	Atmospheric Boundary Layer			
AS	Arabian Sea			
AATSR	Advanced Along Track Scanning Radiometer			
BoB	Bay of Bengal			
BOBEX	Bay Of Bengal EXperiment			
BOBPS	Bay of Bengal Process Studies			
ECC	Electrochemical Concentration Cell			
EPA	Environmental Protection Agency			
GC-FID	Gas Chromatograph-Flame Ionization Detector			
GOME	Global Ozone Monitoring Experiment			
ICARB	Integrated Campaign for Aerosols, gases and Radiation			
	Budget			
IGP	Indo Gangetic Plain			
IMD	Indian Meteorological Department			
INDOEX	INdian Ocean EXperiment			
IPCC	Intergovernmental Panel on Climate Change			
ISRO-GBP	Indian Space Research Organization-Geosphere Biosphere			
	Program			
LRT	Long Range Transport			
MBL	Marine Boundary Layer			
METEX	METeorological data EXplorer			
MLH	Mixed Layer Height			
MOLEX	MObile Lab Experiment			
MOPITT	Measurements Of Pollution In The Troposphere			
MOZAIC	Measurements of OZone and water vapor by Airbus In-			
	service airCraft			
MOZART	Model for OZone And Related Tracers			
NASA	National Aeronautics and Space Administration			
N-AS	Northern Arabian Sea			
N-BoB	Northern Bay of Bengal			

NCEP	National Center for Environmental Prediction			
NIR	Northern Indian Region			
NMHCs	Non-Methane HydroCarbons			
NOAA	National Oceanic and Atmospheric Adminstration			
OMI	Ozone Monitoring Instruments			
ORV	Oceanic Research Vessel			
PRL	Physical Research Laboratory			
ppbv	parts per billion by volume			
ppmv	parts per million by volume			
pptv	parts per trillion by volume			
PSCF	Potential Source Contribution Function			
S-AS	Southern Arabian Sea			
S-BoB	Southern Bay of Bengal			
TES	Tropospheric Emission Spectrometer			
TPSCF	Total Potential Source Contribution Function			
UV-B	UltraViolet- B radiation (280-315 nm)			
WICARB	Winter ICARB			
WMO	World Meteorological Organization			
VC	Ventilation Coefficient			
VOCs	Volatile Organic Compounds			
VPT	Virtual Potential Temperature			

## **List of Publications**

- S. Srivastava, S. Lal, D. Bala Subrahamanyam, S. Gupta, S. Venkataramani, and T. A. Rajesh (2010), Seasonal variability in mixed layer height and its impact on trace gas distribution over a tropical urban site: Ahmedabad, *Atmos. Res.*, 96, 79-87, doi:10.1016/j.atmosres.2009.11.015.
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- 3. S. Srivastava, S. Lal, S. Venkataramani, Y. B. Acharya and S. Gupta, Transport of elevated land plume above marine boundary layer during ICARB: tracking of source regions, *Journal of Geophysical Research*, *(revision under progress)*.
- S. Srivastava, S. Lal, M. Naja, S. Venkataramani, T. A. Rajesh, S. Gupta and Y. B. Acharya, Influences of regional pollution and long range transport to western India: Analysis of ozonesonde data, (*Manuscript under preparation*).

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# Seasonal variability in mixed layer height and its impact on trace gas distribution over a tropical urban site: Ahmedabad

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#### ABSTRACT

Altitude profiles of virtual potential temperature ( $\theta_v$ ) and specific humidity (q) derived from meteorological data obtained from balloon-borne radiosonde ascents are used to investigate the seasonal variations in mixed layer height over Ahmedabad (23.03°N, 72.54°E), an urban site located on the western part of India. A total of 82 balloon ascents were conducted fortnightly in the morning hours during a period of about four years spanning from April 2003 to July 2007. Analysis of the vertical profiles of  $\theta_v$  and q reveals a systematic seasonal variability in the mixed layer height (MLH), showing the decreasing trend from summer–monsoon to winter season. The MLH is observed to be maximum (~1170 m) in summer–monsoon while a minimum (~160 m) is observed to be maximum from summer–monsoon seasons. This variability is observed to be comparatively lower in the post–monsoon and winter months. Effects of MLH have been investigated on the variations in surface ozone and MOPITT derived surface and vertical distributions of CO. The reverse trend is observed in surface ozone and CO with mixed layer seasonal variability. The impact of MLH over CO vertical distributions is observed up to an altitude of 3–4 km.

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#### 1. Introduction

The atmospheric boundary layer (ABL) is characterized by its inherent turbulent properties, which in turn play an important role in dispersion of pollutants through various dynamical processes. Due to extensive turbulent mixing, the concentrations of water vapor and trace gases remain reasonably steady within this layer whose vertical thickness is referred to as the mixed layer height (MLH) (Zeng et al., 1998; Subrahamanyam et al., 2003; Alappattu et al., 2008). The quantitative estimate of MLH (termed as "h" in this paper) is one of the crucial elements in studies related to trace gas distribution. Accurate quantification of h depends on several factors such as — the prevailing meteorological conditions, strength of atmospheric convection, local time of the observation, geographical location of the experimental site, to name a few. Earth's strong surface heating and cloudtopped radiative cooling are the two prime mechanisms which generate thermal instability and turbulence, which in turn helps in formation of the mixed layer (Stull, 1988; Garratt, 1992). The MLH variations over a site are largely driven by the diurnal and seasonal changes in these parameters. These temporal variations in MLH affect the levels of pollutants produced from natural and anthropogenic activities within the ABL and their mixing in the free troposphere (Lal et al., 2000; Naja and Lal, 2002). Several remote sensing techniques like SODAR, LIDAR, LAWP and other direct measurement techniques like dropsonde and balloon-borne radiosonde have been used to explore the spatial and temporal variations of MLH in continental and marine regions (Holt and Raman, 1986; May and Wilczak,



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1993; Hashiguchi et al., 1995; Zeng et al., 1998; Manghanani et al., 2000; Subrahamanyam et al., 2003). Few long term extensive investigations were focused on the seasonal changes of ABL heights and its structure (Gamo, 1984; Fujitani, 1986; Lee, 1986; Dayan and Rodnizki, 1998; Chen et al., 2001). Several studies with special emphasis on boundary layer structural characteristics and dynamics have been pursued over the tropical Indian sub-continent (Parasnis and Morwal, 1991; Devera et al., 1999; Prabha et al., 2002; Reddy et al., 2002).

Devera et al. (1999) have studied the nocturnal structure and stratification of boundary layer and its effect on local air quality by using ventilation coefficient, a parameter governed by local wind and boundary layer height. Extensive studies of seasonal variation of mixed layer and ventilation coefficient have been made over many places in India (Vittalmurti et al., 1980; Krishnan and Kunhikrishnan, 2004). In these studies, researchers have presented different seasonal pictures of mixed layer and ventilation coefficients attributed to different synoptic conditions over these sites. The marine atmospheric boundary layer and its spatio-temporal variability has been examined by using meteorological data collected from Cross-chained LORAN (Long- Range Aid to Navigation) Atmospheric Sounding System (CLASS) (Ramana et al., 2004) and balloon-borne GPS Loran Atmospheric Sounding System (GLASS) sondes launchings (Subrahamanyam et al., 2003; Subrahamanyam and Ramachandran, 2003) during INDOEX (INDian Ocean EXperiment) over the Indian Ocean and the Arabian Sea.

While most of the results obtained from these studies were helpful in broadening our understanding on various aspects of mixed layer like its formation, characteristics and its impact on local air quality, they were constrained to shortduration field campaigns and were season-specific. Even after various scientific field experiments and observational campaigns focusing the ABL dynamics and its characterization, a systematic investigation covering full year observations on the seasonal variability in MLH and its impact on trace gas distributions have not been done in India. It is in this regard that the present investigation is focused to study the seasonal variability of MLHs and its impact on trace gases distributions over a tropical urban site like Ahmedabad. The main objective of the present study is to make use of a large meteorological database of about four years obtained from balloon-borne radiosonde ascents over the site in conjunction with surface and satellite derived trace gas measurements (ozone and carbon monoxide respectively) for understanding the MLH variations and its effects on their distributions. A total of about 82 radiosonde ascents having meteorological measurements over Ahmedabad from April 2003 to July 2007 form the database for the present investigation.

#### 2. Experimental details and data analysis

The meteorological and ozone measurements obtained from the balloon-borne radiosonde and ozonesonde ascents are the backbone of this piece of research. As part of the ISRO-GBP (Indian Space Research Organization's Geosphere– Biosphere Program) activities, this experiment was initiated to study the vertical structure of ozone and different processes affecting its distribution in the lower atmosphere (up to 30–35 km). The balloon flight experiment was conducted fortnightly from the main campus of Physical Research Laboratory, Ahmedabad (23.03°N, 72.54°E; 49 m above the mean sea level) from April 2003 to July 2007 in coordination with the local air traffic controller (ATC). The balloon launch window was permitted from 0900 to 1000 h local time (LT) by the ATC because of the local air traffic. The radiosonde high resolution meteorological data are used to investigate the mixed layer height characteristics. Though the MLH achieves its maximum during afternoon hours, the mixed layer top observed at 0900–1000 LT will be in proportion to the maximum MLH of the day. Thus these MLH values obtained at almost similar timings are considered as the representative of maximum MLH and are compared on the seasonal basis.

Fig. 1 depicts the geographical location of the experimental site. Two payloads, namely an Electrochemical Concentration Cell (ECC) Ozonesonde (EN SCI Corporation, USA) and a RS-80 Radiosonde (Vaisala, Finland) with GPS were attached to the balloon and measurements were made till the balloon burst altitude. Vertical distributions of ambient temperature, pressure and relative humidity were measured by standard capacitance based sensors of the radiosonde (Vaisala Inc., 1989). These payloads transmitted the relevant data which were received by ground-based receiver at a sampling frequency of 1.2 s. Table 1 provides a detailed description of different sensors, their type, measurement range and accuracy.

On an average, most of the ascents provided good quality data up to an altitude of about 32 to 35 km (balloon burst altitude). The balloon ascent rate was typically 3 to 5 m/s. The raw meteorological data obtained from these ascents include ambient atmospheric pressure, temperature and relative humidity. Information on wind speed and direction are extracted from GPS data. Linear interpolation technique is adapted to regrid the raw data at 10 m regular interval. Such a regridding of raw data helps us in bringing uniformity to all the ascents and a comparison among any two such ascents becomes quite easy. The linearly interpolated meteorological data are used for the determination of virtual potential temperature ( $\theta_v$ ) and specific humidity (q), the key parameters for the determination of MLH top, by the following equations:

$$\theta_{v} = \theta \ (1 + 0.61 \ r)$$
  
 $q = 0.623e / (p - 0.377e)$ 

where  $\theta$  is the potential temperature (K), *r* is the mixing ratio (kg/kg) of water vapor, *p* is the ambient pressure (mbar) and *e* is the vapor pressure (mbar) of air parcel.

#### 3. Results and discussion

#### 3.1. Seasonal variation of mixed layer over Ahmedabad

An accurate value of MLH (h) is one of the crucial parameters for the treatment of ABL processes and its impact on trace gas distributions. It is also linked to the maintenance of low-level clouds. When the magnitude of h is very low, the ABL is taken to be decoupled from the cloud layer, which in turn inhibits the vertical transport of heat, moisture and



Fig. 1. Location of observational site Ahmedabad (23.03 °N, 72.54°E; 49 m above the mean sea level).

turbulent kinetic energy from the Earth's surface to the cloud layer. On the other hand, when the magnitude of *h* is very high, cumulus clouds would form instead of stratiform clouds. The strength of pollutant dispersion and trace gas distribution within the ABL are governed mainly by the magnitude of *h*, thereby providing a direct and strong justification on the accuracy of h in observational and modeling studies. While an observationally based climatology of h over Ahmedabad or a tropical inland station is not available at present, most of the observational studies merely depend on the vertical profiles of thermodynamic parameters obtained from radiosonde ascents. The definition of h in most of the observational studies tends to be more intuitive rather than quantitative. Due to extensive turbulent mixing, virtual potential temperature (VPT) and specific humidity values remain almost constant in the mixed layer. In most of the altitudinal profiles of these parameters a sharp increase in  $\theta_{v}$  is noticed with a concurrent decrease in specific humidity just above the top of the mixed layer. In the present investigation, we have identified the top of the mixed layer as the height at which the first significant inversion of virtual potential temperature and specific humidity profiles is evident (Subrahamanyam et al., 2003). To be more precise, the term 'significant' indicates a VPT gradient of 2 K/km or more (Parasnis and Morwal, 1991). The accuracy of the identification of MLH depends on the vertical resolution of the VPT. The gradient method generates a maximum uncertainty of  $\pm 50$  m in the identification of MLH. Demonstration of top of the mixed layer in typical plots of  $\theta_{\rm v}$  and *q* observed on two different days in different years are shown in Fig. 2. The top of the mixed layer is marked with horizontal dashed lines in both the profiles. It was not possible to determine the top of the mixed layer in all the profiles, and about fourteen ambiguous profiles were discarded from the analysis in which a clear-cut identification of the mixed layer was not evident as per above mentioned criteria.

 Table 1

 Specifications of RS 80-15 radiosonde (Vaisala, Finland) meteorological sensors.

Measured parameter	Sensor Type	Range of measurement	Accuracy	Resolution
Temperature	Capacitive bead	– 90 to 60 °C	$\pm$ 0.2 °C (below 20 km)	0.1 °C
Pressure	Capacitive aneroid	3 to 1060 mbar	$\pm$ 0.5 mbar (below 20 km)	0.1 mbar
Relative humidity	Thin Film Capacitor	0 to 100% RH	$\pm$ 2% (below 5 km)	1% RH



Fig. 2. Typical virtual potential temperature and specific humidity profiles observed over Ahmedabad for two days of different years. Solid line represents the VPT profile and dash dot line shows the specific humidity profile. Horizontal dash line shows the top of the mixed layer.

The local weather over the study domain is mostly influenced by seasonal winds which are shown in Fig. 3. The wind field data are obtained from NCEP/NCAR reanalysis (http://www.cdc.noaa.gov/data/reanalysis/reanalysis.shtml). The figure consists of four panels, showing the average wind fields for five years from 2003 to 2007 at 925 mbar for different seasons. This represents the general meteorological conditions which prevail during different seasons over the Indian region. During the summer-monsoon (also known as south-west monsoon) period of June to August over the Indian sub-continent, the south-westerly winds blowing from the Indian Ocean and Arabian Sea to the land-mass bring the moist air resulting into heavy rainfall. The relative humidity is observed to be very high up to 70-80% during this time. On the other hand, the sub-continent experiences drier northerly and north-easterly winds (relative humidity about 20-30%) during the winter season from December to February. Pre-monsoon (March to May) and post-monsoon (September to November) seasons are referred to as the transition periods, when the sub-continent undergoes a wind reversal from north-easterly to south-westerly and vice versa. The difference between summer and winter temperatures is observed to be ~13 °C in the present investigation. Changes in meteorological conditions particularly the moisture levels and temperature due to changes in the wind patterns can significantly affect the extent of vertical mixing and thus control the MLH.

Fig. 4 consists of four panels representing the variation of mixed layer top in the four seasons respectively. In order to accommodate January and February months along with December (winter season) in the same plot, the day numbers of January and February are biased by 365. Fig. 4a represents the MLH variation for pre-monsoon season (MAM). The mixed layer height varies within a range of about 200 m to 1120 m during these months. Though a clear-cut trend is not seen, the first half of this season (March to mid of April) experiences lower heights of mixed layer as against higher

heights seen in the later half of the season. Barring a low height of about 250 m in May 2004, the second half of the season consistently experiences the mixed layer height above 700 m.

Fig. 4b depicts the variation of mixed layer for summermonsoon season (JJA) which happens to have enormous moisture within the atmosphere and the experimental site experiences associated rainfall. Depending on the convective conditions of the atmosphere, the study domain undergoes active and break phases of the monsoon during these months. On a given convective day, if the strong solar heating supports the upward mixing, the mixed layer height can be very high and on the other hand a sudden rainfall can bring down the mixed layer height. Signatures of active and break phases of monsoon are quite clearly seen in the variation of mixed layer height in the summer-monsoon. The mixed layer height, in general, is seen to be higher (>700 m) in the beginning of the season and drops to lower values with the advancement of summer-monsoon. In a broad sense, the variability in mixed layer height is very large in this season and can be attributed to strong convective activities associated with heavy rainfall in this region.

A decreasing trend in the mixed layer height is seen to be emerging in the post-monsoon season (Fig. 4c), where the magnitude of mixed layer drops to low values below 250 m. These variations can be attributed to weakening of convective activities in this season. This is also the season that happens to be a transition period from the wet south-westerly wind to the drier north-easterly wind (Fig. 3). In the beginning of this season, mixed layer heights are found to be in a range of 400 m to 700 m which decrease to a range of about 150 m to 350 m at the end of the season.

Fig. 4d shows the MLH variation for winter season. During winter months, the mixed layer height does not show a large variability. Winds come from drier northerly region so the moisture content is minimum in the atmosphere during these months (Fig. 3). In this season, the solar heating of the earth's



Fig. 3. Average seasonal wind (m/s) at 925 mbar over Ahmedabad (marked in the map) during 2003–07. The wind field data is obtained from NCEP/NCAR reanalysis.

surface is too weak to raise the MLH deeper in the atmosphere. The MLH magnitudes are confined to be in the range of about 150 m to 400 m.

Variation in monthly mean air temperatures observed at 100 m altitude from these balloon ascents is shown with the monthly mean of mixed layer heights for the individual months in Fig. 5. The temperatures at 100 m were obtained from each flight and averaged on monthly basis. The 100 m altitude is chosen to avoid the effect of radiation from the building on the surface temperature. The maximum temperature of  $31.6 \pm 2.1$  °C is observed in May and minimum of  $20.1 \pm 2.3$  °C is observed in December, which is quite similar to MLH variation. This reveals that temperature of earth's surface directly influences the depth of mixed layer in the atmosphere. It is known that warmer earth's surface forces the turbulent mixing deeper in the atmosphere resulting in higher mixed layer. Similar variation can be observed in the average mixed layer height and air temperature except for the summer-monsoon when higher MLHs were observed on clear sunny days and lower on cloudy/rainfall days.

Average seasonal variability of mixed layer top, based on all the five years data, is depicted in Fig. 6. The average mixed layer heights for pre-monsoon, summer-monsoon, postmonsoon and winter are found to be  $518 \pm 264$ ,  $756 \pm 270$ ,  $425 \pm 147$  and  $260 \pm 65$  m respectively. The maximum and minimum values of MLHs are also shown in this figure for all the four seasons. The lowest mixed layer height is observed during winter season (~160 m) and highest in summermonsoon (~1170 m). While the seasonal variation follows the general trend, the interesting feature observed is the large variability during pre-monsoon and summer-monsoon seasons as demonstrated by the higher standard deviation. The smaller standard deviation projects less variation in mixed layer height during post-monsoon and winter months. These variations in mixed layer heights for the four seasons are quantified and summarized in Table 2.

## 3.2. Comparison of mixed layer heights over Ahmedabad with other locations

Several attempts have been made to understand the seasonal variation of mixed layer height over different locations. In one of them, Vittalmurti et al. (1980) had shown the seasonal variation of mixed layer height over some urban locations in India by considering only one month as a



Fig. 4. Mixed layer top variation for different seasons observed over Ahmedabad. The winter season (DJF) panel contains the January and February days biased by 365.

representative of each season. Their study showed that maximum mixed layer height is observed during April (premonsoon) as well as during October and January at several sites in India. Minimum values of MLH were observed during August (summer/monsoon) and October (Post-monsoon). These trends are quite different from the present observations obtained over Ahmedabad where maxima occur during summer/monsoon, minima during winter and secondary



**Fig. 5.** Average monthly variation of temperature at 100 m (obtained from radiosonde temperature sensor) and ABL over Ahmedabad during 2003–07. The error bars represent one sigma standard deviation.

minima during post-monsoon season. This may be due to different meteorology at different locations. It is also possible that the monthly MLH values discussed in Vittalmurti et al. (1980) are not representing the real seasonal picture over the above mentioned locations.

Gamo et al. (1994) have reported the daytime maximum mixed layer height variation over an urban site Delhi during 1997-98. Their study showed that MLH attained highest altitude during pre-monsoon (~3000 m), low during monsoon (<2000 m), moderate during post-monsoon (~2000 m) and lowest during winter (<1000 m). Similar variation is also reported by Krishnan and Kunhikrishnan (2004) over Gadanki (13.5°N, 79.2°E), a rural site in South-East India. They have made use of UHF wind profiler observations for studying the seasonal variation of MLH. They reported reasonably higher values of MLH for pre-monsoon  $(2.2 \pm$ 0.42 km) and post-monsoon  $(1.68 \pm 0.35 \text{ km})$  months as against slightly lower values in the summer-monsoon (1.65  $\pm$ 0.33 km) and winter months  $(1.50 \pm 0.34$  km). Whereas over Ahmedabad, MLH is maximum during summer/monsoon. In context to our observations over Ahmedabad, the MLH values over Delhi and Gadanki are observed to be considerably higher and one of the possible reasons for this seems to be the time of observations. All these observations at Ahmedabad were confined to early noon hours whereas Delhi and Gadanki observations were valid for mid-afternoon hours when the ABL



**Fig. 6.** Average seasonal variation of mixed layer height with one sigma standard deviation is depicted over Ahmedabad during 2003–2007. The maximum and minimum MLH are also shown for each season.

becomes highly convective and turbulent thereby attaining maximum values in the afternoon hours.

Spatio-temporal variability in MLH over the marine regions surrounding the Indian sub-continent has been the subject of investigation during the Indian Ocean Experiment (INDOEX). During the first two campaigns (also referred to as Pre-INDOEX, 1997) and First Field Phase (FFP, 1998) of the INDOEX, the MLH variations were confined to a range of 400 m to 1100 m (Ramana et al., 2004). During the Intensive Field Phase (IFP-99) of the INDOEX campaign, Subrahamanyam et al. (2003) reported a variation of MLH in a range of about 200 to 900 m. These observations were taken from a moving ship during various phases of INDOEX field campaign

#### Table 2

Variation of mixed layer top parameters for different seasons during 2003–07 observed over Ahmedabad.

Years	MLH parameters	Pre- monsoon	Summer– monsoon	Post- Monsoon	Winter
2003	Mean (m)	-	793	405	253
	Std Dev	-	222	209	86
	Max (m)	-	1050	700	330
	Min (m)	-	650	250	160
	No of Profiles	-	3	4	3
2004	Mean (m)	352	690	394	240
	Std Dev	140	268	140	-
	Max (m)	550	850	570	300
	Min (m)	200	380	250	180
	No of Profiles	5	3	5	2
2005	Mean (m)	547	716	400	260
	Std Dev	178	316	149	-
	Max (m)	760	1170	700	270
	Min (m)	310	370	250	250
	No of Profiles	7	5	7	2
2006	Mean (m)	655	786	536	-
	Std Dev	-	77	100	-
	Max (m)	1120	900	650	-
	Min (m)	190	700	460	-
	No of Profiles	2	5	3	-
2007	Mean (m)	574	765	-	260
	Std Dev	237	-	-	76
	Max (m)	850	940	-	360
	Min (m)	290	590	-	180
	No of Profiles	5	2	-	4
Average	Mean (m)	518	756	425	260
	Std Dev	264	217	147	65
	Max (m)	1120	1170	700	360
	Min (m)	190	370	250	160
	No of Profiles	19	18	19	12

and location and time of the observations were continuously varying. Nonetheless, the range of MLH reported over the marine region is found to be similar to that observed over Ahmedabad.

#### 3.3. Ventilation coefficient

Distributions of trace gases are highly influenced by dynamics of MLH near the earth's surface. Ventilation coefficient (VC) is a parameter which quantifies the effects of MLH variation and wind speed on local air pollution (Krishnan and Kunhikrishnan, 2004). This represents the rate by which pollutants within the mixed layer will be blown off from its location. It is given by the following equation:

$$VC \ (m^2/s) = h \times \frac{\sum_{i=1}^{l=n} v_i}{n}$$

where *h* is the mixed layer height and v<sub>i</sub> is the wind velocity at different heights (*i*) within the MLH. High values of VC reflect the strong dispersion so that it is a representative of good air quality, whereas low VC shows poor ventilation and it corresponds to accumulation of locally emitted pollutants. The VC has highest value (~5640 m<sup>2</sup>/s) during June and lowest (~1140 m<sup>2</sup>/s) during December period. It remains high for summer/monsoon and decreases during postmonsoon and attains its minimum during winter. This trend is quite similar to MLH, which reflects the dominance of boundary layer processes on this parameter.

3.4. Impact of seasonal variation of MLH and ventilation coefficient on the distribution of trace gases over Ahmedabad

Surface ozone and some of the precursors have been measured at this site for a long time (Lal et al., 2000). They have explained the diurnal behavior of trace gases on the basis of assumed diurnal variation of MLH. In the present study, we are trying to correlate the seasonal variation of trace gases with seasonal variation of MLH. Full year surface ozone data are available for the year 2002 at the earliest. Ozone is measured using a standard UV based analyzer. These data, collected at each 5 min interval, are averaged for the daytime window of 1200 h to 1400 h when it attains its daily maximum. We have used CO data from MOPITT (Measurement of Pollutants in the Troposphere), which is onboard NASA's Earth Observing System's (EOS) Terra satellite. The gridded CO data (level 3) are used at seven different pressure levels (1000, 850, 700, 500, 350, 250 and 150 mbar) with a spatial resolution of  $1^{\circ} \times 1^{\circ}$  in the present study. Even though these data are more accurate for the middle and upper troposphere but are also being used for the pollution events within the lower atmosphere (Kar et al., 2008). The monthly day time averaged CO data are taken at location 23.5°N, 72.5°E for a period of January 2003 to December 2007.

High ozone (~40–60 ppb) is observed during late autumn and winter, whereas its concentration was observed to be low (<25 ppb) for the entire summer/monsoon season. The surface CO concentrations are around 200 ppb during postmonsoon and winter months, start decreasing from April onwards and attain its minimum (~60 ppb) in July month. The CO data are not available for August possibly due to cloudy days in this month. Average monthly concentrations of surface ozone and CO along with ventilation coefficient are shown in the Fig. 7. It shows the reverse trend in ozone and CO variation with VC. To investigate the impact of VC on the distribution of these gases, the correlation of monthly variation of ozone and CO are examined with VC. The exponential fit is used to demonstrate the dependence of pollution concentration on MLH dynamics as discussed by the Schäfer et al (2006). The square of correlation coefficients of VC with ozone and CO are found to be 0.87 and 0.40 respectively. Ozone is photochemically produced by CO, methane and non-methane hydrocarbons in the presence of NO<sub>x</sub> and sunlight whereas major sources of CO are the anthropogenic emissions, mainly the vehicular emission and biomass burning. Apart from that, the only chemical source of CO is formaldehyde (HCHO) but its contribution is negligible in comparison to direct emission over this location (Lal et al., 2000). Thus, it is better to study the effects of VC on CO rather than ozone as it will give a clear picture of dispersion of locally emitted pollutant. The mixed layer height defines the upper limit of vertical mixing of trace gases. When the mixed layer height is low and VC is also low, the anthropogenically emitted CO will get trapped within a smaller volume, which will increase its concentration. This is the prime cause of high CO concentration during autumn and winter. On the contrary, mixed layer height remains high during summer season resulting in high VC, and CO mixes within a larger volume. The surface air enriched with CO mixes with the cleaner air aloft, having lower concentration of CO as the mixing height increases. This results in the dilution of CO within the mixed layer. The photochemical ozone production is highly dependent on CO concentration, thus it also follows the similar seasonal trend. During autumn/winter season air mainly transported from polluted continental region carrying higher amount of CO whereas during summer season, air comes from cleaner marine region with poor CO concentration. However, it is difficult to separate out the contributions of MLH dynamics and air transport effects on the distributions of these gases.

Seasonal variation of CO at seven different pressure levels (1000, 850, 700, 500, 350, 250 and 150 mbar) along with mixed layer height is depicted in Fig. 8 to study the extent of



Fig. 7. Average monthly variation of ozone and CO along with ventilation coefficient over Ahmedabad. The error bars represent one sigma standard deviation.

boundary layer effect on its vertical distribution. These pressure levels correspond to the altitudes of 0, 1.5, 3, 5, 8.5, 11 and 14 km approximately. The lower MLH shows higher concentration of CO and vice versa. Seasonally averaged values of CO for the lower heights (1000, 850, 700 mbar) show significant effect of mixed layer variation. The percentage changes of CO mixing ratios for seasons of maximum and minimum concentrations are found >25% for these pressure levels. However, no significant seasonal variation of CO concentrations is observed for 500, 350, 250 and 150 mb levels (upper troposphere). The changes in CO mixing ratios were observed to be <15% for these pressure levels. This indicates that MLH variation plays an important role in the transport and mixing of trace gases in lower atmosphere up to around  $\sim$ 3 km (700 mbar pressure level), whereas this effect diminishes with increasing altitude.

#### 4. Summary

The seasonal variation of mixed layer height over Ahmedabad is presented during morning hours using the meteorological data obtained from balloon-borne radiosondes covering a period of 4 years. Significant seasonal variations are observed in the height of the mixed layer top. The maximum MLH (~1170 m) is observed during summer (IJA) and minimum (~160 m) during winter (DJF). The variation of MLH is unpredictable during summer/monsoon and very small variations are observed during winter. Large variability observed in MLH (~±250 m) during pre-monsoon and summer-monsoon seasons when convective activity dominates, while this variation is significantly lower in post-monsoon( $\sim \pm 150$  m) and winter season( $\sim \pm 60$  m). The seasonal variation of mixed layer affects the distributions of trace gases like ozone and CO for different seasons. It is seen that higher mixed layer heights (~750 m) result in lower trace gas concentrations during summer season (CO<100 ppb and O<sub>3</sub><25 ppb). On the other hand, mixed layer height touches its minimum(~250 m) in winter, restricting the vertical mixing of CO and O<sub>3</sub> and resulting in higher concentrations of these gases (CO>200 ppb and O3>60 ppb). Variation of CO at different heights shows that the boundary layer effect is limited to an altitude of ~3 km at this site.



**Fig. 8.** Average seasonal variation (with one sigma standard deviation) of CO at different pressure levels for the study period (2003–2007) along with mixed layer height.

This work presents, for the first time, complete seasonal variation of MLH based on in-situ measurements of temperature and relative humidity and its impact on trace gases over an urban site in India. These observations may be used as input in the modeling of the lower atmosphere to separate the contribution of local chemistry and atmospheric dynamics on the distribution of different trace gases.

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### Emission characteristic of ozone related trace gases at a semi-urban site in the Indo-Gangetic plain using inter-correlations

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**Abstract** Measurements of surface  $O_3$ , CO,  $NO_x$  and light NMHCs were made during December 2004 at Hissar, a semi-urban site in the state of Haryana in north-west region of the Indo-Gangetic Plain (IGP). The night-time  $O_3$  values were higher when levels of CO, NO and  $NO_2$  were lower but almost zero values were observed during the episodes of elevated mixing ratios of CO (above 2000 ppbv) and  $NO_x$  (above 50 ppbv). Slopes derived from linear fits of  $O_3$  versus CO and  $O_3$  versus  $NO_x$  scatter plots were also negative. However, elevated levels of  $O_3$  were observed when CO and  $NO_x$  were in the range of 200–300 ppbv and 20–30 ppbv, respectively. Slope of CO- $NO_x$  of about 33 ppbv/ppbv is much larger than that observed in the US and Europe indicating significant impact of incomplete combustion processes emitting higher CO and lesser  $NO_x$ . Correlations and ratios of these trace gases including NMHCs show dominance of recently emitted pollutants mostly from biomass burning at this site.

Keywords Emissions · NMHCs · IGP · Trace gases · Biomass

#### **1** Introduction

Asian countries such as China and India are most populated regions in the world and are currently experiencing higher industrial and economic growth rates. Increasing emissions of pollutants from industrial, transport and agricultural sectors can lead to environmental and climatic changes. Trace gases such as carbon monoxide (CO), oxides of nitrogen ( $NO_x=NO+NO_2$ ), non-methane hydrocarbons (NMHCs) etc., emitted by man-made activities play important roles in the chemistry of the lower atmosphere and in the photochemical production of O<sub>3</sub>. Tropospheric O<sub>3</sub> is a potential greenhouse gas and it is a major source of highly reactive hydroxyl (OH)

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radicals in this region of the atmosphere. Tropical atmosphere is characterised by strong upwelling, which can lift these pollutants into the free troposphere, where they can get transported to other parts of the global atmosphere (Folkins et al. 2002).

The Indo-Gangetic Plain (IGP) in north India is densely populated region with major agricultural and industrial activities. Anthropogenic emissions of both trace gases and aerosols from biomass burning, industries, power plants and vehicles are present throughout the year in this region. Relatively higher levels of  $NO_2$  column have been observed over this region as compared to other parts of India (http://www.doas-bremen.de/no2 from gome.htm). Similarly, higher levels of black carbon (BC) have been observed over this region (Ramanathan and Ramana 2005). In rural parts, especially in the northern part of India biomass and biofuels (mostly dry branches of trees and dry cow/buffalo dung) are commonly used in the villages for cooking. Impact of these emissions on regional climate has been a cause of concern. The prevailing wind pattern over this region is mostly from west to east throughout the year. This wind pattern transports pollutants emitted from this region over to the Bay of Bengal and the Indian Ocean (Lelieveld et al. 2001). Fog formation takes place during winter period whenever cold air from higher latitudes mixes with moist air. Often fog in this region is very strong and visibility reduces drastically (Gautam et al. 2007). Frequent temperature inversions during winter period not only enhance fog formation but accumulation of pollutants also takes place. This causes disruption in travel services (air, rail and road) and also causes health effects in the entire IGP belt.

There have been several field campaigns to study transport of pollutants over the marine regions surrounding India such as INDOEX, BOBEX, BOBPS etc. (Lelieveld et al. 2001; Chand et al. 2003; Lal et al. 2006; Sahu et al. 2006; Lal et al. 2006). However, there have been limited measurements by individual groups to study levels of aerosols and trace gases over the IGP (Singh et al. 1997; Fishman et al. 2003; Jain et al. 2005; Sahoo et al. 2005; Beig and Ali 2006; and Tripathi et al. 2006). In view of the importance of this region, a campaign was organised by Indian Space Research Organization-Geosphere Biosphere Programme (ISRO-GBP) to study levels and variations of pollutants (aerosols and trace gases) at eight different sites covering wide regions of the IGP from west to east during December 2004. The month of December was chosen as it is the period when both clear days and foggy days occur. Thus, the changes in trace gases and aerosols could be studied during clear as well as foggy days. These measurements were made by a large number of groups covering all these sites.

In this paper we present, for the first time, detailed results obtained from surface level measurements of  $O_3$ , CO, NO and NO<sub>2</sub> at Hissar in the north-west part of IGP. In addition to these continuous measurements, measurements of light hydrocarbons (CH<sub>4</sub>, NMHCs) were also made twice daily. A comparison of these results is made with similar kind of measurements at Ahmedabad in addition to other international studies. Ahmedabad is an urban site in central west India, where measurements have been made using similar techniques by the same research group.

#### 2 Measurement site and meteorology

Hissar (25° 5'N, 74° 46'E) also known as Hisar, a town of the Haryana state of India, is situated at a distance of about 160 km from Delhi in the north-west direction. It is a semiurban town with a population of about 1.2 million. Agriculture is the main occupation of the people of Haryana as well as that of Hissar. It is now an important industrial centre having steel and cotton industries. The Haryana Agriculture University (HAU) located at Hissar is one of Asia's biggest agriculture universities. The building of the Haryana State Remote Sensing Application Centre (HAR-SAC) located in the campus of the HAU was used to house the analysers. The site is located in a relatively remote place in the university, where anthropogenic activities are minimum. However, the university itself is located in the city.

A teflon tube of 1cm diameter was used as a sample inlet tube. One end of it was fixed at one side of the terrace of the building facing open fields while the other end was connected to a multi-port glass buffer kept inside the laboratory. Inlets of various analysers were connected to this buffer. Surface O<sub>3</sub>, NO, NO<sub>2</sub> and CO data were collected at every 5 min interval.

In addition to these continuous measurements, air samples were also collected in evacuated glass bottles of about 300–400 ml volume through a 2 m long stainless steel tube using an oil free compressor (Metal Bellow, USA) from the terrace of the building daily in the morning around  $8_{AM}$  and in the evening around  $8_{PM}$ . These samples have been analysed at Physical Research Laboratory (PRL), Ahmedabad using gas chromatographic techniques for CO, CH<sub>4</sub> and NMHCs (C2-C3).



Fig. 1 Daily average air temperature, relative humidity and atmospheric visibility observed at Hissar, India during December 2004 (Data taken from http://www.ncdc.noaa.gov)

Daily averaged meteorological parameters viz., temperature, relative humidity (RH), and atmospheric visibility are plotted in Fig. 1 (data are taken from http://www.ncdc.noaa.gov). Surface air temperature and RH were in the ranges of 15–20°C and 50–60%, respectively during 3–19 December. Later, air temperature decreased to around 12°C while RH increased to 70–90% during 20–24 December (foggy days). Dense fog on 22 December was marked by lowest visibility and highest RH values. The wind rose diagram (Fig. 2) shows dominance of winds from north-west direction. However, wind flow from all the directions was observed. Often, the wind speed was low or calm.

Daily mean 7-day back trajectories for 0700 h GMT (1230 h Indian Standard Time-IST) were calculated for each day of December month using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory version 4) model (Draxler 1998). These trajectories (Fig. 3a) during 3–19 December indicate transport of air mass from the west or south-west direction. However, air movement was confined near the measurement site during 20–24 December (Fig. 3b). Also, the analyses of back trajectories show slow movement of air parcel within the boundary layer during these days. Two major sources of pollutants at this site are local vehicular exhaust and agriculture waste or biomass burning in the surrounding regions. Since anthropogenic sources in this region are unevenly distributed, we expect that air masses coming from different regions may have different chemical signatures and loading. Wind flow was from higher latitudes on 27 and 28 December, which reflected in the lower values of temperature and RH (Fig. 3c).



Fig. 2 Wind rose diagram showing wind speed and direction as well as percentage frequency of occurrence for December 2004 at Hissar, India





Fig. 4 Hourly averaged mixing ratios of  $O_3$ , CO, NO,  $NO_2$  and total solar radiation observed at Hissar burning December 2004

#### 3 Measurement techniques

Continuous in-situ measurements of surface  $O_3$ , CO, NO and NO<sub>2</sub> were made using online analysers. Measurements of  $O_3$  were made using an analyser based on the absorption of UV radiation (Thermo Electron Corporation, USA; Model # 49C). The absolute accuracy of this analyzer is ~5%. Oxides of nitrogen (NO and NO<sub>2</sub>) were measured by a separate analyser (Environment S. A. France; Model # AC32M). It is based on chemi-luminescence corresponding to the oxidation of NO with  $O_3$  in a reaction chamber. NO<sub>2</sub> is measured by first converting it into NO using molybdenum heated at 320°C. However, this converter also reduces other oxides of nitrogen such as PAN, HNO<sub>3</sub> etc. Hence, the actual concentrations of NO<sub>2</sub> and NO<sub>x</sub> may be lower than those measured and reported here. Carbon monoxide was measured by a standard analyser based on absorption of IR radiation (Monitor Europe UK; Model # M9830). Detailed descriptions of these analysers including calibration methodology are given by Naja and Lal (2002).

Air samples collected during the campaign were analysed for  $CH_4$  and CO by a gas chromatograph (GC) (Varian, USA). Calibration mixtures supplied from NIST (1.0  $\pm$  0.01 ppmv) and Matheson (2.1  $\pm$  0.01 ppmv) were used to calibrate  $CH_4$  and CO, respectively. Analyses of  $CH_4$  and CO showed better than 1% and 3% of reproducibility, respectively. Light NMHCs were also analyzed from these air samples using another GC (Hewlett Packard USA). The reproducibility in NMHCs analyses ranged from 3% to 10%. A detailed description of such measurements and calibration techniques are given in Sahu and Lal (2006).

#### 4 Time series distributions

Hourly averaged mixing ratios of  $O_3$ , CO, NO,  $NO_2$  and total solar radiation flux in spectral range of  $0.31-2.8 \ \mu m$  are shown in Fig. 4. Diurnal distributions of O<sub>3</sub> show large variations with amplitudes ranging from 5–78 ppbv measured during different days of the campaign. The amplitude was as high as about 70 ppbv during 11-12 December and as low as 25 ppbv or even almost zero on 22 December, which was a foggy day (Fig. 1). Surface CO, NO and NO<sub>2</sub> all show similar variations. Mixing ratios of CO were generally up to 1,000 ppbv, but often crossed 2,000 ppbv and went up to 3,800 ppbv on 11 December. Mixing ratios of  $NO_2$  were generally within 20 ppbv but often crossed 40 ppbv and were as high as 55 ppbv on 7/8 and 11 December. Similarly, levels of NO were generally 3–4 ppbv but showed sharp increases corresponding to increases in CO and NO<sub>2</sub>. Levels of NO also crossed 20 ppbv and the highest was about 90 ppbv on the night of 10-11 December. The average value of the ratio of  $NO/NO_2$  was about 0.3 for the entire period of measurements. This ratio increased whenever levels of CO, NO and NO<sub>2</sub> increased, indicating the influence of fresh emissions from nearby sources. Also most of these increases were during evening/night hours. Emissions from diesel power generators could dominate as there were frequent electric power failures/cuts (for half an hour to a few hours) during these hours.

It is interesting to note that whenever  $NO_x$  (both NO and  $NO_2$ ) levels were higher, the night time and early morning  $O_3$  levels were much lower and vice versa. This shows that loss of  $O_3$  took place during night hours due to the reaction of  $O_3$  with freshly emitted NO. Higher levels of NO and NO<sub>2</sub> events coincided with the higher levels of CO as mentioned



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earlier. These higher levels of  $NO_x$  and CO also produced higher levels of  $O_3$  during the day and the diurnal amplitudes were also higher.

Figure 5a shows average diurnal patterns (box plot) of trace gases and solar radiation flux measured during the campaign period except for a dense fog day on 22 December. Diurnal photochemical build-up of ozone is observed and the average value goes as high as 55 ppbv at 1500 h. These features are similar and typical to those observed in other urban or polluted sites. Other gases like CO, NO and NO<sub>2</sub> show morning increase around 0900 h and a major increase in the evening hours.

There was an occurrence of intense fog on 22 December. The diurnal patterns of  $O_3$ , CO, NO and NO<sub>2</sub> got disturbed (Fig. 5b). This could be due to diminished level of solar radiation as well as descending air motion during foggy periods. Maximum total solar flux was about 15 mW cm<sup>-2</sup> compared to 60 mW cm<sup>-2</sup> on clear days of observations. Levels of  $O_3$  increased to about 11 ppbv during noon hours from early morning values of about 2–3 ppbv on this day. There was no morning rush hour peak and no noontime decrease in CO or NO<sub>x</sub>.

The average mixing ratios of surface  $O_3$ , CO and  $NO_x$  at Hissar on clear days were  $33.4 \pm 9.6$  ppbv,  $553.5 \pm 292$  ppbv and  $15.7 \pm 7.3$  ppbv respectively. Similar to this study, the average data for Ahmedabad for the month of December 2002 were  $28 \pm 18$  ppbv,  $539 \pm 35$  ppbv and  $15.1 \pm 7.4$  ppbv respectively (Sahu and Lal 2006). This shows that while average  $NO_x$  and CO levels are almost same at both the sites, the average  $O_3$  is slightly higher at Hissar.

#### 5 Correlations and source identification

#### 5.1 O<sub>3</sub>-CO and O<sub>3</sub>-NO<sub>x</sub> relations

Carbon monoxide and NO<sub>x</sub> are two important precursors for the photochemical production of O<sub>3</sub> in the troposphere and have been used as tracers for anthropogenic emissions. The correlation study of O<sub>3</sub> and CO can be used to demonstrate the photochemical activities at regional scale (Parrish et al. 1998). Similarly, NO<sub>x</sub> (or NO<sub>y</sub>) species play important role in the formation of ozone in the presence of CO and hydrocarbons. Therefore, the slopes  $\Delta O_3/\Delta$ CO and  $\Delta O_3/\Delta NO_x$  can be used to estimate the photochemical production efficiency of O<sub>3</sub> (Olszyna et al. 1993; Glavas et al. 1999). In highly polluted regions near the emission sources, O<sub>3</sub>-NO<sub>x</sub> gives better estimate for the O<sub>3</sub> production efficiency than O<sub>3</sub>-CO due to shorter lifetime of NO<sub>x</sub>. The linear regression fits of O<sub>3</sub>-CO and O<sub>3</sub>-NO<sub>x</sub> plots represent negative slopes, however, with poor correlation coefficients (r<sup>2</sup> < 0.25). The photochemical production of O<sub>3</sub> is a non-linear process, usually the higher levels of O<sub>3</sub> mixing ratio were observed when CO was in the range of 200–300 ppbv and NO<sub>x</sub> of 20–30 ppbv at Hissar (see Fig. 6).

The scatter found in the  $O_3$ -CO slope in winter season has been speculated due to results of vertical mixing and dry deposition of  $O_3$  (Poulida et al. 1991). Also, weaker correlations are indications of partially processed air entering the observational site (Olszyna et al. 1993)

#### 5.2 CO-NO<sub>x</sub> relation

The CO/NO<sub>x</sub> ratio can be used as one of the parameters to study the sensitivity of precursors in the photochemical production of  $O_3$  rather than their concentrations which can be influenced by changes in meteorological parameters, changing traffic density etc. These two gases get almost equally perturbed by such events. Hence, their ratio will not be



**Fig. 5 a** Box plots showing average diurnal variations of O3, CO, NO,  $NO_2$  and total solar radiation observed at Hissar during December 2004. In the box, the dotted and thick lines represent average and median of the data respectively. The lower and upper edges of these boxes represent 25th and 75th percentile of the data sets. The whiskers below and above are 10th and 90th percentile and the outliers (circles) show 5th and 95th percentile in the hourly average data for all the clear days during December 2004. **b** Diurnal variations of hourly average  $O_3$ , CO, NO,  $NO_2$  and total solar radiation observed at Hissar on 22nd December 2004 when heavy fog was observed



Fig. 5 (continued)

affected much. Apart from this, the slope  $(\Delta CO/\Delta NO_x)$  is related to primary emission sources of these species. In high temperature combustion processes (e.g., use of fossil fuel in vehicles and power plants) these slope values are lower than those emitted from biofuel and biomass burning. In other words, slope of CO-NO<sub>x</sub> scatter plot decreases from incomplete to complete combustion of fuels. Mixing ratios of CO and NO<sub>x</sub> show moderate correlation at Hissar. The calculated  $\Delta CO/\Delta NO_x$  values are 33 ppbv/ppbv and 25 ppbv/ppbv during clear sky and foggy periods, respectively. Such studies in the air parcels originated from the US and Europe showed lower  $\Delta CO/\Delta NO_x$  values of 5–10 ppbv/ppbv due to near complete combustion of fuels. This slope value decreased in the US at a rate of about 7–9% during 1987–1999 (Parrish et al. 2002). In general, the values are significantly higher in the Asian plumes caused by extensive use of biofuel and biomass burning. The  $\Delta CO/\Delta NO_x$ 



**Fig. 6** Contour plot among CO,  $NO_x$  and  $O_3$  observed during 0800 h to 1600 h at Hissar in December 2004. Color codes indicate ozone mixing ratios in ppbv

values of 30–40 ppbv/ppbv are observed near some rural sites in China (Wang et al. 2002). These results indicate that emission from biomass burning play major role in the observed distributions of various trace gases at Hissar.

#### 5.3 NMHCs and CO

NMHCs are released into the atmosphere from a variety of anthropogenic and biogenic sources, while, lighter molecular weight NMHCs are contributed mainly from anthropogenic sources.

In this study, the levels of various light hydrocarbons ( $C_2$ - $C_3$  NMHCs) are similar to those observed at Ahmedabad. But the mixing ratios of NMHCs are higher than reported data for some sites in China but lower than those observed at many urban sites of the world (see Table 1). The Chinese values are for rural areas and for Hongkong, which is a coastal city.

In addition to their importance in the in-situ photochemical production of  $O_3$ , NMHCs data can be used to identify dominant emission sources. The ratios of NMHCs have also been used to estimate the age of the air parcels. In this section, we have attempted to identify the major sources using correlation studies between different pairs of NMHCs, CO and CH<sub>4</sub> at Hissar. The scatter plots showing the linear regression fits for four pairs of anthropogenic species viz. C<sub>2</sub>H<sub>2</sub>-CO, C<sub>2</sub>H<sub>4</sub>-C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>-C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub>-CO are depicted in Fig. 7, and are discussed below.

#### 5.3.1 $C_2H_2$ -CO relation

The slopes  $\Delta C_2 H_2/\Delta CO$  (pptv/ppbv) and  $\Delta C_3 H_8/\Delta C_2 H_6$  (ppbv/ppbv) have been used as measures of photochemical processing of the air mass after emission from anthropogenic

Gas average	Hissar (this work)	Ahmedabad <sup>a</sup> (winter)	China <sup>b</sup> (winter)	Karachi <sup>c</sup> (winter)	Taipei <sup>d</sup> (winter)	US <sup>e</sup> 39 cities
O <sub>3</sub>	33.4±9.6	28±18				
CO	$553.5 \pm 292$	$539 \pm 35$	800			
NO <sub>x</sub>	15.7±7.3	$15.1 \pm 7.4$	18			
C <sub>2</sub> H <sub>6</sub>	$8.6 \pm 3.8$	$9.2{\pm}6.4$	3.3	93	8.3	11.7
$C_2H_4$	9.3±11.4	$4.6 {\pm} 4.8$	3.1	19	14.1	10.7
$C_2H_2$	$3.1 \pm 3.3$	$6.4 \pm 4.4$	2.6	18	15.1	6.5
C <sub>3</sub> H <sub>8</sub>	$4.7 \pm 4.9$	$12.5 \pm 8.8$	1.6	41	6.4	7.8
C <sub>3</sub> H <sub>6</sub>	$2.8{\pm}2.6$	$1.3 \pm 1.3$	0.5	5.5	4.6	2.6
$\Delta CO/\Delta NO_x$	33		36			6–9 <sup>f</sup>
$\Delta C_2 H_2 / \Delta CO$	7.8		0.37, 0.4 <sup>g</sup>			5.5 <sup>g</sup> (Tropical Pacific)
$\Delta C_3 H_8 / \Delta C_2 H_6$	0.69		0.37			

Table 1 A comparison of mean values of trace gases (ppbv) and their slopes observed at Hissar with available data from other sites in the world

<sup>a</sup> Sahu and Lal 2006

<sup>b</sup> Wang et al. 2001, 2002, 2003

<sup>c</sup> Barletta et al. 2002

<sup>d</sup> Ding and Wang 1998

<sup>e</sup> Seinfeld 1989

<sup>f</sup> Parrish et al. 2002

g Xiao et al. 2007

activities (Smyth et al. 1996). The combustion products acetylene  $(C_2H_2)$  and CO represent a pair of compounds that have common anthropogenic emission sources and common sink via reactions due to OH radicals. Similarly, propane  $(C_3H_8)$  and ethane  $(C_2H_6)$  have common anthropogenic sources and both have major loss with OH radicals.

For a typically polluted continental type of air mass, the  $\Delta C_2 H_2/\Delta CO$  values greater than 1.5pptv/ppbv are considered as having influenced by relatively recent emissions, while lesser values are indicative of significantly processed (aged) air mass (Gregory et al. 1996; Smyth et al. 1996; Sahu et al. 2006). Scatter plot of  $C_2H_2$ -CO for Hissar is shown in Fig. 7(a). The observed  $\Delta C_2H_2/\Delta CO$  value of 7.8 ppbv/ppmv with excellent correlation ( $r^2 =$ 0.9) suggests influence of very recent emissions from combustion related local sources. However, from this correlation study alone it is difficult to find out whether the emission from fossil fuel combustion or from biomass burning (mostly dry wood and dry cow/buffalo dung) is dominant in the observed distributions of trace gases at Hissar.

#### 5.3.2 $C_3H_8$ - $C_2H_6$ relation

The scatter plot of  $C_3H_8$ - $C_2H_6$ , which is another indicator of photochemical processing of air mass, is depicted in Fig. 7(b). A study in outflow of air pollution from Hong Kong (a tropical Asian site) reports a value of about 0.37 ppbv/ppbv for  $\Delta C_3H_8/\Delta C_2H_6$  as representative of recently emitted continental air mass (Wang et al. 2003). However, this slope value may change depending upon dominant source of emissions. The higher  $\Delta C_3H_8/\Delta C_2H_6$ value of 0.69 ppbv/ppbv observed at Hissar indicates recent emissions. The lower slope value can be explained in part by faster removal of  $C_3H_8$  than  $C_2H_6$  after released into the atmosphere. So far our analyses have indicated that recent emissions from combustion related processes have played major role in the distributions of these trace gases.



**Fig. 7** Scatter plots between **a** CO and  $C_2H_2$  **b**  $C_2H_6$  and  $C_3H_8$  **c**  $C_2H_6$  and  $C_2H_4$  and **d** CO and CH<sub>4</sub> based on all the hourly averaged data observed during the campaign at Hissar

Observations show good correlations between different primary pollutants, CO and acetylene, while these could be due to several types of combustion processes. Propane and butanes are generally associated with leakages of liquid petroleum gas (LPG) and natural gases. The moderate to poor correlations of these two species with CO and  $C_2H_2$  indicate their emissions from non-combustion sources.

#### 5.3.3 $C_2H_4$ - $C_2H_6$ relation

From various observational studies near biomass burning and biofuel combustion sources, it has been observed that the slope of ethene to ethane  $(\Delta C_2 H_4 / \Delta C_2 H_6)$  is always higher than 1.0 ppbv/ppbv (Goldan et al. 1995). The scatter plot of this relation is depicted in Fig. 7(c). The observed higher slope value of 1.29 ppbv/ppbv supports the dominance of emissions from biomass burning activities.

#### 5.3.4 CH<sub>4</sub>-CO relation

Methane and CO are emitted from biomass burning and biofuel combustion (Blake et al. 1996) but have no significant common sources from fossil fuel combustion. The scatter plot between mixing ratios of  $CH_4$  and CO is shown in Fig. 7(d). Strong interrelation between the two gases with correlation coefficient values of  $r^2 = 0.58$  respectively suggests dominant role of biomass burning and biofuel combustion processes. In comparison to these measurements, data from Ahmedabad, where fossil fuel is being used extensively,
show very poor correlation ( $r^2 = 0.08$ ) between these two gases (Sahu and Lal 2006 and references therein). Thus supporting the interpretation that biomass burning is the major source of various primary pollutants at Hissar. This explanation is coherent with emission inventory study reporting seasonal high of biomass burning emission in south Asia in the winter months. (Streets et al. 2003).

## 6 Summary and conclusions

The continuous surface level ambient measurements of  $O_3$  and related trace gases like CO,  $NO_x$  and light NMHCs were conducted at a semi-urban site in the north-west of the IGP in India during the full month of December 2004. The observations were influenced by both clear sky and foggy conditions. Typical for a clear sky day, the diurnal distributions show the noontime elevated  $O_3$  but lower mixing ratios of CO, NO and  $NO_2$ . On the other hand, diurnal patterns of trace gases were not so strong during the foggy days. Mixing ratios of  $O_3$ , CO and  $NO_x$  are almost same as those observed at Ahmedabad, even though Hissar is a semi-urban site whereas Ahmedabad is a major urban site.

The slope  $\Delta CO/\Delta NO_x$  of 33 ppbv/ppbv observed in this study is similar to the values reported for the rural sites in China. But both these values are much larger than the average value of about 6–9 observed at few sites in the US (Parrish et al. 2002). The comparison implies that both India and China have more CO emissions compared to  $NO_x$  emissions. This is expected as the incomplete combustion processes like biomass-biofuel burning are major sources of many primary pollutants in these two countries. However, with accelerated industrial growth and increasing numbers of automobiles, levels of  $NO_x$  are likely to increase further. This may cause higher levels of surface ozone in future as predicted by models (Prather et al. 2003).

These studies based on the correlations and ratios of many primary pollutants indicate that the observations at Hissar were influenced by fresh emissions mostly from local biomass burning sources. These results will be useful for model validation and budget estimates. There is a need for long term measurements at many sites in this region to study chemistry and emission characteristics of these important trace gases and related changes in the environment and climate.

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