Atmospheric Trace Gases: Transport and Emission Effects

A Thesis

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by Chinmay Mallik



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DECLARATION

I, Chinmay Mallik, S/o Mr. Lambodar Mallik, resident of RN-102, PRL Student Hostel Campus, Thaltej, Ahmedabad 380059, hereby declare that the research work incorporated in the present thesis entitled, "Atmospheric Trace Gases: Transport and Emission Effects" 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.

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Countersigned by Head of the Department

Dedicated to My Loving Parents and My Beloved Brother

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ABSTRACT

This thesis work aims to investigate the role of atmospheric processes on trace gas distributions in different environments. The diurnal and seasonal variations in atmospheric trace gases have been studied in urban (source) regions located in Western India and the Indo-Gangetic Plain, at remote high altitude sites as well as over oceanic regions to understand the impacts of emissions, atmospheric transport, boundary layer dynamics as well as atmospheric chemistry and photo-chemistry towards these variations. Information on dominant sources has been derived by investigating the inter-relationships among various trace gases, made possible by simultaneous measurements of multiple trace gases. This is the first comprehensive study of atmospheric SO_2 , the major anthropogenic precursor of radiatively important sulfate aerosols, over different regions of India. Further, a new gas-chromatographic set-up has been developed at PRL to study the levels and variability of reduced sulfur gases, mainly atmospheric COS (which is an important component of the global sulfur cycle), over the Indian region. The impacts of South Asian emissions on the O_3 variability over the Bay of Bengal has been investigated from simultaneous, in-situ measurements of O_3 and its precursors (CO, NO_x , CH_4 and NMHCs) along with meteorological parameters during a post-monsoon cruise. Further, O_3 diurnal variations over the Bay of Bengal has been studied in detail using a photochemical box model.

Keywords: Trace gases, Emission ratios, Atmospheric transport, Sulfur dioxide, Ozone, Indo-Gangetic Plain, Bay of Bengal

LIST OF PUBLICATIONS

A. Referred Journals

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- "Enhanced SO₂ concentrations observed over Northern India: Role of long-range transport" Mallik, C., S. Lal, M. Naja, D. Chand, S. Venkataramani, H. Joshi and P. Pant Int. J. Rem. Sens. 34, 2749-2762 (2013).
- "Study of a high SO₂ event observed over an urban site in western India" Mallik, C., S. Venkataramani and S. Lal Asia-Pac. J. Atmos. Sci. 48, 171-180 (2012).
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Acronyms and Abbreviations

AMSL	Above Mean Sea Level
AOD	Aerosol Optical Depth
BM/BF	Biomass/Biofuel
BoB	Bay of Bengal
CPCB	Central Pollution Control Board
DU	Dobson Unit
EDGAR	Emissions Database for Global Atmospheric Research
FID	Flame Ionization Detector
\mathbf{FF}	Fossil Fuel
GC	Gas Chromatography
GMT	Greenwich Mean Time
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory Model
IGP	Indo Gangetic Plain
INDOEX	Indian Ocean Experiment
IPCC	Intergovernmental Panel on Climate Change
IST	Indian Standard Time
LPG	Liquefied Petroleum Gas
LPS	Large Point Sources
MACC	Monitoring Atmospheric Composition and Climate
MLD	Mixed Layer Depth
MODIS	Moderate Resolution Imaging Spectroradiometer

MOPITT	Measurements Of Pollution In The Troposphere
NASA	National Aeronautics and Space Administration
NCEP	National Centers for Environmental Prediction
NMHC	Non-Methane Hydrocarbons
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
OMI	Ozone Monitoring Instrument
PBL	Planetary Boundary Layer
PCA	Principle Component Analysis
PFPD	Pulsed Flame Photometric Detector
PMF	Positive Matrix Factorization
PMT	Photon Multiplier Tube
ppbv	parts per billion by volume
PRL	Physical Research Laboratory (Ahmedabad, India)
PSCF	Potential Source Contribution Function
RSC	Reduced Sulfur Compounds
TG	Trace Gas
VOC	Volatile Organic Compounds

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Chapter 1

Introduction

The Earth's climate is changing and 'anthropogenic influence' is likely to be the most dominant cause (Stocker et al., 2013). The Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5) states that 'human influence has been detected' in warming of the atmosphere and the ocean, in changes in the global water cycle, in reductions in snow and ice, in global mean sea level rise, and in changes in some climate extremes. The AR5 further states that the level of confidence pertaining to causal attributions regarding several aspects of climate change has increased since the previous report (AR4, Solomon et al., 2007). The increased confidence is a result of sustained efforts devoted to climate studies that includes measurements and modeling of atmospheric components, processes and phenomena. However, our understanding of the chemical and physical processes occurring in the atmosphere is still shrouded with considerable uncertainty which limits our ability to model and forecast them at local, regional and global scales. In particular, research on atmospheric trace gas chemistry and air quality forecasting is still in its infancy particularly over the Indian region, due to lack of representative in-situ measurements of important gaseous constituents and poor understanding of their sources and sinks as well as other dynamical processes impacting their local and regional budgets.

The genesis of chemical species in the atmosphere and the chemical composition of the atmosphere resulting from the interactions among these species, driven by various energetic (thermodynamics) with major influence of solar radiation (photochemistry), the sources and sinks of these gaseous and particulate species, ions and radicals is studied under the aegis of 'atmospheric chemistry'. The distribution of these chemical species in the atmosphere is strongly influenced by 'atmospheric dynamics'. Atmospheric dynamics is a major component of 'meteorology' which is responsible for more visible impacts like formation of high and low pressure systems, formation of weather systems, clouds, monsoon, El-Nino, Hadley (meridional) and Walker (zonal) circulations, genesis of different wind regimes, etc. Atmospheric dynamics is also responsible for transport and distribution of gases and aerosols and consequent sustenance of the water, carbon, nitrogen and sulfur cycles. An important influence on these chemical and physical components is exerted by solar radiation which provides the basic energy for atmospheric circulations, for seasons, weather phenomena, atmospheric photochemical and chemical reactions, etc. Thus, a plethora of interactions (physical and chemical) at different scales (temporal and spatial) spanning orders of magnitudes makes the investigation of atmospheric chemistry and dynamics and ultimately the climate, 'challenging'. The understanding of these systems becomes more complicated due to feedback mechanisms as a result of scale interactions, errors and their propagation etc. An added complexity is generated by human influence on the climate system, the starting point of which are anthropogenic emissions of trace gases and aerosols into the atmosphere and subsequent perturbation of atmospheric chemistry and associated feedback.

The present thesis work is aimed at exploring some of the linkages between emissions (mainly anthropogenic) and atmospheric composition (influenced by atmospheric dynamics and chemistry) over the Indian region and thus advance our understanding of the interactions between emissions and transport processes controlling levels of trace gases at local and regional scales (Figure 1.1). While each of the myriad trace gases in the atmosphere has its own importance, during this thesis work, emphasis has been on the measurements of a select few trace gases (ozone, its precursors and sulfur dioxide). Surface ozone (O_3) and its major precursors are involved in major part of atmospheric trace gas chemistry. Thus, study of their levels and variability at local scales can explain local processes and their subsequent impacts on regional processes and reduce disparity between observations and models. Moreover, changing concentrations of precursors due to increased emissions from various anthropogenic activities have necessitated the investigation of their impacts on O_3 levels.



Figure 1.1: Schematic of factors influencing atmospheric composition.

The levels and variability of atmospheric sulfur dioxide (SO_2) , its relation with atmospheric processes resulting in its transport and transformation, and its subsequent impacts on the sulfur cycle is poorly understood over the Indian region. Since SO_2 and its thermodynamic end point viz. sulfate have major influence on both atmospheric chemistry and climate studies, extensive measurements of SO_2 over different regions of India have been attempted during this thesis work. Additionally, measurements of carbonyl sulphide, a major component of the sulfur cycle and stratospheric aerosols, have been initiated over an Indian site. Simultaneous measurements of carbon monoxide (CO), methane (CH_4) , non-methane hydrocarbons (NMHCs), nitrogen oxides and SO_2 are aimed at identifying source signatures pertaining to trace gas compositions in different regions of India. In subsequent sections, there will be discussions related to the general atmospheric chemistry of O_3 involving its precursors, SO_2 , sources and sinks of these trace gases as well as the atmospheric processes influencing their distributions in the atmosphere. This would be followed by discussions on the study locations highlighting the importance of South-East Asia and India in perspective of global emissions. Finally, an overview of subsequent chapters of the current thesis will be presented.

1.1 Importance of the study of atmospheric trace gases

The atmosphere is chemically complex and temporally evolving with continuous interactions with the hydrosphere, the biosphere, the lithosphere, and the anthroposphere as well as solar radiation. As evident from the latest IPCC report, anthropogenic emissions of trace gases have been increasing faster during the last few decades, particularly over the Asian region (*Stocker et al.*, 2013; *Lu et al.*, 2011; *Ohara et al.*, 2007 and references therein), and are projected to increase further. These emissions have profoundly modified the atmospheric composition leading to local and regional air quality issues. Further, they have been associated with perturbation of regional and global climate with potential impact on biogeochemical cycling of various elements, monsoon systems etc (Jacob and Winner, 2009). Some of the emitted trace gases also affect vegetation and crop yields. Further, they can also affect human health in several ways. The impacts of these emissions on air quality and radiative forcing can be direct as well as indirect (through formation of secondary species). Further, atmospheric levels of some of the climatically and biogeochemically important secondary species viz. O_3 and secondary organic aerosols (SOA) are influenced by primary emissions of CO, nitric oxide (NO), volatile organic compounds (VOCs), SO₂, particulate matter (mainly PM 2.5) etc. Due to important consequences of these primary and secondary gases and aerosols to the environment and climate, their monitoring has become necessary, over regions of different climatic regimes.

In the above perspective, trace gas and aerosol measurements over urban regions assume significance because of potentially large fluxes and consequently more severe impacts on air quality and atmospheric chemistry. Studies estimate an increase in surface O_3 by 1-10 ppbv over urban areas due to climate change (Jacob and Winner, 2009). Apart from urban regions, trace gas measurements over remote regions are also required to provide the information about background levels of these gases on a regional scale. Measurements made over high altitude stations and over oceans are necessary to provide information on various transport and transformation processes. Once there is sufficiently reliable information regarding levels of atmospheric constituents over different representative regions of the globe and the role of various physical and chemical processes in controlling levels of these constituents at various scale sizes, modeling of future scenarios of atmospheric composition and climate would become more reliable and pave way for effective policy making. Further, the model physics needs to be tuned to represent actual physical and dynamical processes which vary from region to region. Once the chemical and physical processes are well represented and reliable estimates of emissions and concentrations are available, we can hope to actually arrive at budget closures for important species that drive the chemistry of O_3 , sulfur gases etc.

1.2 O_3 chemistry in the troposphere

 O_3 is one of the key species that drives tropospheric chemistry, mainly because it is the only source of the primary atmospheric oxidant in the troposphere viz. the hydroxyl radical (OH). The production of atmospheric O_3 occurs via reaction R1.

$$O + O_2 + M \to O_3 + M \tag{R1}$$

where M is any third body, primarily N_2 or O_2 molecules, but also other gas molecules and particles which absorb energy from the reaction as heat.

The difference between stratospheric and tropospheric O_3 is in the source of atomic oxygen (O). Whereas, in general, at ($\lambda < 242 \ nm$), molecular oxygen breaks into atomic oxygen, this wavelength is not able to penetrate into the troposphere. In fact, much of the solar radiation with ($\lambda < 290 \ nm$) is absorbed above the troposphere. Consequently, the O atoms in the troposphere are produced primarily from photolysis of nitrogen dioxide (NO₂) by the ultraviolet portion of solar radiation ($\lambda < 424 \ nm$).

$$NO_2 + h\nu \rightarrow NO + O$$
 (R2)

The cycle is completed by conversion of O_3 and NO to O_2 and NO₂ respectively.

$$O_3 + NO \rightarrow NO_2 + O_2$$
 (R3)

The R1-R3 reactions sequence is not supposed to have any net effect on O_3 . However, the O_3 -NO-NO₂ photochemical steady state is perturbed by presence of CO and hydrocarbons (R-H; R: C_nH_{2n+1} , e.g. CH₄ and NMHCs) which leads to net production of O_3 in the troposphere. The photochemical production of O_3 occurs from the oxidation of CO and R-H, catalyzed by hydrogen oxide (HO_x = OH + H + peroxy) radicals in the presence of nitrogen

 $\mathbf{7}$

oxides (NO_x=NO+NO₂). The reaction is initiated by the production of HO_x via photolysis of O₃ at ($\lambda < 320 \ nm$).

$$O_3 + h\nu \to O_2 + O(^1D) \tag{R4}$$

While most of the $O(^{1}D)$ formed recombines with O_{2} to form O_{3} , about 10% is converted to OH. OH initiates the atmospheric oxidation of a wide range of compounds in the atmosphere and is thus referred to as 'detergent of the atmosphere'.

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
 (R5)

The reaction propagates by cycling of HO_x between its OH and peroxy forms via oxidation of hydrocarbons involving organic peroxy radicals (RO₂) and CO involving hydroxyl radicals.

$$CO + OH + O_2 \rightarrow CO_2 + HO_2; RH + OH + O_2 \rightarrow RO_2 + HO_2$$
 (R6)

The reactions are followed by

$$HO_2 + NO \rightarrow OH + NO_2; RO_2 + NO \rightarrow RO + NO_2$$
 (*R*7)

$$\mathrm{RO} + \mathrm{O}_2 \to \mathrm{RCHO} + \mathrm{HO}_2$$
 (R8)

The aldehydes (RCHO) formed may further oxidise to produce O_3 or photolyze to produce HO_x . The chain is terminated by removal of HO_x and NO_2 via

$$\mathrm{HO}_{2}/\mathrm{RO}_{2}/\mathrm{OH} + \mathrm{HO}_{2} \rightarrow \mathrm{H}_{2}\mathrm{O}_{2}/\mathrm{R} - \mathrm{HO}_{2}/\mathrm{H}_{2}\mathrm{O} + \mathrm{O}_{2}$$
(R9)

$$OH + NO_2 + M \rightarrow HNO_3 + M$$
 (R10)

R10 acts as a sink for both NO_2 as well as radicals. While O_3 production is facilitated only during sunlit hours (R7, R2, R1), O_3 loss (which occurs both during the day as well as during night) proceeds via R5 or R11-R12.

$$O_3 + HO_2 \to OH + 2O_2 \tag{R11}$$

$$O_3 + OH \to HO_2 + O_2 \tag{R12}$$

Generally, in regions of high NO (e.g. urban regions), R7 predominates resulting in O₃ production while in NO poor regions like oceans; R11 prevails leading to O₃ destruction. Under assumption of simple O₃-NO_x chemistry, for net O₃ production, production rate (in R7) should be more than the loss rate of O₃ (in R11). Assuming the rate constants for R7 and R11 as k_7 and k_{11} , the following equation leads to O₃ production:

$$k_7 \ge HO_2 \ge NO > k_{11} \ge HO_2 \ge O_3 \text{ implies } NO/O_3 > [k_{11}/k_7]$$
 (1.1)

Since k_{11}/k_7 is about 0.23×10^{-3} , it leads to the fact that at 50 ppbv of ambient O₃, NO concentrations should be at least 11.5 pptv for O₃ formation to take place. The ratio of NO/O₃ to cross the threshold of NO for O₃ production is in the range of 0.23×10^{-3} to 4.0×10^{-3} depending upon the environment. Extensive description of tropospheric O₃ chemistry is provided in *Finlayson-Pitts and Pitts Jr* (1999), *Jacob* (2000) and *Seinfeld and Pandis* (2006). *Liu et al.* (1987) have defined the O₃ production efficiency as the total number of odd oxygen molecules (O_x= O₃ + O + NO₂ + HO₂NO₂ + (2x) NO₃ + (3x) N₂O₅) produced per molecule of NO_x oxidized to HNO₃. It accounts for each NO molecule emitted to the atmosphere that undergoes a number of reactions, producing O₃, before being lost as HNO₃. About 90% of O_x is accounted by O₃ (*Jacob*, 2000). The chemical lifetime of O_x ranges from about a week in the lower troposphere to several months in the upper troposphere.

The above reactions can be used to explain the typical diurnal pattern of O_3 in the urban atmosphere. NO concentrations are relatively high in the early morning because the free radicals needed to convert the NO to NO_2 are not present at that time in sufficient quantities. After sunrise, photolysis of formaldehyde (HCHO) and other compounds starts the volatile organic compounds (VOC) oxidation cycle for the various organic gases present in the atmosphere. Subsequent conversion of NO to NO_2 by RO_2 (R7) results in NO_2 becoming the dominant NO_x species. Build-up of O_3 occurs when
the NO₂ to NO ratio becomes high enough. Meanwhile, NO₂ concentrations decrease via the sink reaction R10. Simultaneously, during the day, NO_x is also diluted under the regime of a rising inversion layer. During the night, NO and O₃ combine to form NO₂ via R3 until either the NO or O₃ is completely consumed. Gas phase nitrous acid (HONO), present at night in polluted urban air, breaks apart at sunrise, to provide NO and OH, initiating formation of O₃.

Apart from its pivotal role in atmospheric chemistry, O_3 is a greenhouse gas (because of its strong absorption band centred at 9.6 μ m), with significant impacts at the cold upper troposphere (Hansen et al., 1997). O_3 changes have the potential to affect climate significantly. As per the 4^{th} IPCC report, the radiative forcing (RF) of tropospheric O_3 was estimated (with a medium level of scientific understanding) at 0.35 Wm^{-2} with an uncertainty range of 0.25-0.65 Wm⁻² (Forster et al., 2007), making it the third most important greenhouse gas perturbed by human activity, next to carbon dioxide (CO_2) and methane (CH_4) . As per the latest IPCC estimates, the emissions of shortlived gases certainly contribute to the total anthropogenic RF, emissions of CO are virtually certain to have induced a positive RF, while emissions of NO_x are likely to have induced a net negative RF (AR5, Stocker et al., 2013). Further, O_3 is a pernicious, secondary pollutant (as it is not directly emitted into the atmosphere) and toxic to both human beings and vegetation. Studies evince that elevated ground-level O_3 not only causes deleterious human health effects ranging from eye irritation to severe respiratory distress, but also results in crop and forestry losses (Mauzerall and Wang, 2001). As per the World Health Organization (WHO) Air Quality Guideline (AQG), the 8-hour daily average O_3 should be less than 50 ppbv for adequate protection of public health (*WHO*, 2006). Owing to its adverse health effects, tropospheric O_3 has become one of the most widely researched topics in recent decades (Bell et al., 2004).

1.3 Tropospheric sulfur chemistry and sulfur cycle

Sulfur is ubiquitous in all spheres of the globe. It is emitted from the soil and the oceans into the atmosphere in various states of oxidation. The biogeochemical cycling of various sulfur species between various ecosystems (Figure 1.2) has important implications to the climate, to the pH of rainwater, to the health of human beings, fauna and flora. The most conspicuous form of sulfur in the atmosphere is SO_2 . However, its several precursors in lower oxidised state called reduced sulfur compounds (RSCs), contribute significantly to the global budget. The atmospheric sources of SO_2 are natural as well as anthropogenic but over the years, the anthropogenic component has increased overwhelmingly. The primary source of SO_2 is combustion of coal and oil due to various anthropogenic activities. Natural sources of SO_2 include volcanic emissions and oxidation of RSCs.

The major atmospheric RSCs are dimethyl sulfide (DMS, CH₃SCH₃), hydrogen sulfide (H₂S), carbonyl sulfide (COS), carbon disulfide (CS₂) etc. The most preferred reagent for oxidation of RSCs into SO₂ is OH with rate constants (x10⁻¹² cm³ molecule⁻¹ at 298 K) of 9.1, 5.0, 0.43 and 0.04 for DMS, H₂S, CS₂ and COS respectively (*Warneck*, 1999). In several cases, the reactions are accelerated in the presence of molecular oxygen. Further, the reaction rates of RSCs with atomic oxygen are also quite rapid, but due to lower number densities of O in the lower troposphere, the reactions do not make significant impact to the overall budget. Based on their reactions with OH, the lifetimes of DMS, H₂S, CS₂ and COS would be about 0.6 days, 4.4 days, 12 days and 44 years, respectively at surface level. Thus, except COS, the RSCs released into the troposphere are ultimately converted into SO₂ in the atmosphere in a time span of a few days and contribute to its budget. While COS is also converted into SO₂, some of it is able to reach the upper troposphere and may even penetrate into the stratosphere where its photolysis at $\lambda < 250 \ nm$ and oxidation lead to formation of SO₂ and ultimately sulfate (SO₄²⁻). Thus, COS is a source of stratospheric sulfate layer (*Andreae and Crutzen*, 1997; *Notholt et al.*, 2003). The stratospheric aerosol layer has an important impact on the radiation budget of the stratosphere, its dynamical structure, and its chemistry (*Brasseur et al.*, 1999). COS accounts for about 43% of the stratospheric aerosol, while the stratospheric SO₂ oxidation and upward-transported tropospheric sulfate account for 27%, and the remaining 30% respectively (*Pitari et al.*, 2002). The importance of DMS in the Earth's atmosphere was realized since *Charlson et al.* (1987) proposed a hypothesis (CLAW) in which DMS is released by marine phytoplankton, enters the troposphere, and is ultimately oxidized to sulfate particles, which then act as cloud condensation nuclei (CCN) for marine clouds. Globally, DMS accounts for most of the non sea-salt sulfate (*Chin and Jacob*, 1996). However, the role of DMS in climate regulation needs further investigation (*Woodhouse et al.*, 2010).



Figure 1.2: The atmospheric sulfur cycle. Source:http://www.atmosphere.mpg.
de/media/archive/8066.jpg

A typical reaction sequence from CS_2 to SO_4^{2-} , (the thermodynamic end point of sulfur in the atmosphere) is initiated via formation of SH, the sulfur analog of OH (*Warneck*, 1999).

$$OH + CS_2 \rightarrow COS + SH$$
 (R13)

The SH can react with O_2 or even O_3 , finally forming SO, which reacts with O_2 to form SO_2 .

$$SH + O_2 \rightarrow OH + SO(-102 \text{ kJ mol}^{-1})$$
 (R14)

$$\rightarrow \mathrm{SO}_2 + \mathrm{H}\left(-225 \text{ kJ mol}^{-1}\right) \tag{R15}$$

$$SH + OH \rightarrow S + H_2O$$
 (R16)

$$S + O_2 \rightarrow SO + O$$
 (R17)

$$SO + O_2 \rightarrow SO_2 + O$$
 (R18)

The oxidation of SO_2 to sulfate can occur via gas phase oxidation, in cloud droplets, at the surface of aerosol particles etc. Direct photo-oxidation of SO_2 in the troposphere is a weak prospect due to loss of the excitation energy to collisions with air molecules. The most dominant oxidation mechanism is by OH, leading to formation of an adduct (HOSO₂), which reacts with O₂ to form the sulphuric acid anhydride (SO₃), a gaseous pollutant and a primary agent in acid rain. The anhydride reacts with water to form H₂SO₄, in a rapid, exothermic reaction (-88 kJ mol⁻¹). In the formation of H₂SO₄, R19 is the rate-limiting step.

$$SO_2 + OH + M \to HOSO_2 + M$$
 (R19)

$$HOSO_2 + O_2 \to HO_2 + SO_3 + M \tag{R20}$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4$$
 (R21)

The H_2SO_4 formed subsequently condenses, almost irreversibly, on the preexisting particles (*Kulmala et al.*, 2004). It also forms new particles by nucleating with water vapor (H_2O) and gaseous ammonia (NH_3) to form sulfate aerosol (*Khoder*, 2002).

 SO_2 also dissolves in the liquid water of clouds and fogs, to form $HSO_3^$ and SO_3^{2-} ions, which are oxidised by O_2 , O_3 , hydrogen peroxide (H₂O₂) etc and catalyzed by iron (Fe) and manganese (Mn) ions, sourced to mineral fraction of aerosol particles (*Seinfeld and Pandis*, 2006). SO_2 is not especially soluble in water, but subsequent equilibria during heterogeneous oxidation to sulfate increases the partitioning of gas and aqueous phases towards cloud water (*Brimblecombe*, 2003). However, the production of H_2SO_4 decreases the pH of the liquid water in clouds/fogs, shifting the gas-liquid partitioning in favour of the gas phase. Further, oxidation of SO_2 also occurs on surface of fly ash particles of power plant plumes, which are also rich in oxides of heavy metals. The reaction rate increases with increasing relative humidity (RH). While average atmospheric lifetime of SO_2 due to gas phase oxidation is about a week, dry deposition (average of 1 cm s^{-1}) in the boundary layer (average height of 1 km) limits its lifetime to about a day (Seinfeld and Pandis, 2006). A recent estimate of the average tropospheric lifetime of SO_2 is about 1.8 days (Faloona, 2009). Further, wet deposition due to washout (removal processes within clouds) and rainout (removal by falling precipitation and diffusional uptake of SO_2) also acts as a sink of SO_2 .

Measurements of SO₂ are highly desirable as it covers important aspects of air pollution, atmospheric chemistry and climate. It is a primary criteria pollutant with potentially adverse health effects from acute exposures (*WHO*, 2006; *Longo et al.*, 2008) and concomitant deleterious impacts on the flora and fauna (Alberta Environmental, 2003). It leads to acidification of precipitation, although, the problem of acid rain is naturally alleviated over the Indian region due to alkaline soil (*Banerjee*, 2008). As illustrated above, SO₂ also plays a pivotal role in the global sulfur cycle (*Delmas and Servant*, 1988). It is a precursor to the formation of sulfate aerosols that are potential candidates for CCN and impact the number concentrations and size distributions of cloud droplets. Due to their large hygroscopicity, sulfuric acid aerosols undergo substantial hygroscopic size growth, which strongly increases their light scattering efficiency and ability to act as water vapor condensation nuclei in liquid water cloud formation. Changes in the abundance of SO₂ (and hence SO₄²⁻) will impact the radiation field, and consequently the climate (*Solomon et al.*, 2007; *Tsai et al.*, 2010). The direct RF of sulfate aerosols is estimated to be -0.40 ± 0.20 W m⁻² (the negative sign indicates a net cooling of the Earth's climate) (*Forster et al.*, 2007) and one-half to two-thirds of this RF is attributable to anthropogenic sulfur.

1.4 Sources of atmospheric trace gases

Apart from its photochemical production, the atmosphere also has a certain background level of O_3 , which varies with region. The background O_3 , which is not attributed to anthropogenic sources of local origin, is also an important sphere of research (*Vingarzan*, 2004). Its sources include (1) downward transport of stratospheric O_3 , (2) in situ O_3 production from CH_4 emitted from swamps and wetlands reacting with natural NO_x (from soils, lightning and downward transport of NO from the stratosphere), (3) in situ production from reactions of biogenic VOCs with natural NO_x and (4) long-range transport of O_3 from distant pollutant sources. Modelling studies indicate that during the winter and spring at northern mid-latitudes, approximately 10% of O_3 in the lower troposphere is estimated to be of stratospheric origin (Fusco and Logan, 2003). Although O_3 was found to rise during the last century, in recent decades, divergent trends in tropospheric O_3 have been observed over different regions of the globe (*Vingarzan*, 2004). Recent studies indicate that O_3 mixing ratios over most part of the world show little or no growth (Oltmans et al., 2012). However, an increase in surface O_3 by 1-10 ppbv over urban areas is attributed to climate change (Jacob and Winner, 2009). Model results indicate that increase in NO_x emissions since the 1970s account for a 10-20% increase in background O_3 over certain areas of the globe. Further, rising CH_4 levels from industry and agriculture are believed to have increased global O_3 levels

by 3-4% (*Vingarzan*, 2004). A global tropospheric O_3 budget for the year 2000 estimates chemical production, chemical destruction, dry deposition and stratospheric input fluxes to be 5100, 4650, 1000 and 550 Tg-O₃ per annum (a⁻¹), respectively (*Stevenson et al.*, 2006).

The importance of NO_x , CO and NMHCs in controlling tropospheric O_3 is very well documented. These gases also wield substantial influence on air quality and global climate. Being important consumers of hydroxyl radicals, these gases can enhance the lifetime of atmospheric greenhouse gases. CO does not absorb terrestrial infrared radiation strongly enough to be counted as a direct greenhouse gas, but its role in determining tropospheric OH indirectly affects the atmospheric burden of CH_4 and leads to O_3 formation. Documentation of their levels over major emission regions e.g. urban areas, is very important due to potentially large fluxes. Fluxes of biogenic VOCs (isoprenes, terpenes etc) and CO emitted due to biomass burning could be large over forested as well as rural areas. The major anthropogenic sources of CO, HCs, NO_x and SO_2 are presented in Table 1.1.

The global anthropogenic emissions of CO vary between 476-611 Tg-CO a^{-1} as per various inventory estimates (*Lamarque et al.*, 2010). For biomass (BM) burning emissions of CO, estimates agree fairly well and the range is 427- 467 Tg-CO for the year 2000. Most of the global CO emissions come from the Asian region (279 Tg-CO; *Streets et al.*, 2003). Out of this, 67 Tg, or 24%, comes from open BM burning. Further, China contributed 121 Tg-CO during 2000 as per Climate Model Intercomparison Program (CMIP5) estimate. However, CO emissions in Asia are not known with great confidence because emission factors are highly dependent on the efficiency of the combustion processes. The CO emissions for the Indian region were estimated at 63 Tg for the year 2000 (*Streets et al.*, 2003) which is about 22.6% of Asian emissions. However, *Garg et al.* (2006) estimated CO emissions in India to be about 41.7 Tg, majority of which is accounted by the residential sector (86%) and the transport (13%) sector. CO in the residential sector comes from biofuel

(BF) burning (fuel-wood, dung-cakes and agriculture crop residue), especially through cooking activities in the rural households. However, over India, CO emissions from transport, power and brick kilns have been growing at over 5% a^{-1} (compounded)(*Garg et al.*, 2006).

Table 1.1: Anthropogenic sources of CH₄, C₂-C₅ NMHCs, CO, NO_x and SO₂. Biomass (BM), Biofuel (BF), Fossil Fuel (FF). OH rate constants at 298 K are in $x10^{-12}$ (cm³ molec⁻¹ s⁻¹).

Species	ОН	Sources		References
	rates		-	
		Major	Other	
CH_4	0.0063	Agriculture/ Live-	Landfill, Coal-	Streets et al., 2003; Wang
		stock/ Wetland	mines, NG, BM/BF	<i>et al.</i> , 2004a
C_2H_6	0.26	BM/ BF/ NG	FF (Coal), Oceans	Rudolph, 1995
C_2H_4	8.52	BM/ BF	FF (Ethanol),	Sawada and Totsuka,
			Petrochemical	1986; Horowitz et al.,
			(Plastic)	2003
C_2H_2	0.82	Transport sector $(BM/$	BM	Xiao et al., 2007
		BF/ NG)		
C_3H_8	1.15	FF (LPG)	Petrochemical, NG	Duncan et al., 2007; Blake
				and Rowland, 1995
C_3H_6	26.30	FF/BF	BM, Petrochemical	Duncan et al., 2007
			(Plastic)	
C_4H_{10}	2.44	FF(LPG), Petrochemi-	BM/BF, Solvent	Horowitz et al., 2003; Guo
		cal	use	et al. (2007)
C_5H_{12}	3.90	Vehicle (Gasoline)		Guo et al., 2007; Xie and
				Berkowitz, 2006
CO	0.15 -	BF/BM/ Incomplete	Oxidation of	Streets et al., 2003; Dun-
	0.21	burning of FF	$\rm CH_4/HC$	can et al., 2007
NOx		Vehicles/ Power	BM	Garg et al., 2001
		plants/ Industry		
SO_2	1.1	Coal burning in power	Refineries	Garg et al., 2001
		plants/ industries		

The global anthropogenic and biomass burning emissions of VOCs are estimated at 129.5 Tg and 78.3 Tg for the year 2000 (*Lamarque et al.*, 2010). Asian and Chinese NMHC emissions were estimated at 52.2 and 17.4 Tg respectively for the year 2000 (*Streets et al.*, 2003). The CH₄ and NMHC emissions for the Indian region were estimated at 32.8 and 10.8 Tg respectively for the year 2000 (Streets et al., 2003). The major contributors to CH_4 emissions in India were enteric fermentation followed by paddy cultivation (Garg et al., 2006). Among the NMHCs in India, alkanes and alkenes contributed almost equally (2.8 Tg or 26% each), followed by aromatics (1.8 Tg or 17%) and aldehydes/ ketones (0.95 Tg or 9%) (Streets et al., 2003). This is in contrast to developed countries in Asia and the world, where alkanes are emitted in higher percentages due to larger contribution of petroleum products in transportation.

The global anthropogenic and biomass burning emissions of NO_x are estimated at 56.8 Tg and 11.7 Tg for the year 2000 (*Lamarque et al.*, 2010). Asian and Chinese NO_x emissions were estimated at 26.8 and 11.4 Tg for the year 2000 (*Streets et al.*, 2003). The NO_x emissions for the Indian region were estimated at 4.6 Tg for the year 2000 (*Streets et al.*, 2003) which is about 17% of Asian emissions. For NO_x emissions in India, which has been growing at over 5% pa, the road and power sector constitute 34% and 31% respectively (*Garg et al.*, 2006). BM burning accounts for 13% of NO_x emissions in India (Table 1). An important component of the NO_x group is NO_2 , a major gaseous pollutant arising from combustion of fossil fuels (FF) and BM. While only a small part of NO_2 is formed by photo-oxidation of NO (the major nitrogenous product of combustion). The largest natural sources of NO are lightning and microbial activity in soils (*Bond et al.*, 2002; *Bouwman et al.*, 2002).

Both NO_x and SO₂ have precarious associations with acid deposition (*Hidy*, 1994). As mentioned above, the primary source of SO₂ is coal burning in power plants and industries. However, over certain locations, vehicular and sometimes even natural sources of SO₂ could make substantial contributions to its levels. Natural sources of SO₂ include volcanoes and oxidation of RSCs. Globally, volcanoes contribute about 15 Tg a⁻¹ of atmospheric SO₂, which is shared between active volcanoes and post-eruptive, passive degassing. The global anthropogenic and biomass burning emissions of SO₂ were estimated at

92.71 Tg and 3.84 Tg respectively for the year 2000 (Lamarque et al., 2010). Asian and Chinese SO₂ emissions were estimated at 34.3 and 20.4 Tg respectively for the year 2000 (Streets et al., 2003). The SO₂ emissions for the Indian region were estimated at 5.5 Tg for the year 2000 (Streets et al., 2003) which was less than 6% of global emissions. During 2010, the SO₂ emissions in India were estimated at 8.8 Tg with 5.8 Tg from power sector and 2.8 Tg from industries. Among this, coal and oil contributed 76% and 19% to the national SO₂ emissions (Lu et al., 2011). The SO₂ emission from power sector in India have gone up from 37% in 1995 to 57% in 2005 to about 66% in 2010 (Garg et al., 2006; Lu et al., 2011). The major sinks of SO₂ are oxidation, dry-deposition and wet-deposition, with global average contributions of 53%, 36% and 8% respectively (Faloona, 2009). In polluted urban regions, dry deposition can sometimes be a more effective scavenger of SO₂ than oxidation.

Among the RSCs, COS and DMS are major natural contributors to atmospheric SO_2 over continents and oceans respectively. COS is the most abundant and long-lived sulfur gas in the troposphere, because its slow gas phase oxidation gives rise to long tropospheric residence times. However, the global atmospheric COS budget seems to have either an overestimation of sources or underestimation of sinks. Modelling investigations have highlighted the weaknesses in current understanding of the temporal and spatial fluxes of COS from the oceans, vegetation, soils and the atmospheric oxidation of COS (Kettle et al., 2002). The global emission of COS is estimated at 1.31 ± 0.35 Tg a⁻¹, out of which CS₂ oxidation contributes 0.42 ± 0.12 Tg a⁻¹, outgassing from oceans contributes 0.30 ± 0.15 Tg a⁻¹, DMS oxidation contributes 0.17 ± 0.04 Tg a^{-1} , and anthropogenic emissions account for 0.12 ± 0.06 Tg a^{-1} (*Watts*, 2000). The major anthropogenic contributors of COS are coal combustion, vehicular emissions and aluminium production. There has been some debate as to whether the oceans are a source or a sink for COS, but in the analysis of Watts (2000) the oceans are taken as a source. Uptake by vegetation $(0.56 \pm 0.10 \text{ Tg a}^{-1})$ and deposition to soils are important loss processes for COS apart from its oxidation $(0.13 \pm 0.10 \text{ Tg a}^{-1})$, although the large uptake by oxic soils $(0.92 \pm 0.78 \text{ Tg a}^{-1})$ is particularly uncertain. Nevertheless, longterm measurements are desired for a clear picture of how background surface mixing ratios of COS in the northern hemisphere vary across broad scales in response to ocean emissions and vegetation uptake (*Kettle et al.*, 2002). Further, there has been speculation regarding whether atmospheric concentration of COS is increasing due to human activities. It is pertinent to mention here that measurements of COS levels over the Indian region are yet to be reported.

Reliable information regarding levels of atmospheric constituents on appropriate temporal and spatial scales from emission inventories, can facilitate mathematical modeling of atmospheric chemistry, air quality, and climatic conditions of the past, present and future. However, the production and evaluation of these inventories is still an area of active research. A very recent development is the Regional Emission inventory in ASia (REAS) 2.1, which estimates the emissions from all of Asia in 2008 (growth rate from 2000 to 2008) as 56.9 Tg (34%) for SO₂, 53.9 Tg (54%) for NO_x, 359.5 Tg (34%) for CO, 68.5 Tg (46%) for NMVOC and 182.2 Tg (32%) for CH_4 (Kurokawa et al., 2013). The estimates for India for 2008 are 10.08 Tg SO₂, 9.68 Tg NO_x, 61.8 Tg CO and 15.95 Tg NMHCs (Kurokawa et al., 2013). These estimates for India by Emission Database for Global Atmospheric Research (EDGAR 4.2) were 8.52 Tg SO_2 , 6.39 Tg NO_x , 46.3 Tg CO and 10.61 Tg NMHCs (EDGAR4.2, 2009). Thus, it is clear that discrepancies exist between estimates of various inventories, particularly over the data sparse Asian region. Further, due to increasing emissions fuelled by population and economic growth, the contribution of Asian emissions to the global total, and hence to the global chemistry and climate, is significant. Since the accuracy of modelling results is vital to policy making, the inventories need to be supplemented by systematic and reliable inputs of constituent levels as well as activity values. It is to be noted that systematic representative measurements of SO_2 , NO_x , CO and NMHCs are still limited to very few locations in India, and hence knowledge about their

abundance and variability could have cornerstone implications to the understanding and modelling of tropical, atmospheric chemistry and its subsequent impacts on climate.

1.4.1 Emission ratios and source signatures

While emission inventories rely heavily on activity data (number of vehicles, type of fuel etc) and emission factors, another way to gauge the sources affecting the ambient trace gas composition is by studying inter-relationships among various trace gases. Identification of sources is possible because individual sources will emit a particular species more pre-dominantly. For example coal burning emits large amount of SO_2 , vehicular emissions are rich in NO_x and BM burning results in preferential release of CO. C_2H_2 is preferentially emitted from the transport sector, natural gas emissions are rich in C_2H_6 while paddy fields emit a lot of CH_4 (Table 1.1). Sometimes, instead of a single gas, the covariation of two gaseous species is a better indicator of emission sources and/or atmospheric processes. The relationships among CO and VOCs is popularly exploited to identify various emission sources due to unique emission signatures of different sources e.g. more C_2H_6 is emitted from BM compared to FF combustion (http://www.ipcc.ch/ipccreports/tar/wg1/140.htm). In contrast, the predominant source for C_4H_{10} is FF combustion. On the other hand, C_3H_8 emissions from FF are roughly 1.5 times that of BM. However, due to problems arising out of co-locations and co-emissions specially over urban regions, source signatures can be difficult to interpret using measurements of a limited number of species, unless measurements of specific tracers like 3-methyl pentane (gasoline marker) or acetonitrile (CH_3CN ; biomass burning indicators) are available.

Sometimes, correlation and the slope linear regression between two species are used for source attribution e.g. good correlation among butane isomers (i- C_4H_{10} and n- C_4H_{10}) are indicative of evaporative emissions from petrol station refuelling and refinery operations (*Derwent et al.*, 2000). In general, emissions of the butane isomers are strongly coupled and are largely attributed to the use of fossil fuels (natural gas, LPG, gasoline). The rates of reaction of C_4H_{10} isomers with OH are nearly equal, and considering OH as the major sink, the ratio between these two isomers is expected to change little with photochemical processing during transport. Thus, this ratio is a strong tracer of the actual emission ratio (*Baker et al.*, 2011). Further, a higher slope of C_3H_8 -CO alludes to LPG emissions while a very low slope indicates emissions rich in CO viz. BM burning. Likewise, CH_3CN -CO slope close to 2% is considered as BM burning indicator (*Lelieveld et al.*, 2001). Whether BM burning dominates over FF combustion can be further verified by simultaneous estimation of slopes between more numbers of species like C_2H_6 , C_2H_2 and CO. However, these values are subject to lifetime effects (the time during which concentration of an emitted species decreases to 1/e of its initial value) and hence the distance of the approximated source must be considered before arriving at an inference. To arrive at a more quantitative estimation of the transport time (age) of air parcels from source locations to a receptor site, the ratios of VOCs with different photochemical lifetimes (or reactivities) against OH have been used as a measure of the 'photochemical age'. These, so-called 'hydrocarbon clocks' (De Gouw et al., 2004) are based on the following equation

$$[C_t] = [C_0] \exp\left(-k_C \mathbf{x} \left[OH\right] \mathbf{x} \mathbf{t}\right)$$
(1.2)

where, k_C is the reaction rate coefficient for the reaction of a hydrocarbon with OH radical, C_0 is the concentration of the hydrocarbon at the time of emission and ' C_t ' is its concentration at time 't' after the emission. To make the estimation more robust and assuming that dilution effects are equal for the components (light hydrocarbon species), estimation of photochemical age 'T' of an air mass is made from the simultaneous measurements of two hydrocarbons A and B, having comparative atmospheric cycles but different reactivities towards OH radical.

$$t = \frac{\left[\ln\left(A_0/B_0\right) - \ln\left(A_t/B_t\right)\right]}{\left[OH\right]\left(k_A - k_B\right)} \tag{1.3}$$

where A_0/B_0 is the initial ratio at the emission source and A_t/B_t is the concentration ratio measured at a receptor location. K_a and K_b are the rate coefficients for reaction of A and B with OH radicals Atkinson et al. (1997). The computation of photochemical processing is necessary when the study concerns impacts of a source region on a remote location at a considerable distance.

1.5 Distributions of trace gases in the troposphere: Impact of transport and local meteorology

Global chemical transport model studies indicate that Asian pollution contributes about 3-10 ppbv to background O_3 levels in the western United States during the spring (*Vingarzan*, 2004). A continued rise in anthropogenic emissions from Asia was expected to further increase this background level. The phenomenon highlights the influence exerted by transport processes in modulating trace gas levels over a region, which may have to bear the impacts of emissions from another region. In this context, anthropogenic emissions of SO₂ over China have been found to be transported to Japan (*Igarashi et al.*, 2006, 2004) and Europe (*Fiedler et al.*, 2009a,b). Further, *Arnold et al.* (1997) have observed North American SO₂ plumes over Europe with SO₂ mole fractions as high as 3000 pmol mol⁻¹. Thus, air motions play a key role in determining the distribution of chemical species in the atmosphere allowing different chemical species, with different local sources, to interact. Through transport processes, human activities at local scales have global consequences, changing the chemical balance in remote regions of the atmosphere. The time taken by an air parcel to circulate the Earth under different zonal wind regimes varies from less than 8 days under influence of subtropical winter jet (40 m s⁻¹) to over a month under the regime of trade winds (easterlies <<10 m s⁻¹). The meridional wind (longitude averaged winds) speed is very less due to effect of angular momentum conservation, and hence little transport occurs on Earth due to meridional circulation. In general, west to east (zonal) mixing of the air around the globe takes about 2 weeks, mixing within a hemisphere takes about 1-2 months and inter-hemispheric exchange takes about 1.5 years.

Vertical mixing varies with season and latitude and is supposed to be the fastest in the lower latitudes during periods of convective activity. The strength of convective activity can be estimated by calculating the convective available potential energy (CAPE, $J \text{ kg}^{-1}$). The vertical motion of an air parcel is driven by the temperature difference of the parcel with its surroundings, giving rise to different stability conditions. Presence of moisture makes the computation of lapse rates more intricate. The changes in vertical distribution of temperature and moisture also lead to formation of inversion layers, which can impact the concentration of trace gases within the layer.

Trajectory calculations are often used for the interpretation of source locations of measured atmospheric trace substances. However, it must be taken into account that measurements of trace substances sample finite volumes of air, whereas a trajectory tracks the path of an infinitesimally small particle. Trajectories are, in meteorology, defined as the paths of infinitesimally small particles of air. Such a fluid particle, marked at a certain point in space at a given time, can be traced forward or backward in time along its trajectory. In practical trajectory models, this is done by integrating the trajectory equation

$$\Delta x_i = v_i \Delta t \tag{1.4}$$

where Δx is the position increment during a time step Δt resulting from the wind v, the index 'i' runs from 1 to 3 and denotes the three dimensions of space, using mean (non-turbulent) horizontal and vertical winds from a meteorological model. While forward trajectories describe where a particle will go, backward trajectories (often simply called back trajectories) indicate where it came from and are often used to interpret measurements of atmospheric trace substances, in order to establish relationships between their sources and their receptors (*Stohl et al.*, 2002). Trajectory calculations depend entirely on the input wind fields taken from a meteorological model, and thus inaccuracies in these data are the largest source of error for them. Other sources of errors are the interpolation of the wind velocity from grid points to actual trajectory positions and truncation errors which occur in the numerical solution of the trajectory equation (*Stohl et al.*, 2002 and references therein).

Further, boundary layer dynamics have important implications to flow of air and hence levels of trace gases in source region; e.g. increased height of convective boundary layer (CBL) during daytime can lead to dilution of primary pollutants over source regions (*Stull*, 1987). In most situations, a combination of mixed layer height (MLH) and wind speed plays a crucial role in governing the ambient levels of pollutants over a region. This is referred to as ventilation coefficient (VC, m² s⁻¹), which determines whether local air pollution will accumulate or disperse.

$$VC = h x v \tag{1.5}$$

where h is the height of the mixed layer and v is the wind speed. The MLH is the vertical layer where concentrations of water vapor and trace gases remain steady due to extensive turbulent mixing. Sometimes, wind speed alone can be a governing parameter in dispersing trace gases in a source region or transport to a non-source region. The effects of wind speed and horizontal advection can span broad scale ranges depending on the location.

The net lifetime of an atmospheric constituent is determined by the combined impacts of chemistry and dynamics. Thus, the role of meteorology on trace gas levels needs to be accessed very minutely for good simulations of present and future levels. A recent study over 39 major eastern US urban area confirmed that O_3 has been increasing with increasing temperature and decreasing with increasing RH (*Camalier et al.*, 2007). However, temperature and humidity can have variable effects for different trace gases over different regions. *Camalier et al.* (2007) state that advances in statistical modeling of the relationship between air quality and meteorology should help corroborate the results being obtained from numerical simulations which predict the response of air quality to changes in climate conditions.

While chemistry and meteorology govern the transport and transformation of trace gases in the atmosphere, wet and dry depositions are the ultimate paths by which these gases are removed from the troposphere. The factors controlling dry deposition are the atmospheric turbulence, the chemical property of the species, and the nature of the surface itself (*Wesely and Hicks*, 2000). Further, for trace gases, the solubility and chemical reactivity may affect the uptake at the surface. The vertical dry deposition flux (F; the amount of material deposited on a unit surface area per unit time) is directly proportional to the local concentration (C) of the depositing species at some reference height above the surface (e.g. 10 m or less)

$$\mathbf{F} = -\mathbf{V}_{\mathbf{d}} \mathbf{x} \mathbf{C} \tag{1.6}$$

The proportionality constant, V_d , has the unit of length per unit time and is known as deposition velocity. V_d is estimated on the basis of resistance models and is defined as the inverse of the sum of multiple resistance factors (aerodynamic resistance: R_a , boundary layer resistance: R_b , and surface resistance: R_c) (Wesely and Hicks, 2000). Since C is a function of height above the ground, V_d is also a function of height and must be related to a reference at which C is specified. By convention, the downward flux is negative so that V_d is positive for a depositing substance. Surface deposition is one among the major sinks of tropospheric O₃ as well as SO₂. The large variability in the deposition rates of trace species at different surfaces and in different seasons adds to the uncertainty budgets of those species. In certain cases, wet removal of gases can also play crucial role in determining atmospheric levels. *Igarashi* et al. (2004) had noted that in-cloud scavenging of SO₂ was responsible for depleted concentrations at Mt. Fuji during winter. *Rai et al.* (2010) have calculated a deposition rate of 185 g m⁻² s⁻¹ for SO₂ removal at a rainfall rate of 168 mm hr⁻¹. The quantification of wet removal processes for acidic gases still needs to be systematically represented.

1.6 Trace gas measurements over India

Measurements of surface O_3 were initiated in India as early as 1950s (Ramanathan, 1956). However, measurements on a regular basis can be traced to 1960-70s, which were made by the Indian Meteorological Department (IMD) over Srinagar, Delhi, Pune, Nagpur, Trivandrum and Kodaikanal (Sreedharan and Tiwari, 1971). The brief background of O_3 and precursor measurements over the Indian region has been provided in this section. However, it must be noted that the discussion is not comprehensive but an overall flavor. Measurements of O_3 using electrochemical as well as chemiluminescence methods were being done during the 1990s by groups at Delhi (Varshney and Aqqarwal, 1992), Pune (Khemani et al., 1995) and Thumba (Nair et al., 2002). Systematic measurements of O_3 along with its precursors (CH₄, CO and NO_x) were made over Ahmedabad during 1991-96 (Lal et al., 2000), Gadanki during 1993-96 (Naja and Lal, 2002) and Mt. Abu during 1993-2000 (Naja et al., 2003). The varying patterns of diurnal variations over these sites were linked to precursor levels, meteorology as well as study locations. The role of NO chemistry on O_3 levels during post-sunset time was clearly observed over Gadanki, a rural site. The diurnal patterns of O_3 at Mt. Abu (1680 m amsl) revealed absence of in-situ photochemical production during daytime. Measurements of surface O_3 at a tropical coastal site, Thumba during 1997-98, revealed a typical diurnal variation with a secondary peak during evening related to change in wind pattern from sea-breeze to land-breeze at the site (Nair et al., 2002). Surface O_3 measurements at Tranquebar, a rural coastal site of southeast India, during 1997-2000 showed higher concentrations (23±9 ppbv) in May and lower concentrations (17±7 ppbv) in October due to active (inactive) photochemical production mechanisms along with favorable (unfavorable) meteorological conditions in May (October) (*Debaje et al.*, 2003). Further during this period, the vertical distributions of trace gases (viz. CH₄, N₂O, SF₆, and various halocarbons) in the troposphere and stratosphere were studied using indigenously developed, balloon-borne, cryogenic air samplers flown on high altitude balloons from the national balloon launch facility at Hyderabad (*Lal et al.*, 1996).

To understand the transport and en-route transformation of O_3 , a 'mobile lab experiment-advection' (MOLEX-A) was conducted in the downwind of urban regions of Gujarat during January 2001 and 2002 (Chand and Lal, 2004). The elevated O_3 levels in the downwind of urban regions were observed to be in the range of 70-110 ppbv, about 60% higher than the O₃ observed at Ahmedabad (an urban region). The observations across the Bhavnagar city further confirmed that O_3 levels inside the urban center were much lower than its downwind side. Further 'mobile lab experiment-vertical' (MOLEX-V) was conducted during October-December, 2000. These measurements, covering the height corresponding of 998-840 mb and mostly conducted during the night hours, showed a significant loss of O_3 (60-80%) in the nocturnal boundary layer compared to the free troposphere. Also, in the free troposphere, the daytime O_3 was lower by 10-20% than the night-time O_3 due to chemical destruction and dilution of O_3 poor air from the boundary layer with the air in the free troposphere during daytime. It was observed that over certain locations, dilution played a more significant role towards O_3 levels than chemistry. Over the last decade, measurements of surface O_3 have been reported from different parts of India including Nainital (Kumar et al., 2010), Delhi (Jain et al., 2005), Kolkata (Ghosh et al., 2013), Pune (Beig et al., 2007), Hyderabad (Swamy et al., 2012), Anantpur (Reddy et al., 2012), Trivandrum (David and *Nair*, 2011), etc. These measurements have explained very interesting features in diurnal and seasonal variations of O_3 related to location, meteorology, precursor levels etc. While some of these O_3 measurements were accompanied by NO_x measurements, generally they lacked simultaneous measurements of important O_3 precursors viz. CO, NO_x and NMHCs necessary for a deeper understanding of O_3 chemistry. Measurements of NMHCs along with O_3 , CO and CH_4 were made at Ahmedabad and Mt. Abu during 2002 to study the impacts of large local emissions on the photochemical production of O_3 (*Sahu and Lal*, 2006a,b). Moreover, there have been reports of increased surface O_3 at Delhi (*Jain et al.*, 2005).

In view of the importance of the Indian landmass as potential source of important atmospheric constituents, several land campaigns were organized under the aegis of 'Indian Space Research Organization-Geosphere Biosphere Programme' (ISRO-GBP) to study levels and variations of pollutants (aerosols and trace gases) at different sites in peninsular India (from Ahmedabad to Hyderabad) during February, 2004 (*Reddy et al.*, 2008; *Lal et al.*, 2008a) as well as the Indo-Gangetic Plain (west to east) during December, 2004 (Lal et al., 2008b). Further, extensive measurements of vertical distributions of O_3 and meteorological parameters have been made from Ahmedabad (2003-07), Kanpur (2004) and over marine regions surrounding India (2006) (Gupta et al., 2007; Lal et al., 2013). Aircraft based observations of O_3 and its precursors have been made from several land-marine interfaces during January, 2009 (Srivastava et al., 2012a). Details regarding trace gas measurements over oceanic regions around India are given in Chapter 5 of this thesis. The various land campaigns and ship campaigns, apart from individual station based measurements, conducted over the Indian subcontinent and its surrounding marine regions have highlighted the large spatial and temporal heterogeneity in the distributions of surface O_3 and its precursors over the Indian subcontinent. However, systematic measurements of O_3 along with its various important precursors are still desirable for more accurate simulation of O_3 levels, which are generally found to differ from model estimations. Further, except for a few measurements (*Reddy et al.*, 2008; *Kumar et al.*, 2004), study of sulfur gases over the Indian region are still lacking over the Indian region. While this section presented an overall scenario of trace gas measurements conducted over the Indian region, the next section presents the context and objectives of the thesis to further the issues raised above and to fill some of the gaps in our current understanding.

1.7 A brief overview of the thesis: Context, objectives and chapter details

As discussed above, changing anthropogenic emissions have been clearly found to impact atmospheric chemistry, air quality and climate; resulting in modification of cloud processes, global warming etc. However, much research is still needed to understand the intricacies of emission-chemistry-climate relationship. Further, this relationship is governed by various chemical and dynamical processes occurring in the atmosphere. While on one hand, we need to estimate the emissions very accurately, on the other hand it is necessary to understand the fate of the emitted trace gases after their release into the atmosphere. Since it is not practically possible to measure the emissions at all source locations, measurements need to be made at strategic locations (which include hotspots, remote areas as well as regions with varying environmental conditions). Further, the South-East Asian region, including India, has become very important in the global scenario due to its impact on global atmospheric chemistry and climate. This is related to the prevalent socio-economic conditions, pockets of dense population and uncontrolled emissions. The Indian region contributes significantly to the global emission budget of trace gases. These emissions are lifted up by deep convection and transported over large distances, giving it a global perspective. Satellite observations and emission inventories clearly

show that the Indo-Gangetic Plain (IGP) of India is a major contributor to the national budget of anthropogenic trace gas emissions, with significant impacts from both FF combustions as well as BF/BM burning. Apart from the IGP, the industrial corridor in Western India (Mumbai-Ahmedabad-Delhi axis) is also a major source of several pollutant gases.

The distribution of trace gases over a particular location is influenced by synoptic scale transport and meteorology. (Figure 1.3) shows the wind patterns over the Indian subcontinent and surrounding regions during different seasons. During pre-monsoon (summer, March-May), the westerly winds bring trace gases and aerosols from the Arabian Peninsula, southern Pakistan and northern Arabian Sea to Western India. However, over the central IGP, the air masses mainly come from northern India and western IGP. Over the eastern IGP, the air masses bring pollutants from northern BoB and the eastern coast of India. During monsoon (June-September), the wind speeds are high and the Indian peninsula is swept by oceanic air masses. While the western part of India receives air masses directly from the Arabian Sea, the IGP receives air masses from eastern and peninsular India with the eastern IGP being cleansed by marine air masses from the north BoB. Further, during monsoon and pre-monsoon, the pollutants over the Indian region are uplifted to higher altitudes due to strong convective activity (represented by omega in (Figure (1.3)) and transported to other regions. Reversal of winds takes place during post-monsoon (October-November) as a high pressure region builds up to the north of Indian subcontinent. During this time, western India mainly the Gujarat region receives north-easterly air masses from further east (western India) while the IGP receives air masses from northern India. The eastern part of the IGP receives polluted air masses from the western and central IGP. The change from monsoon to post-monsoon is accompanied by sudden increase in trace gas levels over both western India and the entire IGP due to increased influence of continental sources and reduced influence of marine air masses. The post-monsoon effect is intensified during winter (December-January-February) and accumulation of pollutants takes place due to reduced wind speeds and a shallower boundary layer.

As highlighted in the Section 1.1, study of atmospheric trace gases with respect to emission and transport processes is necessary for better understanding of their variability, distribution and subsequent impacts on our environment and climate. Section 1.6 highlighted the lack of simultaneous measurements of O_3 and its important precursors over the Indian region, which has limited our understanding of the processes controlling their levels and large tempospatial variability. Further, measurements of sulfur gases have become highly desirable over the Indian region due to changing emission patterns and the important role of these gases in atmospheric chemistry and climate studies. Their measurements can also provide useful information regarding the relationship of trace gases and aerosol, source signatures etc. To further the issues raised above and improve our understanding of the links between emissions, atmospheric processes and trace gases, the current thesis work is planned with the following objectives:

1. To understand the diurnal and seasonal variability of atmospheric trace gases over the Indian region with a focus on SO_2 .

2. To investigate the role of dynamical and chemical processes on the distributions of atmospheric trace gases (SO₂, O₃, NO_x, CO and light hydrocarbons) in different environments viz. urban source regions, remote marine regions as well as pristine high altitude sites.

3. To study the impact of various emission sources on the levels of these trace gases at various representative locations over the Indian subcontinent including marine regions.

To accomplish the objectives addressed above, and using information from seasonal wind patterns shown in (Figure 1.3), four locations were selected for detailed study of the transport and emission effects in trace gas composition over the Indian region (Figure 1.4). Two of these sites represent urban source regions in Western and Eastern India viz. Ahmedabad and Kolkata (Figures



Figure 1.3: Wind streamlines (represented by arrows; $m s^{-1}$) at 925 hPa over the Indian sub-continent during different seasons. The colour map on the background represents the variation of vertical velocity (omega, Pa s⁻¹) over the Indian region during different seasons.

1.3 and 1.4) with very different climatic and meteorological conditions. While Ahmedabad is impacted by air masses from the western part of India which move further over the Arabian Sea, Kolkata is impacted by air masses transporting continental pollutants all along the IGP (black arrow in (Figure 1.4) over to the BoB. Kolkata lies in the eastern end of the IGP and can be considered as the end point of continental IGP emissions. The eastern part of India is not as industrialised as the western part, but is densely populated. Kolkata, being located at the extreme eastern end of the IGP is a strategic site to study IGP outflow over to the BoB during winter and post-monsoon against the influence of the BoB and eastern coast of India during pre-monsoon and monsoon (Figure 1.3). Further, the measurements made at Kolkata megacity with its unique blend of domestic and industrial emissions provide an opportunity to study the effects regional IGP emissions *vis. a vis.* local urban emissions. On the other hand, Ahmedabad represents a semi-arid, urban region which is relatively free from the influence of IGP emissions. However, measurements over this site are representative of emissions from the highly industrialised part of western India. Further, trace gases measurements over Ahmedabad during the changing wind regime from summer to post-monsoon is supposed to provide useful information on source characteristics as well as the response of O_3 to changing precursor levels.

Further, the levels and variability of SO₂, NO₂ and CO are studied over several urban regions in and around the IGP, using already available surface and satellite data, to understand their seasonal patterns with respect to emissions, winds and other seasonally varying physical processes. Apart from studies carried over urban source regions (which have significant local emissions), a pristine high altitude site in the central Himalayas, represented by Nainital, was selected to study the impacts of IGP emissions when they are transported to higher altitudes. While measurements made in Nainital can provide information on how trace gas levels vary when they are originated from different surface sites in the IGP, the site is also a strategic location for gauging the impact of surface emissions during their uplifting into higher atmosphere and subsequently the free troposphere. It is pertinent to mention here that while wind borne transport brings trace gases from IGP into Nainital during premonsoon and monsoon, during winter nights, the site is entirely cut off from the IGP due to boundary later dynamics and acquires free tropospheric characteristics. Lastly, ship borne measurements over the Bay of Bengal (BoB; Figure 1.4) can provide information on the chemical and dynamical processes on trace gas composition of continental plumes sourced to different regions in Asia (with different emission characteristics). Ship borne measurements of O_3 and its several precursors over the BoB during this study provided an opportunity to explore the role of dynamics and chemistry on O_3 levels over marine regions.



Figure 1.4: The measurement sites: Ahmedabad (23.0°N, 72.6°E, 49 m amsl, semi-arid, urban), Nainital (29.4°N, 79.4°E, 1958 m amsl, sub-humid, background), Kolkata (22.6°N, 88.4°E, 6 m amsl, humid, urban) and the Bay of Bengal. The yellow lines mark the cruise track over the BoB. The pink and yellow dotted lines border the densely populated plains in India and Pakistan. The black arrows show two major pathways for outflow of trace gases from continental India into the surrounding ocean.

The thesis comprises six chapters including this introductory discussion (Chapter 1) on the importance of trace gas studies in the present-day context, their sources and sinks and role of chemistry and dynamics in governing their distributions.

Chapter 2 will describe the measurement principles of the instruments used for online measurements of trace gases (O_3 , CO, NO_x and SO_2) during this study and their calibration procedures. There will be discussions on gas chromatographic (GC) measurements of CH₄, CO and NMHCs as well as a detailed description of a GC set-up for measurement of RSCs.

Chapter 3 will discuss the role of atmospheric processes on the levels and variability of O_3 , CO, NO_x and SO_2 over Ahmedabad (a representative site for the highly industrialised western India) on a local (spatial) scale and a short, temporal scale (May-October, 2011) with rapid changes in meteorology. Source signatures based on inter-species correlations of measured concentrations will be discussed. This chapter will also include results on diurnal and seasonal variability of atmospheric COS and CS₂ during January-October, 2013, obtained for the first time in India, with a new GC set-up for measurements of RSCs at Physical Research Laboratory (PRL), India.

Chapter 4 would begin with results from a road experiment (from Ahmedabad to Nainital) to highlight the changes in emissions patterns as one moves from Western India into the IGP. This would be followed by a survey of the variability of SO_2 , NO_2 and CO emissions over a few urban locations using existing surface measurements and satellite retrievals. Next, the influence of IGP emissions over Nainital, a pristine mountain site in the Himalayas, will be investigated using SO_2 as a tracer. Measurements of SO_2 , CO and hydrocarbons over Kolkata, a megacity in the IGP outflow region, would be used to gauge the relative contribution of the IGP emissions against local, urban emissions. Finally, an evidence of free tropospheric, long-range transport of volcanic SO_2 from Africa to the IGP would be presented using multiple satellite observations.

Chapter 5 will be based on cruise measurements of O_3 and some of its precursors over the Bay of Bengal (BoB) during the post-monsoon of 2010. An insight into the O_3 chemistry and dynamics during different parts of the campaign will be provided using a photo-chemical box model. Source signatures, based on trace gas levels and ratios, in air masses coming from different source regions, will be investigated.

Chapter 6 would highlight important results from the present thesis and also attempt to put them in a national and international perspective.

Chapter 2

Experimental Techniques

The core part of the current thesis work is constituted by the measurements of trace gases conducted over various locations. Measurements form the basis on which our understanding of the atmosphere is built. Thus, the more accurate our measurements, the better will be our understanding of the atmosphere. On the same note, the more we are able to improve our measurement capabilities, the more information we will be able to derive. The measurements during this study can be broadly classified into two categories: in-situ online measurements and offline sampling of ambient air. Most of the online measurements of O_3 , CO, NO_x and SO_2 were conducted using in-situ trace gas analyzers. Online measurements were also made for estimating the levels of RSCs over Ahmedabad, using a gas chromatographic (GC) setup developed in-house at PRL. Offline sampling was conducted for estimating CH₄, CO and NMHCs concentrations in air samples, collected in glass sampling bottles, at locations outside Ahmedabad and the samples were analyzed by using gas chromatographic setup at our laboratory in Ahmedabad. Apart from this, measurements of SO_2 and NO_2 , conducted by the Central Pollution Control Board (CPCB) of India, using chemical methods were also used for part of this study. Further, space based measurements of tropospheric O_3 , surface and columnar CO, columnar SO_2 and NO_2 , by various satellite sensors were

used for this study. A description of the techniques involved in the measurements of trace gases used in the current thesis work is described in the following sub-sections.

2.1 In-situ measurements of trace gases using online analyzers

For continuous in-situ monitoring of trace gases, a suite of online analyzers were used. Most of the data were acquired using on-line analyzers from Thermo Fisher Scientific (USA) [O₃ (49i), CO (48i-TLE), NO_x (42i-TL) and SO₂ (43i-TLE)]. However, intermittently, we have also acquired data using in-situ analyzers from Teledyne Instruments (USA) and Environment SA (France). For monitoring at Ahmedabad, ambient air was drawn through a 2 m long perfluoroalkoxy (PFA) Teflon tubing (5 mm ID) into a glass manifold. The O₃ instrument drew sample air directly from this manifold through a 3 m long heated inlet tube. The CO, NO_x and SO₂ analyzers drew the same air from the manifold through an additional Peltier-based moisture removal unit. PTFE (polytetrafluoroethylene) filters (5 μ ; Sartorius AG, Germany), placed in the filter housings at the inlet of each analyzer, were used to remove dust and particles. The residence time in the manifold and tubing is assumed to be negligible due to a fast flow of air of about 2.5 litres per minute (lpm), generated by the four analyzers.

2.1.1 Measurements of surface SO₂

Among the three primary UV absorption regions for SO₂, the band between 190-230 nm is best suited for fluorescence measurements. In its fundamental state, each SO₂ molecule can absorb energy from photons to access the first excited state (a vibrational or rotational energy level). Absorption of ultraviolet radiation by SO₂ occurs at a frequency $\nu 1(\lambda \sim 214 \text{ nm})$ and yields an excited species SO_2^* . The excited SO_2 molecules then release the excess energy by three main processes. The most important of these is fluorescence, typically between 240 - 420 nm, with a rate constant k_f , as given by the following reaction (Figure 2.1).

$$SO_2 + h\nu 1 \rightarrow SO_2^* \rightarrow SO_2 + h\nu 2$$
(fluorescence, k_f) (R22)

Positive interference can occur due to NO and hydrocarbons which fluoresce in the same region as SO₂ (*Mohn and Emmenegger*, 2001). Hence, it would be necessary to selectively excite single vibronic states of SO₂ without absorption by NO (this becomes more important in a high NO scenario). Extinction (quenching) and dissociation (photolysis) are two other processes that compete with fluorescence for the fate of the excited SO₂ intermediates. Quenching (by O₂ or H₂O) of the excited species can lead to an underestimation of the SO₂ concentration (*Mohn and Emmenegger*, 2001).

$$SO_2^* + M \rightarrow SO_2 + M$$
 (quenching, k_q) (R23)

$$SO_2^* \to SO + O \text{ (photolysis, } k_p)$$
 (R24)

 k_f , k_q and k_p denote quantum yields associated with each form of deactivation and thus express probability of occurrence of these processes. Since k_q and k_p remain relatively constant over a wide range of temperatures, the fluorescence intensity is only affected by the concentration of the quenching compound M. Hence probability that the molecule will fluoresce is given by

$$Probability = k_f / (k_f + k_q [M] + k_p)$$

$$(2.1)$$

Quenching can be accounted for by calibrating with a standard that contains the same concentration of 'M' as the sample. Thus, calibrating with a SO_2 standard balanced by zero air is more suitable than a standard balanced with nitrogen. Further, the radiation intensity absorbed by SO_2 contained in a cell of length 'L' is governed by Beer-Lambert law:

$$Intensity = I_0 \{1 - \exp\left(\alpha L \left[SO_2\right]\right)\}$$
(2.2)

where I_0 is the intensity of incident radiation at the cell inlet after it is emitted by the flash lamp, α is the absorption coefficient of SO₂, [SO₂] denotes the concentration in the illuminated path.

Assuming steady state conditions in the optical cell, the intensity of the fluorescent radiation F received by the PMT can be deduced:

$$F = Gk_f I_0 \{1 - \exp(\alpha L [SO_2])\} / (k_f + k_p + k_q [M])$$
(2.3)

where G represents a geometric factor characteristic of the design of the instrument optical cell, When the magnitude of the exponent is small (i.e. $[SO_2]$ is low and L short), the relationship $e^{-x} \sim (1-x)$ as $x \to 0$ holds, and the above equation reduces to

$$F = Gk_f I_0 \alpha L \left[SO_2 \right] / \left(k_f + k_p + k_q \left[M \right] \right)$$

$$(2.4)$$

because G and L are constants and depend only upon cell design. The rate constants k_f , k_q and k_p are essentially constant as long as temperature does not vary markedly, the fluorescence intensity is linearly proportional to SO₂ concentration at relatively low levels (*Luke*, 1997).

An outline of the measurement principle of SO_2 analyzer is shown in Figure 2.1 while a detailed layout of the same is shown in Figure 2.2. The process of estimation of SO_2 in ambient air by the analyzer is elucidated in the following steps:

1. Ambient air (preferably freed from moisture using a Nafion dryer) passes through a 5 micron teflon filter to remove coarse mode particles that can potentially coagulate the flow path including a flow restrictor on the pump side.

2. The gas then flows through a "kicker" which removes hydrocarbons (interfering compounds which are excited with white light and consequently emit fluorescence) from the gas stream through a selective permeation membrane due to differential pressure. Hydrocarbon molecules are forced to permeate through the tube wall leaving the SO_2 concentration unaffected. The gas, sup-



Figure 2.1: Schematic for the measurement principle of the SO_2 analyzer (based on Thermo Scientific 43i-TLE manual).

posedly free of moisture, hydrocarbons and coarse mode particles enters the fluorescence (measurement) chamber.

3. In the measurement chamber, SO_2 molecules of the sample gas are preferentially excited by a UV light between 195 - 235 nm (Figure 2.1). The excitation light is produced by a xenon flash lamp pulsing at around 10 Hz and focussed into a mirror assembly by a condensing lens. The assembly consists of interference mirrors to selectively filter the UV to around 214 nm. This reflective filtering serves to intensify and stabilise the emission reaching the chamber through a relay lens. The UV source can also be a Zn vapour lamp (213.8 nm). The pulsing of UV lamp helps to increase the optical intensity and producing greater UV energy throughput to detect lower SO_2 concentrations. The fluorescence chamber has a structure to efficiently emit the fluorescence of SO_2 .

4. The SO_2 molecules (that have been excited by UV) decay to lower en-

ergy states and fluoresce in a broad band continuum from 240-420 nm, with an emission peak at approximately 320 nm. The emitted light passes through an emission filter (generally a combination of band-pass filters). The band-pass filter at right angles to the SO_2 fluorescence allows selected wavelengths from SO_2 fluorescence (between 340 and 410 nm) to pass into the orthogonally oriented UV responsive photomultiplier tube. It also blocks any scattered incident light which impinges on the PMT. Additionally, the filter serves to preferentially filter the fluorescence radiation of the interfering compounds, specifically NO. Reflective band pass filters are less subject to photochemical degradation and more selective in wavelength isolation compared to transmission filters.

5. The intensity of the emission is measured by the PMT. The intensity of fluorescence is proportional to the concentration of SO_2 as elucidated in Equation E4. Electronic signal processing transfers the light energy impinging on the PMT into a voltage. The PMT signal is amplified and measured by a photon counter. The values along with other house-keeping parameters like instrument background and span coefficients are used to give the SO_2 concentration in ppbv/ μ g m⁻³.

6. The sample gas, after leaving the chamber, passes through a flow sensor, the capillary and the shell side of the kicker through the pump to the exhaust. The flow is maintained by the flow restrictor and a pump at the rear end of the analyzer. The flow restrictor is a capillary that maintains the suction of the pump between 0.5 - 1 lpm depending on the ambient pressure. It has been observed that the hydrocarbon kicker works more effectively at lower flow rates. Simultaneously, as flow is reduced from 2 lpm (2000 sccm) to about 0.3 lpm, rejection ratio of interfering compounds (NO, CS₂, benzene, toluene, xylene, ethyltoluene, ethylbenzene etc) increases, thus making the measurements more reliable (*Luke*, 1997).

7. A photodetector continuously monitors the UV light intensity from the lamp. Its signal is compared to a reference signal and used to control the lamp intensity. The lamp intensity provides an indication of the quality/age of the



Figure 2.2: Schematic of working of the SO₂ analyzer (based on Thermo Scientific 43i-TLE manual).

2.1.1.1 Calibration of the SO₂ analyzer

Periodic calibration is critical to ensure measurement precision. In this section, the calibration of the SO₂ analyzer is described in detail. Similar procedures are followed for NO_x and CO analyzers and therefore they have not been discussed separately in this thesis. Span calibration is normally performed by reproducing the zero point and a gas with known concentration. Two point calibration (using zero air and a span gas in the range of ambient variation) is recommended once/twice a week depending on analyzer drift and feasibility of calibration. If the difference between the preset and measured span levels is greater than 2%, the cause must be investigated. The instrument is checked for linearity and stability every three to four weeks by performing a multipoint calibration (several span concentrations) (*Tscherwenka et al.*, 1998). The response of the SO_2 analyzer to changing span concentrations is shown in Figure 2.3. It must be noted that when concentration of span gas passing into the analyzer is gradually increased, it takes time to stabilise. This is because the walls of the analyzer and tubing take some time to equilibrate with the higher concentrations until the sub-systems are saturated with respect to absorption effects, if any. However, as concentration of the span gas is gradually decreased, it quickly attains a set value. It is recommended that zero and span gases are made to pass through the same path used for ambient air (manifold, particle filter etc). In case this is not possible, care must be taken to maintain similar conditions like using PTFE tubes, use of a similar particulate filter in the calibration line etc.



Figure 2.3: Response of the SO_2 analyzer to changing span concentrations during an experiment on 05 July, 2011.
2.1.1.2 Measuring the background concentration

Different options (given below) are available to create a zero air with SO_2 concentration reduced below the detection limit of the analyzer:

1. A commercially available zero air generator capable of producing a gas with SO₂ concentration below detection limit of the trace level analyzer (available from Teledyne (701H), Ecophysics (PAG003) etc). The PAG003 can reduce NO_x, SO₂ and O₃ to below 10 pptv. Further, it can reduce CO and hydrocarbons to below 3 ppbv. An external compressor feeds oil free air to an internal dryer through a condensate trap. A Peltier-effect based cooling module dries the air to a dew point of 15°C. A heated palladium catalyst module at 350° C oxidises all hydrocarbons (including CH₄) and the resulting air is passed through a copper cooling coil to equilibrate to ambient temperature. Next, NO and other oxidisable gases are oxidised by reactive O₃ from an ozonator. Further, the air is purified by adsorption through an activated charcoal filter and a particle filter.

2. Zero air for SO_2 analyzer can also be generated by passing through purafil / puracarb and/or molecular sieve/liquid nitrogen trap. Purafil contains powdered activated alumina and other binders impregnated with potassium permanganate to provide optimum absorption, adsorption and oxidation of SO_2 to about 4% of its own weight. The gases are trapped within the pellet due to chemisorption which converts them into solids to eliminate desorption.

3. Removing SO₂ by passing through Cu tubing (6.4 mm o.d.; *Faloona et al.*, 2009) or granulated activated copper as bulk adsorbent (http://www.restek.com/catalog/view/6605).

4. Zero air can also be produced by pressing ambient air through a series of cartridges filled with silica gel, activated carbon, sodium chalk and a molecular sieve (6Å) (*Tscherwenka et al.*, 1998) or activated charcoal filter (Sofnocarb, Molecular Products; *Hanke et al.*, 2003)

5. Chemical zeroing by a sodium carbonate (Na_2CO_3) coated denuder using

an annular arrangement (coating glass pellets should extend the life of a given trap). Glycerol is added to a 50:50 methanol:water solution to bring it up to 5% glycerol by weight and then Na_2CO_3 is added to have a clearly saturated solution. The saturated Na_2CO_3 solution is used to coat the inside of a glass tube (with packed beads) and dried under a slow flow of N_2 until it is ready to use. The trap can be tested by monitoring its ability to remove SO_2 by periodically adding calibration gas upstream and downstream of the SO_2 trap and calculating the percent removed. Method (i) is found to be most suitable for regular background calibration with periodic checks using other methods.

2.1.1.3 Measuring the span concentration

The pre-requisite for span calibration is a stable, calibration gas stored in an aluminium cylinder and traceable to international standards (NIST, USA; NPL, UK). For regulating gas flows, smaller volume stainless steel (SS; preferably passive) regulators are preferred with sample flow rates exceeding 500 mL min⁻¹. Regulator materials may not be as critical as for storage because of decreased contact times. However, materials with brass should be avoided at all costs (*Benesch and Jacksier*, 2002).

The span gas can be diluted using a commercial diluter which employ a set of mass flow controllers for multi-point calibrations. Avoiding SS surfaces as much as possible during dilution is recommended. The span gas must be passed for sufficient time for readings to stabilise. The linearity of the instrument ($\pm 1\%$) must also be taken into consideration.

Span gas concentration generated by dilution can be calculated using the formula:

$$S = (V_1 S_1 + V_2 S_2) / (V_1 + V_2)$$
(2.5)

where 'S' is the span gas concentration in ppbv achieved by diluting a span gas of concentration S_1 ppbv flowing at V_1 lpm using a diluting gas with S_2 concentration (in ppbv) flowing at V_2 lpm. The diluting gas is generally a zero air (SO₂ free air); so $S_2=0$. The calibration curve for SO₂ analyzer is shown in Figure 2.4.



Figure 2.4: Calibration curve for the SO_2 analyzer (logarithmic scale is used only for visualizing a range of concentrations).

For the Thermo SO₂ analyzer, the minimum detection limit is 50 pptv (300 s averaging time), response time is 320 s (300 s averaging time) the zero noise is about 25 pptv RMS (300 s averaging time), zero drift is less than 200 pptv per day and span drift is $\pm 1\%$) of full scale per week. The measurements are precise to 1% of the readings or at least 200 pptv.

2.1.2 Measurements of surface O₃

The photometric method for surface O_3 measurements has gained in popularity over the chemiluminescent and electrochemical methods due to higher accuracy, lower drifts, and negligible interferences from other air molecules. The method involves absorption of UV radiation at wavelength of 253.7 nm by O_3 molecules (Figure 2.5). The degree to which the UV light is absorbed is measured by a UV photometer. The UV photometer in O_3 analyzer consists of a stable UV light source which is placed at one end of the optics bench, and a UV detector which is placed at the opposite end. The detector is 'solar blind' Cesium Telluride photodiode with a broad pass-band centred near 253.7 nm. It generates an electrical output which is directly proportional to the amount of UV radiation striking its sensitized surface. Quartz windows allow the beam of UV radiation to pass through the chamber from the lamp to the detector, both of which are mounted externally.



Figure 2.5: Schematic of a dual beam O_3 analyzer (based on Thermo Scientific 49i manual).

The sample is drawn and split into two gas streams; one flows through an O_3 scrubber (MnO₂) to the absorption cell to provide signal Io (reference cycle) and the other stream of sample gas flows directly into the absorption cell to provide signal I (measurement cycle). To remove the effect of artefacts due to flow path, air sample is passed alternatively through the above mentioned two paths in small temporal cycles (about 10 seconds) using 3-way solenoid valves. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The absorption cells, one filled with ambient air and the other containing the same air but without O_3 , are illuminated by a low pressure, cold cathode mercury vapour lamp with most of its output concentrated at the 253.7 nm emission line. The attenuation in the signals due to the absorption and/or scattering by the air samples are measured by photodiodes. The relation between UV light intensity and ambient O_3 concentration is described by the Beer-Lambert Law:

$$I_1/I_2 = \exp\left(-\sigma LC\right) \tag{2.6}$$

where: σ is the absorption cross-section, L is the optical path length (length of cell, 38 cm for Thermo 49i), C is O₃ number density (molecules cm⁻³), I₁ is the UV light intensity measured in the sample cell with O₃ (sample gas) and I₂ is the UV light intensity measured in the reference cell with O₃ scrubbed (reference gas).

The ratio of I_1 with I_2 eliminates the contribution of absorption and/or scattering by species other than O_3 , and thus is a function of O_3 only. Simultaneous measurements of cell temperatures and pressures enable corrections due to changes in temperature and pressure in the absorption cell. Drift in the intensity of the UV lamp is also compensated in the analyzer. The minimum detection limit of different UV photometric O_3 analyzers is better than 1 ppbv and their response time is about 10-20 seconds. The absolute accuracy of these types of systems is reported to be about 5% (*Kleinman et al.*, 1994). The O_3 instruments were calibrated with a traceable O_3 generator (Sonimix 3001, LN Industries, Geneva, Switzerland).

2.1.3 Measurements of surface CO

CO in the atmosphere has been measured using spectroscopic methods as early as the 1950s. A good review of various methods commonly used for measuring the atmospheric CO is compiled by *Novelli* (1999). As of today, methods for measurements of atmospheric CO vary from GC technique to cavity ring down spectroscopy. Modern commercial CO analyzers are based on a combination of gas filter correlation (GFC) and infrared absorption at 4.67 μ m vibration-rotation band of CO (*Nedelec et al.*, 2003). The direct absorption measurements using this approach are considered absolute and are in contrast to other measurement techniques such as fluorescence for SO₂. The uniqueness of gas correlation spectroscopy is that a cell filled with the gas of interest is used instead of grating. Comparison of the attenuated signals from these cells filled with different gases reduce the absorption interference from other gases and separate the absorption signal of desired gas (*Roscoe and Clemitshaw*, 1997), in this case, CO.



Figure 2.6: A simplified block diagram of the CO analyzer (based on Thermo Scientific 48i-TLE manual).

The analyzer consists of an IR source, which generates broadband radiation (Figure 2.6). The radiation, modulated by a revolving chopper wheel, reaches optical measurement cell through a GFC wheel. The GFC unit consists of two cells filled with CO and N_2 along with a dummy metallic (opaque) cell for getting the correlated signals. The cells are filled at high pressure to achieve maximum optical attenuation in a small path of the cell. The N_2 filter is transparent to IR radiation and it allows the radiation to reach the measurement

cell where absorption of 4.67 μ m by CO occurs. Absorption of radiation also takes place in the measurement cell where sample air is filled. The radiation then passes through a narrow band pass filter and detected by a lead selenide IR detector, which is kept chilled at sub-zero temperatures. This provides the measurement signal. The CO gas filter produces a reference beam, which cannot be further attenuated by CO in the sample cell. Other gases do not cause modulation of the detector signal since they absorb the reference and measurement beams equally.

The minimum detection limit for various trace level commercial CO analyzers is reported to be less than 50 ppbv with a daily zero drift of less than 0.1 ppmv. This requires daily zero calibration of the analyzer using a pure air generator which is able to supply a zero air below detection limit of the analyzer (Ecophysics, PAG003). The PAG003 can supply pure air containing less than 3 ppbv CO by employing a palladium catalytic scrubber. For single point span calibration, a calibration mixture (1995 ppbv CO in N₂) from Intergas (International Gases & Chemicals), UK is used. Multi-point calibrations are done by diluting a 50 ppmv mixture of CO using zero air from the PAG003. Further, since H₂O has strong absorption features in the CO spectral range and significant concentrations of water vapour exists in the lower troposphere, a Nafion dryer is used to remove the water vapour.

2.1.4 Measurements of surface NO_x

Techniques for surface NO₂ and NO_x measurements vary from wet chemical methods (Jacob and Hochheiser modified method) to laser induced fluorescence. However, one of the most popular methods is based on 'chemiluminescence' (*Williams et al.*, 1998). Chemiluminescence is the emission of electromagnetic radiation from the transition to lower state of an electronically excited molecule, as the result of a chemical reaction. This method of detection has very high sensitivity and achieves very low limits of detection.

A schematic of the NO_x analyzer is shown in Figure 2.7. Ambient air is dried (using a Nafion dryer) and freed of particles (using a 5 μ m pore size PTFE filter) and sent to the analyzer where it has to pass through one of the two modes: NO_x mode where NO_2 is converted to NO using a molybdenum (Mo) converter at about 325°C or NO mode when it by passes the thermal conversion. Unfortunately, the reduction of NO_2 to NO is not specific for NO_2 , so that other nitrogen species such as peroxyacetyl nitrate (PAN) are also reduced to NO and act as interferences in the NO_2 measurement (Wendel et al., 1983). The molybdenum oxide (MoO) converters do not efficiently reduce N_2O , HCN, CH_3CN or CH_3NO_2 at typical operating converter temperatures lower than 400° C (Williams et al., 1998). However, they have the advantage over gold converters as they respond to aerosol nitrate. A third mode routes the sample (from either NO mode or NO_x mode) to a pre-reactor to create a dynamic zero reading for the analyzer by the consumption of NO using O_3 (generated from a silent discharge ozonator). The pre-reactor is sized so that greater than 99%of a 200 ppbv NO sample will react prior to entering the reaction chamber but is small enough to allow interferents (olefins) to pass onto the chamber. The combination of the three modes generates three signals for NO, NO_x , and the difference between the two.

Finally, at the reaction chamber, the O_3 reacts with the NO in the sample to produce excited NO₂ molecules (NO₂*).

$$O_3 + NO \rightarrow NO_2^* \rightarrow NO_2 + h\nu \quad (580 \text{ nm} < \lambda < 2800 \text{ nm}) \tag{R25}$$

The spontaneous deactivation of NO_2^* produces a characteristic luminescence with intensity linearly proportional to the NO concentration. The luminescence peaks at 630 nm radiation (*Navas et al.*, 1997). The signal is also directly proportional to the total flow and inversely proportional to the pressure due to dominance of quenching over fluorescence. Further, chemiluminescence is favoured by slightly elevating the reaction chamber temperature. However, too high temperature will increase the background count and result in heat transfer to the red sensitive PMT, which must be kept cool (using a thermoelectric cooler). In general, the measurements are certified to be precise till 1% of reading or 0.2 ppbv (whichever is greater). Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions.



Figure 2.7: Schematic of the NO_x analyzer (based on Thermo Scientific 42i-TL analyzer).

2.2 Measurements of NMHCs, CO and CH_4 using gas chromatography

The method of gas chromatography (GC) allows separation of thermally stable components in an air mixture if the individual components exhibit reasonable volatility. Further, the technique combined with a suitable detector, offers superior selectivity for compounds having similar spectroscopic properties. GC based measurements can quantify gaseous compounds in complex matrices present both in high and low concentrations. The principle of GC separation involves an air sample (containing compounds of interest or analytes) being transported through a column by the flow of inert, gaseous mobile phase known as carrier gas e.g. He, N₂ etc. The column contains a solid, stationary phase which provides a surface for interaction of the individual compounds of interest in the air sample. Depending on how the stationary phase exists, columns are classified into packed (tube filled with a solid support material coated with a liquid stationary phase) or capillary (inner walls of a tube of low diameter coated with stationary phase). The different rates of migration of individual components due to their repeated adsorption and desorption in the column results in their temporal separation. Separation of different compounds is achieved in the column because of their individual interactions with the stationary phase ("like-dissolves-like"-rule). The stronger the interaction for a compound, the longer it remains attached to the stationary phase, and consequently it takes more time to move (elute) through the column (longer retention time). The interactions could be a result of polarity (polar compounds interact strongly with a polar stationary phase), temperature (higher the temperature, the more of the compound is in the gas phase and hence lower interaction), carrier flow (lower the flow rate, more the interaction), column length (longer length, better separation but also longer retention time), and amount of material injected (very large samples can result in tailing). Once optimum separation is achieved between the individual compounds of interest by achieving a trade off between above mentioned parameters, they must be detected by employing a common physical or chemical property.

A very common detector is flame ionisation detector (FID) where signal is related to the rate at which solute molecules enter the detector. The effluent from the column is mixed with hydrogen and air, and ignited. The resulting flame burns at a temperature so as to pyrolyze most organic compounds, producing positively charged ions and electrons. In order to detect these ions, two electrodes are used to provide a potential difference. The nozzle head (where the flame is produced) acts as the positive electrode. The negative collector electrode is located above the flame. The ions thus are attracted to the collector plate and upon hitting the plate, induce a current. This current resulting from the pyrolysis of individual organic compounds in the air sample is measured with a high-impedance picoammeter and fed into an integrator. The current measured corresponds roughly to the proportion of reduced carbon atoms in the flame. The response of the detector is determined by the number of carbon atoms (ions) hitting the detector per unit time. This makes the detector sensitive to the mass rather than the concentration, which is useful because the response of the detector is not greatly affected by changes in the carrier gas flow rate. The FID is robust, easy to use, has high sensitivity and large linear response range. A schematic of an FID is shown in Figure 2.8.



Figure 2.8: Schematic of a Flame Ionization Detector.

Measurements of CH_4 and CO during this study were done using a Varian Vista 6000 GC, USA with FID. The air samples were collected in preevacuated, 900 ml borosilicate glass sampling bottles and injected into the GC with the help of a six port switching valve (VICI, USA). Separation of CH_4 and CO was achieved by passing the air sample through a 5 m long packed SS column (OD: 3.2 mm; ID: 1.9 mm) with a stationary phase of Molecular Sieve 13X kept at an isothermal temperature of 70°C using high purity helium gas (99.9999%) with a flow of 35 ml min⁻¹ as a carrier gas. Since CO cannot be directly identified by a FID, it is reduced to CH₄ by reaction with H₂ at 325°C in a methanizer containing Ni catalyst. The FID is very sensitive towards organic molecules e.g. CH₄ (10^{-12} g s⁻¹, linear range: 10^6 - 10^7). H₂ and zero air are the flame gases with their respective flows of 30 ml and 300 ml. A typical chromatogram for CH₄ and CO in ambient air is shown in Figure 2.9. The calibration of CH₄ and CO was done with 1.07 ± 0.01 ppmv and 2.17 ± 0.01 ppmv calibration mixtures supplied by NIST (USA) and Matheson (USA) respectively. The reproducibility of CH₄ and CO was found to be better than 1 and 5%, respectively. A secondary standard, prepared at PRL (Std#2), was also analyzed at regular intervals during the sample analysis period to see the stability of the systems.



Figure 2.9: A typical chromatogram for CH_4 and CO in an air sample.

The quantification of C_2 - C_5 NMHCs was achieved using a Hewlett-Packard 5890 series 2 GC with a FID. Since NMHCs in ambient air occur at trace lev-

els (low ppbv and sub ppbv), their direct determination requires injection of a prohibitively large sample volume into the column, in order to obtain a detectable amount of the analyte. This calls for on-line coupling of chromatographic separation with a sample pre-treatment step e.g. cryotrapping which utilizes differences in freezing points of the analytes and that of the matrix gas (atmospheric air in our case). The cryotrap for NMHCs, placed as a precolumn, consists of a 1/8 inch ID SS loop filled with 75-100 μ m size glass beads immersed in a vessel containing a cooling agent (liq. N₂ in our case for separation of volatiles). During passage of a stream of gaseous sample through the cryotrap, the analytes are frozen out and quantitatively caught in the trap. After completion of the concentration stage, the entrapped analytes are directly injected into the column by rapid heating of the trap with boiling water. The sample loading, isolation and injection processes are controlled by six port and eight port, electrically actuated valves (Valco Instruments limited).



Figure 2.10: A typical chromatogram for C₂-C₅ NMHCs of an air sample.

Separation is achieved by a 50 m porous layer open tubular (PLOT) capil-

lary column with an ID of 0.32 mm. The solid stationary phase is KCl/Al2O₃, providing one of the least polar interfaces to separate C₂-C₅ hydrocarbons including isomers in (approximate) boiling point order. PLOT columns differ from wall coated open tubular (WCOT) columns in that the coating on the inner wall of the column is solid in case of former but liquid in case of latter. He, at a flow rate of 8 ml min⁻¹, is used as the carrier gas. To separate the C₂-C₅ hydrocarbons over a wide range of boiling points effectively, the GC temperature was programmed as follows:

 $-1^{\circ}C(3 \text{ min hold}) \rightarrow 4^{\circ}C \text{ min}^{-1} \rightarrow 40^{\circ}C(4 \text{ min hold}) \rightarrow 3.5^{\circ}C \text{ min}^{-1} \rightarrow 110^{\circ}C \rightarrow 35^{\circ}C \text{ min}^{-1} \rightarrow 200^{\circ}C(10 \text{ min hold})$



Figure 2.11: Calibration curves for C₂-C₅ NMHCs.

High purity H_2 and zero air, produced by H_2 generator (Parker, model: H2PD-300-220) and zero air generator (Parker, model: HPZA-7000-220), are used as the flame gases in the detector with the flow rates of 30 ml min⁻¹ and 300 ml min⁻¹ respectively. Analytical data are processed by the Hewlett Packard integrator (model HP3395). The gases are identified by injecting pure samples of these gases. A typical chromatogram of NMHCs is shown in the Figure 2.10.

The system was calibrated with the standard reference gas supplied by Intergas, UK. Calibration curves for a few NMHCs are shown in Figure 2.11. The response of the FID detector was found to be linear over the range 100 pptv to 60 ppbv (which accounts for NMHC variability in ambient air of both pristine and urban environments). The reproducibility in NMHCs analyses ranged between 3 to 10% depending upon the compounds, in general lower molecular weight hydrocarbons showed better reproducibility.



Figure 2.12: Variation of C_2 - C_5 NMHCs concentrations due to storage over a period of 55 days.

The stability of hydrocarbons in glass sampling bottles were tested for storage at intervals of 2, 5, 14, 30, 44 and 55 days (Figure 2.12). The variation was of the order of 4-5% w.r.t. the mean during this period for most of the C_2 - C_5 hydrocarbons.

2.3 Measurements of reduced sulfur gases by gas chromatography

Interest in the trace analysis of RSCs in ambient air has grown considerably because of their significant role in atmospheric sulfur cycle which has significant implications to the global atmospheric chemistry, hydrological cycle and climate change. Despite developments of several methods for detecting RSCs viz. spectrophotometry, fluorescence, coulometry, impregnated filter tapes, application of these methods to actual environmental samples suffers from several limitations viz. the lack of detectability, interfering substances, procedural complexity and weak reproducibility. However, the most serious issue is 'sensitivity' (analytically defined as the signal response to analyte amount) due to the low abundance of RSCs (sub ppbv levels) in most environmental samples. The most popular approach for quantitative determination of RSCs in ambient air has been gas chromatography (Wardencki, 1998; Kim, 2005; Pandey and Kim, 2009). However, depending on the RSCs of interest and sampling location, the GC systems must be optimised with respect to sample collection, pre-concentration, separation and detection. Nevertheless, determination of RSCs in ambient air with reliable accuracy is highly challenging due to natural as well as laboratory related factors. As mentioned before, natural factors include low concentrations of RSCs in ambient air, rapid oxidation of sulfur (S) compounds and reactions with any of the large number of chemical compounds present in the air sample. Laboratory related factors include adsorption onto glass and stainless steel linings within the analytical system, unpredictable diffusion related memory effects even on inert materials like Teflon, in-situ transformation etc. A brief description of the instrument development, for RSC measurements at Ahmedabad, with respect to various challenges is outlined below.

2.3.1 GC and column selection

The analysis was done with a fully automated, Varian CP-3800 GC, which facilitates both manual pneumatics as well as full Electronic Flow Control (EFC), and can accommodate up to 3 injectors and 3 non-MS detectors, operating concurrently. Further, Varian injection liners are deactivated using gas phase silanization to reduce sample degradation. Ultra high purity He (99.9999%, Scott speciality gases, Netherlands) was used to carry the analytes from through the column to detector. 'He' has a larger range of flow rates that are comparable to H₂ in efficiency, with the added advantage that helium is non-flammable, and works with a greater number of detectors. In some studies, use of N₂ as carrier gas was not pursued as it was found to be contaminated with COS (*Catalan et al.*, 2006). The interface between the 10 port valve and capillary column was done with a dual split vent injector (Varian CP-1177 with both split and splitless options) which also controls the column flow.

The back-pressure regulated injector serves additional purposes of maintaining a constant flow in the column and transferring a homogeneous mixture of analytes to the column head at a constant temperature (injector is operated at 210°C). Further, a uniform temperature profile across the injector body eliminates cold spots (which could result in mass discriminations). The dual vent design of the CP-1177 facilitates rapid sample transfer (reduces residence time) necessary for reproducible split performance. The injector, designed to accommodate large injection volumes, is operated in split mode with a 1:1 split ratio to ensure maximum analyte flowing into the column. The split ratio is the sum of column flow and split vent flow divided by the column flow. Since we do not often use syringe delivered samples (except testing pure gases), the septum purge flow is kept to the minimum by adjusting a needle valve suitably. The septum needs to be periodically replaced due to it being always under high temperature.

CP-1177 can be operated at an isothermal temperature between $4-450^{\circ}$ C

while the EFC can operate effectively between 0-100 psig. The analytes are brought into direct connection with column by switching a 10 port valve (Restek coated Vici valve) to inject position (Figure 2.15). At this point, a pressure drop occurs due to the time taken by the EFC regulated carrier gas to build the required pressure into the empty tubing in the 10 port valve and the tubing connecting the valve to the column head. The problem can be countered by operating the back-pressure regulated injector (CP1177) in split mode. In backpressure-regulated systems, the split vent flow rate is changed by adjusting the flow controller. A decrease in the total flow being delivered to the injection port will be compensated by a lower split vent flow rate. The column flow rate is not affected by changes in the total flow being delivered to the injection port, but by the backpressure regulator.

The heart of gas chromatography is the column selection. The first choice has to be made between capillary and packed columns. Capillary columns are more efficient than packed columns because they have more theoretical plates (a measure of column resolving power or efficiency) per meter and can be made longer as they offer less resistance to flow than packed columns. Further, packed columns are more prone to losses due to adsorption and catalytic reactions and rearrangements. While analyte mass is severely restricted for a capillary column, the limitation can be offset by sample pre-concentration. Further, inertness and selectivity (elution of sulfur gases away from hydrocarbon matrix) were important criteria for column selection. PLOT columns possess higher retention, selectivity and exhibit acceptable elution patterns for sulfur compounds. However, they also exhibit unwanted stationary phase surface activity which can affect the sensitivity of the system for active sulfur compounds, producing higher detection limits. Development of fused silica capillary columns has provided more inert surfaces for required for trace sulfur analysis. Due to high vapour pressure of sulfur gases, columns possessing high degree of retention are preferred for their separation. Generally, columns with thicker films provide increased separation of volatile sulfur compounds and are better suited for analysis of low level volatile sulfur compounds (Wardencki, 1998). On such non-polar columns, retention times are governed primarily by boiling points and the retention sequence can be predicted from boiling-point data. However, care must be taken to optimise sample injection amounts so as to not overload the columns. DB1 (100% dimethyl polysicoxane stationary phase), BP1 (60 m, 0.32 mm, 5.0 μ m, SGE) and GS-Gaspro (Silica based plot phase; 30 m, 0.32 mm, 0.25 μ m) columns have often been used in combination with pulsed flame photometric detector (PFPD) to separate and detect RSCs (Trabue et al., 2008; Kim, 2005). Possible quenching of response for low-level sulfur compounds may occur if they elute at the same time as large hydrocarbon peaks. Quenching makes accurate quantitation difficult due to detector response reduction and may also cause difficulties in compound identification. Thus, column selectivity is critical if accurate results are to be obtained. Thick-film CP-Sil 5CB from Chrompack, Varian offered guaranteed elution of "difficult" sulfur compounds at trace levels. Several studies have employed this column for direct online analysis of RSCs (Kim et al., 2007; Catalan et al., 2006; Cheskis et al., 1993). In our case also, the thick film CP-Sil-5CB, WCOT column (Fused silica; Length = 50 m; ID = 0.32 mm; df = 5 μ m) was found to suitably elute various RSCs with acceptable separation and has been used for this study.

2.3.2 Detector for RSCs

Several detectors have been developed for quantitative estimation of RSC concentrations in various sample matrices. Some of the popular detectors include flame photometric detection (FPD), PFPD, sulfur chemiluminescence detection (SCD) and atomic emission detection (AED). The FPD is plagued by nonlinear (exponential) response (to sulfur compounds) and compound-specific response characteristics. The SCD is a good low-level sulfur detector with negligible quenching. However, it suffers from severe drifts. Performance wise, the AED is one of the best sulfur detectors with low ppbv sensitivity, no quenching and equimolar response. However, being expensive due to high costs incurred by a plasma excitation source, it is not suitable for laboratories where multiple element detection is not a necessity. The PFPD is the detector of choice for sulfur analysis due to its simple, self cleaning, low maintenance design, negligible drifts, high selectivity, consumption of conspicuously less detector gases and stability. A comparison of various sulfur detectors can be found in *Firor and Quimby* (2001) whereas details about their working can be found in *Pandey and Kim* (2009) and references therein.



Figure 2.13: Schematic of the Pulsed Flame Photometric Detector (Source: PFPD for CP-3800 Operators Manual, Varian Inc. 2001).

A schematic of the PFPD is shown in Figure 2.13. The detector can be divided into two main chambers: ignition and combustion. The analytes are carried into the combustion chamber by the carrier gas. The air: H_2 mixture enters the PFPD at two points: around the outer wall (called wall flow)

and through the centre of the combustor tube. The wall flow is used to refill the upper ignitor chamber of the detector after each pulse. Meanwhile, the combustion chamber is filled with additional flow of air and H_2 , which mix with column effluent to form a combustible mixture which flows upwards from the bottom side of the detector. For proper operation of the PFPD, the combustor should refill slightly faster than the ignition chamber. Meanwhile, ignition occurs in the light-shielded, ignition chamber by a continuously heated, Cr/Fe/Al alloy ignitor (*Cheskis et al.*, 1993). While the flame propagates down into the combustor, it extinguishes as the flow rate of H_2 and air are insufficient to support a continuous flame. Thus, the flame pulses at about 2-4Hz. The flame (2200°C) results in formation of excited-state sulfur dimers (S_2^*) , which release a characteristic light energy (300 to 500 nm) as they return to the ground state The emitted light is transferred with a light pipe through a broad band filter (25 mm diameter, 2 mm-thick BG-12 for sulfur; 340-460 nm) and detected with a PMT. During each pulse background, chemiluminescent emissions associated with the hydrogen rich flame emit over a period of only 4 ms since combustion of H_2 molecules is very exothermic and thus fast and irreversible. Meanwhile, emissions from $\mathrm{S}_2{}^*$ are delayed and occur between 4 to 16 ms (Figure 2.14). The delayed emission is monitored by a delayed electrometer gate where gate delay and width are optimized for the sulfur emissions. Since the flame background is significantly eliminated, the sulfur signal is optimized.

When using a conventional FPD, the flame is static and sulfur-hydrocarbon selectivity is achieved by using a narrow-band transmission filter that transmits a single band of light at 394 nm; all other emissions are blocked. Since time separation of the emissions adds selectivity in case of PFPD, wide band-pass optical filters can be used, permitting more light to be detected and resulting in increased sensitivity. The differences in specific emission lifetimes, combined with the kinetics of the propagating flame, allow both time and wavelength information to be used to improve the selectivity of the PFPD and to decrease the observed noise. The sensitivity of the PFPD can be 5X to 7X better than the FPD. Quenching is reduced due to the hotter post pulsed flame conditions and through the ability to inject smaller samples due to its improved sensitivity. However, it can accept very limited column flow (1 ml min⁻¹ with a margin of only $\pm 10\%$; *Firor and Quimby*, 2001), thus column choices are very limited. A detectivity of 1 pgS s⁻¹ and a selectivity of 10⁶ S/C (since carbon accounts for principle background emission in air-H₂ flame) are obtained with a PFPD. The dynamic range is 10³ making the PFPD suitable for a relatively wide concentration band while providing equimolar response irrespective of sulfur compound identity. The superior PFPD sensitivity is attributed to the reduction of flame background and chemical noise due to its filtration in time, dark current reduction due to its current gating, higher signal brightness due to lower combustible gas flow rate and smaller combustor volume as well as the use of broad band colour glass filters.

For proper response of PFPD, it must be optimised so as to operate just near, but not in, the tick-tock mode. Tick-tock occurs when combustible mixture ignites in the ignition chamber but does not propagate to combustor chamber as it has not yet filled with combustible gas. The PFPD was optimised to operate just out of tick-tock by gradually increasing the combustible mixture (air-H₂ needle valve counter clockwise), thus increasing baseline noise until it rises sharply (tick-tock) and then falls and becomes steady. A wide bore quartz combustor (3 mm ID) was used to increase S/C selectivity although it reduces the sensitivity slightly (less than a factor of 2) by spreading the S₂* emissions over a larger volume. Further, quenching (mainly due to reaction of CO with S atoms) can be minimised with 3 mm ID combustor by increasing the combustor air (Air 1) flow rate. Sulfur detection is favoured by H₂ rich conditions i.e. increasing the H₂-air ratio.

An option for square root function in the PFPD electrometer converts quadratic response (sulfur emission varies as the square of sulfur concentration) to a linear response (sulfur emission varies as a direct function of sulfur

General Characteristics		Operational parameters	
Detectivity	1 pg S s^{-1}	Column flow	1.2 ml min^{-1}
Selectivity	$10^6 \mathrm{S/C}$	PFPD temp.	220°C
Dynamic Range	10^{3}	Air-1 flow	17.0 ml min^{-1}
Drift	10 x peak noise	H_2 flow	13.0 ml min^{-1}
		Air-2 (Wall) flow	9.0 ml min^{-1}
		Operating range	9.0
		Gate delay	6 ms
		Gate width	20 ms
		Trigger level	220 mV
		Gain factor	2
		PMT voltage	550 V

Table 2.1: Operational parameters and characteristics of the PFPD used in thisstudy (Source: PFPD for CP-3800 Operators Manual, Varian Inc. 2001).

concentration). The PFPD was operated at 220°C since sulfur response decreases at very high detector temperatures. Operating the PFPD at range 9 was found to be a good compromise between noise and sensitivity. The PMT was operated at 550 V, trigger level was set at 200 mV, gate delay was 6 ms and gate width was kept at 20 ms. The trigger level serves to initiate the signal processing upon ignition of the flame so that gate window for sulfur signal is monitored consistently despite changes in pulse frequency of the flame. The electrometer gate delay and width help to minimise background noise e.g. for a pulse of 2.5 Hz (duration=400 ms), a 20 ms gate width results in discarding 95% of background noise. It must be noted that above 3 Hz, the standard deviation of peak area is 2%, which is dominated by non-detector effects (*Amirav and Jing*, 1995). The gain factor, which determines the amplification of sulfur signal within the gate width, was kept at 2. The gain factor must be adjusted as a function of the gate width. The gain factor serves to adjust signals to the confines of the integration circuit by attenuating large signals and permitting amplification of smaller signals. The various detector parameters are given in Table 2.1.



Figure 2.14: Selectivity of the sulfur signal in a PFPD. The reoccurring momentary combustion of the flame at ~ 3 Hz, marked by a characteristic 'popping' noise (shown by yellow stars), helps to isolate the sulfur signal from interferences. Source: *Cook* (2006)

2.3.3 Sample collection, removal of water and oxidants

Several methods exist for offline collection of reduced sulfur compounds from ambient air which can then be brought to laboratory for GC analysis. Two main considerations are that loss of RSCs must be avoided during collection and the reliable storage methods be employed to ensure no loss occurs during the time between collection and analysis. While these are general precautions for any analysis, its importance is far more in case of RSCs due to their high reactivity. Tedlar bags (generally made of PVF; polyvinyl fluoride), due to their cost-effectivity and reusability, have been widely used for collection and storage of RSCs with 24 h losses of less than 10% (Mochalski et al., 2009). However, remains of previously stored samples or emissions of previously adsorbed compounds (e.g. on bag walls) may irreversibly modify samples and distort the analysis results and hence, effective bag purging procedure has to be applied between consecutive samplings to maintain the original sample composition. Because of the lower stability, Tedlar bags and electropolished SS canisters are not highly desirable for collecting and storing low-level (sub ppby) S compounds. Another method of sampling involves filling canisters using a robotic autosampler (7500, Entech Instruments Inc.) interfaced with a three stage pre-concentrator (7100, Entech Instruments Inc.) including a cold trap dehydration (-20°C), RSCs trapping by Tenax (-80°C) and cryofocussing (fused silica tube at -150°C) (Trabue et al., 2008). However, the method is expensive. An alternative approach for offline sample collection is drawing air through a PTFE head pump into SS canisters whose interior surfaces are coated with chemical vapor deposited amorphous silicon (e.g. sulfinert cans from Restek) (Khan et al., 2012). However, if GC analysis is done by online method (as the case in the present thesis), it eliminates the need to collect and store samples. In this case, ambient air is directly drawn into the system by using a PTFE gas sampling pump (Model: N726FT29E, KNF Neuberger, with $P_{max} = 1.5$ bar) at an adjustable flow rate. The air is then passed through a Nafion dryer.

The use of Nafion dryer minimises various negative effects that moisture has towards analysis of RSCs. For highly humid samples (e.g. during monsoon), capillary columns can get overloaded with water and result in formation of a layer of an independent, aqueous "stationary phase", obstructing separation of the target analytes. Further, applicability and operation of the cryotrapping is, strongly influenced by the water content of the sample and humid samples rapidly form ice plugs in the trap, leading to a blockage of the whole system. Use of Nafion dryer enables effective use of direct cryotrapping (without use of adsorbents) and eliminates the need of cryofocusing (narrowing the band of analytes introduced onto the head of a chromatographic column). In simple terms, Nafion (copolymer of perfluoro-3,6-dioxa-4-methyl-7octene-sulfonic acid and tetrafluoroethylene) is a Teflon backbone with occasional side chains terminating in sulfonic acid (-SO₃H) groups. The SO₃H groups are immobilized within the bulk fluorocarbon matrix and cannot be removed, but unlike the fluorocarbon matrix, the sulfonic acid groups do participate in chemical reactions (Perma Pure Inc, Tech Note 4). While the fluorocarbon matrix makes Nafion dryer resistant to attack by most chemicals, each SO₃H group can absorb as many as 13 molecules of water, making the dryer a selective, semi-permeable membrane to water vapour. The absorbed moisture from sample air permeates through the Nafion tube wall due to water concentration differential, evaporating into a counter-flowing purge gas stream (dry air), thus effectively freeing the sample air from water vapour but not affecting other analytes of interest.

The Nafion dryer (Model: PD -100T-24MKA) was tested to remove water vapor from about 20000 ppmv to less than 50 ppmv using a Licor 7000 CO_2/H_2O analyzer. Simultaneously, the model provided minimum reactive surface for loss of analytes. The output from the pump was controlled with a needle valve so that the flow rate in the inner tube was 3.1 lpm (measured using a TSI flow meter; Model: 4140D) while dry air flows at a higher rate through the outer tube. Meanwhile, air from a zero air cylinder is passed into a fully automatic heatless dryer (Model: HD) which contains two chambers filled with highly adsorbent desiccant, molecular sieve 4A. One chamber dries the air stream while the other chamber regenerates. The generated dry air is sent to the outer tube of the Nafion dryer at 15 psi using a pressure regulator (Janatics, India; Model: R13614).

A major difficulty in sampling of RSCs is interference caused by atmospheric oxidants (SO₂, O₃, and NO_x) which need to be scrubbed off the sample air before pre-concentration. Many substances have been developed as scrubbers including PTFE, Tygon, glass fiber filters, chromosorb, anakrom, and glass beads with a coating of Na_2CO_3 or MnO_2 (*Pandey and Kim*, 2009). Thus, in our system, in addition to removing water from the sample air, an option to remove oxidants (e.g. O_3 , SO_2 etc) which may cause transformational losses, is provided by passing air through sulfinert tubing packed with cotton wool (*Persson and Leck*, 1994). The cotton wadding oxidant scrubber does not affect COS, H_2S , CS_2 and DMS concentrations (*Hofmann et al.*, 1992); however, it is suitable only in case of continuous operation.

2.3.4 Sample transfer

In a GC analysis, often the first step in the analysis sequence viz. sample preparation and/or analyte enrichment step is the limiting step and the largest source of analytical errors. The major problem in analysis of RSCs is minimizing the losses (physical and chemical) between the point where sample enters the injection system to the point that the analytes reach the detector. It is well known that S compounds have absorptive, adsorptive, photo-oxidative and metal catalytic oxidative features which lead to irreversible adsorption, reaction with each other, catalytic reactions and rearrangements etc (Wardencki, 1998). Studies have shown that wall losses are high for SS as well as glass surfaces (*Kuster and Goldan*, 1987). Among several Teflon materials, FEP Teflon was found to exhibit least wall losses (*Kuster and Goldan*, 1987). Thus, we designed an injection system using mostly FEP and PTFE Teffon tubing and nuts. However, severe peak tailing was observed with this system which could be due to desorption related problems. Apart from memory effects, Teflon also suffers from O_2 permeability. Thus, the Teflon injection system had to be abandoned. Different tubing materials (SS, silicone, PTFE Teflon, Tygon etc) are found to have unique loss patterns for different RSCs (*Kim et al.*, 2006). A very popular method for analyzing reactive sulfur gases is by passivating the inner walls of SS linings and tubing, making them less prone to attack of sulfur gases.

Since sample integrity for RSCs is compromised when air samples flow through sampling or analytical apparatus materials which have not been passivated, we re-designed the entire injection system using sulfinert materials (tubing, valves, nuts, unions, tees and canisters) from Restek, Bellefonte, PA, USA. Sulfinert fittings are found to significantly enhance the stability of very low levels of sulfur compounds under dry or humid storage conditions (Khan et al., 2012). The sulfinert coatings are performed by a chemical vapor deposition (CVD) process at elevated temperatures to deposit amorphous silicon. The inner surface of this material are then functionalized via hydrosilylation (to react with remaining SiH moieties) to create a highly inert surface on the stainless steel substrate (Khan et al., 2012). Further, special care was taken to use tubes of lower diameter (1/8 and 1/16 inch) wherever possible, as well as minimise the length, so as to keep the dead volume to a minimum. During design of the injection system, it was also necessary to avoid sharp bends to minimize the losses of RSCs due to storage in those regions. A schematic of the injection system is shown in Figure 2.15.

A rotary, vacuum pump (from Alcatel, France) was used to flush the lines before and after every analysis and whenever required. A Siltek miniature canister (400 ml) was fitted to a calibrated pressure transducer (Setra; Model: 205-2) and used as the sample bulb that acts as the end point of sample collection. The pressure sensor facilitates volumetric calculations viz. amount of sample/standard/calibration gases injected by using the pressure difference before and after cryogenic trapping. The pressure sensor also facilitates periodic leak testing of the injection system.

2.3.5 Cryogenic trapping and desorption

As mentioned above, due to very low abundances of sulfur gases in ambient air, they must be sufficiently pre-concentrated to send sufficient molecules of



Figure 2.15: Schematic of the sample collection and injection system for RSC measurements at PRL.

analytes to the detector so as to be measured with reliable accuracy. Several methods of pre-concentration exist in literature. Several decades ago, SO₂ and H₂S were trapped using molecular sieve 5A and 80% was recovered by desorbing at 250°C for GC analysis (*Black et al.*, 1978). Similarly, adsorption tubes made of pyrex glass packed with Tenax GR (0.13g, 60/80 mesh) were used to trap CS₂, DMS and DMDS and desorbed at 300°C for subsequent GC analysis with a Gas Pro column and sulfur chemiluminescence (SCD) detector (*Sye and Chen*, 2000). The adsorbent was a Tenax matrix (poly-2,6-diphenyl-p-phenylene oxide) filled with 23% graphitized carbon. Several other methods have been adopted for sample enrichment including (1) sorption on metal surfaces viz. gold, palladium, and platinum, (2) sorption on solid adsorbents such as activated charcoal, silica gel, aluminum oxide, graphitized carbon black, molecular sieves, polydimethylsiloxane and porous polymers, and (3) cryogenic trapping (Pandey and Kim, 2009 and references therein). A recent popular set-up for sample enrichment and cryofocussing is commercially available (UNITY)

model, Markes International Ltd., U.K.). The thermal desorption (TD) system of this model consists of a cold trap (a mixture of silica gel and Carbotrap B) allowing cryofocusing of the S gases via electronic cooling to -15° C by a Peltier cooler (*Kim*, 2005). However, none of these methods are completely free from positive blanks (memory effects) and sorptive loss (*Pandey and Kim*, 2009).



Figure 2.16: Schematic of the sample loading and injection.

Further, we observed that the peak shape also gets distorted by trapping with absorbent e.g. molecular sieve filled sample loop immersed in liquid N₂ and desorbing using hot iron beads preheated at 350°C resulted in severely tailed peaks. After a series of trials with different loops (lengths, diameters and materials) and adsorbents, we found that the best results are obtained using a highly coiled, sulfinert sample loop (1/16 inch OD, 1 ml, Restek coated) immersed in liquid nitrogen. Loop size has been found to be inversely proportional to sensitivity (though non-linearly; *Kim*, 2006). Thus, use of 0.25 and 0.50 ml loops will result in better overall chromatography and peak shape for most applications where maximum sensitivities are not required. Further, we did not find significant difference when desorption of trapped analytes in the sulfinert loop was done using boiling water (100°C) and higher temperatures (using heated silicone oil; 350 cSt i.e. centistokes). Thus, it was more convenient to use hot water to desorb the cryogenically trapped analytes. The desorbed analytes are then transferred into a capillary column for subsequent chromatographic separation (Figure 2.15).

2.3.6 Peak separation, detection and calibration

The efficient column oven design of CP-3800 provides fast heat-up (100°C min⁻¹) and rapid cool-down (400°C to 50°C in 4.5 min) times. Several temperature ramping combinations were tested for separation of RSCs. While COS and CS₂ get separated even at an initial starting temperature of 35°C, the initial temperature has to be decreased further to separate H₂S, SO₂, COS, CS₂ and DMS (in calibration mixtures) on the CP-Sil-5CB. It was found that SO₂ and COS (in calibration mixture) can be reliably separated (by about a minute) when the initial starting temperature is less than -30°C. After testing for several combinations, the final column program is as follows:

 $-40^{\circ}C(2 \text{ min hold}) \rightarrow 5^{\circ}C \text{ min}^{-1} \rightarrow -15^{\circ}C \rightarrow 20^{\circ}C \text{ min}^{-1} \rightarrow$

 $200^{\circ}C(10 \text{ min hold})$

The total run time is about 25 minutes. Sub-zero starting temperatures prevent chromatographic movement of H₂S (BP=-60°C) and COS (BP=-50°C) during sample transfer time. In general, flow decreases with increasing temperature (and vice-versa), hence, care must be taken to ensure that the flow remains constant during the temperature ramping. If the GC is operated in constant pressure mode, the flow will vary during the analysis and result in a fluctuating baseline. The problem can be solved by using a pressure programming resulting in a constant flow of He at 1.2 ml min⁻¹. The pressure program is as follows:

5.9psi
(2 min hold) \rightarrow 0.19psi min^{-1} \rightarrow 6.9psi
 \rightarrow 0.81psi min^{-1} \rightarrow

15.6psi(10 min hold)

The column does not exhibit any bleed (background signal generated by the column stationary phase) in this temperature range. Using this temperature program, H_2S elutes after 9.8 minutes, COS after 11.9 minutes, CH_3SH after



14.6 minutes, DMS after 16.5 minutes, CS_2 after 17 minutes and another peak after 21.9 minutes (probably DMDS; unidentified) of injection.

Figure 2.17: Chromatograms for different sulfur gases obtained in ambient air over Ahmedabad: H_2S (9.8 minutes), COS (11.9 minutes), CS₂ (17 minutes) and an unidentified peak around 21.9 minutes. Column: CP-Sil-5CB; Detector: PFPD.

A typical chromatogram for RSCs in ambient air of Ahmedabad is shown in Figure 2.17. The sample tube is filled to about 2500 mb allowing approximately 1250 ml (STP) sample air for chromatographic analysis. The peaks have been identified with both pure gases as well as calibration mixtures using National Physical Laboratory (UK) traceable calibration mixtures from Intergas, UK. In general, COS and CS₂ are almost always obtained in ambient air. The system can detect less than 100 pptv of COS. These gases (COS and CS₂) are relatively less reactive and less water soluble, so it is more easy to quantify these gases compared to highly soluble and reactive gases like SO₂, H₂S or CH₃SH. Recoveries (efficiency) have been found to be the lowest for H₂S and CH₃SH indicating that there should be a minimum threshold value below which they cannot be detected. Despite this, we find the system to be able to detect H_2S and sometimes even DMS and CH_3SH in ambient air. Another peak is sometimes observed at 21.9 minutes, which is suspected to be dimethyl disulfide, but has not been identified due to lack of calibration gas.



Figure 2.18: Sample pressure vs. peak area for COS.

The linearity of COS w.r.t. sample amount (filled pressure) is shown in Figure 2.18. A nitrogen blank is analyzed before samples to have a feel of the baseline noise and presence of memory effects from previous analysis. Lack of sample carry-over is verified by a featureless baseline. Additional nitrogen blanks are analyzed to meet this requirement. Reproducibility for calibration gases was found to be within 10% of the average value. Calibration curves for COS and CS₂ are shown in Figure 2.19.

Future improvement in the GC may include incorporation of a backflushing system to remove chemical background (and thus matrix noise) and an electrical cryotrapping/thermal desorption system to make faster injections.



Figure 2.19: Calibration curves for left: COS and right: CS_2 with the PRL setup.

2.4 Measurements of trace gases using wet chemical methods

The Central Pollution Control Board (CPCB) has been monitoring ambient air quality across stations spanning the entire Indian region with the help of the State Pollution Control Boards and other agencies under the National Air Quality Monitoring Programme (NAMP). Under NAMP, four air pollutants viz. SO₂, oxides of nitrogen as NO₂, suspended particulate matter (SPM) and respirable suspended particulate matter (RSPM) have been identified for regular monitoring. The monitoring of pollutants is carried out for 24 hours (4-hourly sampling for gaseous pollutants) to have around one hundred observations in a year from each site. The data are available online at http://cpcbedb.nic.in/. The CPCB norms for annual SO₂ (NO₂) levels over India are pegged at 50 (40) μ g m⁻³ for industrial and residential areas and 20 (30) μ g m⁻³ for sensitive areas (*CPCB*, 2011). The 24 hour National Ambient Air Quality (NAAQ) standard for both these gases is 80 μ g m⁻³. The NAAQ refers to the levels of air quality necessary, with an adequate margin of safety, to protect public health, vegetation and other property.

 SO_2 is measured using the 'Improved West and Gaeke' method (*Mallik and Lal*, 2013; *CPCB*, 2011). In this method, SO_2 from ambient air is absorbed in

an aqueous solution of potassium tetrachloromercurate. The SO₂ reacts with the mercuric salt to form a dichlorosulphitomercurate complex, which resists oxidation. Once formed, this complex is stable to strong oxidants such as O₃ and oxides of nitrogen and therefore, the absorber solution can be stored for some time prior to analysis. The complex is made to react with acid bleached para-rosaniline and formaldehyde to form an intensely colored pararosaniline methylsulphonic acid. The absorbance of the solution is determined photomertically. This method is sensitive to low ppbv levels. The minimum detection limit is 4 μ g m⁻³. Relative standard deviation for this analytical procedure at the 95% level is 4.6% using standard samples.

NO₂ is measured by 'Jacob and Hochheiser modified' method (*Harrison* and Perry, 1986; CPCB, 2011). Ambient NO₂ is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion produced during sampling is determined colorimetrically by the reaction of the nitrite ion with phosphoric acid, sulfanilamide and N-(1naphthyl)-ethylenediamine-dihydrochloride and measuring the absorbance of the intensely colored azo-dye at 540 nm. The nominal range of the method is 9 to 750 μ g-NO₂ m⁻³ (5 to 400 ppbv). Further details are given in (*Harrison* and Perry, 1986).

2.5 Gravimetric and volumetric units

The volume of a pure pollutant in a given volume of air, held at its original temperature and pressure, is equivalent to the volumetric mixing (ppbv, pptv etc). Gravimetric units specify the mass of material per unit volume of air (μ g m⁻³) and can be used for both particles and gases. Volumetric and gravimetric units related by Equation E7 and are inter-convertible based on the fact that 1 mole (6.023 x 10²³ molecules) of a pure gas weighs 'X' g, where 'X' is the relative molar mass, and occupies a volume of 0.0224 m³ at STP (0°C, 1

atmosphere).

$$\mu \text{gm}^{-3} = (\text{ppb})^* (12.187)^* (\text{M}) / (273.15 + \text{T}^{\circ}\text{C})$$
 (2.7)

where M is the molecular weight. e.g. SO_2 has M = 64 g, so that pure SO_2 has a density (= mass/volume) of 64 /0.0224 = 2860 g m⁻³ at STP. However, expressing in volumetric unit, pure SO_2 is 109 ppbv. Therefore, 109 ppbv 2860 g m⁻³ at 0°C, implies 1 ppbv 2860 x 10-9 g m⁻³ = 2.86 μ g m⁻³. Conversion between volumetric and gravimetric units for different gases is shown in Table 2.2.

Gas	Moleculat Wt.	ppbv	$\mu {f g} {\ {f m}}^{-3}$
O_3	48	1	2.00
CO	28	1	1.15
NO_2	46	1	1.88
NO	30	1	1.25
SO_2	64	1	2.62

Table 2.2: Conversion between gravimetric and volumetric units at 25° C.

The volumetric concentration is invariant with temperature and pressure and therefore applicable during transport of a gaseous plume. However, if concentration is being determined by extracting the gas onto a treated filter for subsequent chemical analysis, it is better to use a gravimetric concentration.

2.6 Satellite based measurements of atmospheric constituents

Space based measurements of atmospheric composition has improved our understanding of three dimensional distributions of trace gases in the atmosphere. While the measurements alone have provided new insights into the
spatio-temporal distribution and transport of anthropogenic constituents, a combination of space and ground based measurements offers immense scope of probing the transport and transformation processes further. The Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS) instruments on board the Aura spacecraft have been providing global measurements of total and stratospheric column ozone (TCO and SCO) since the launch of NASA's Earth Observing System (EOS) Aura satellite on 15 July 2004, enabling near global measurements on almost a day to day basis.

OMI is a wide angle, non-scanning, nadir viewing near UV/Visible Charge Coupled Devise (CCD) spectrometer orbiting at 705 km in a sun-synchronous polar orbit with 1345 local equator crossing time. It detects backscattered solar irradiance in a swath of 2600 km with a telescope Field of View (FOV) of 115° in across-track dimension, covering visible (350–500 nm) and UV wavelength channels (UV-1: 270–314 nm; UV-2: 306–380 nm) with a spectral resolution of 0.42 to 0.63 nm to measure column O_3 , SO_2 , NO_2 , HCHO, cloud-top pressure, aerosol parameters like aerosol optical depth (AOD) with near global coverage over the Earth (*Levelt et al.*, 2006) with a nadir spatial resolution of 13 km by 24 km. Measurements of total ozone from OMI and National Oceanic and Atmospheric Administration (NOAA) satellites are within 1% of each other for latitudes 60°S to 60°N (*Ziemke et al.*, 2006). OMI retrievals of various atmospheric constituents are available on a 0.125°x0.125° grid with global daily coverage.

The improved sensitivity of OMI permits daily global measurements of passive volcanic emissions of SO_2 and of strong anthropogenic SO_2 pollution (*Krotkov et al.*, 2006). The column integrated SO_2 is expressed in Dobson Units (DU). If all of the SO_2 in a column of the atmosphere is compressed into a flat layer at standard temperature and pressure, one DU would be 0.01 millimeters thick and would contain 0.0285 grams of SO_2 per square meter. SO_2 retrievals are accurate to within 10% for OMI (*Karagulian et al.*, 2010). Because of improved algorithms and sensitivity in OMI, it can also detect lower atmospheric NO₂ pollution (*Boersma et al.*, 2004). The total column and tropospheric column NO₂ is measured in the spectral range of 405-465 nm with an estimated accuracy of 5% ($\sim 0.2 \times 10^{15}$ molec cm⁻²) in unpolluted cases and 20% ($\sim 0.8 \times 10^{15}$ molec cm⁻²) in polluted cases, for a vertical column NO₂ under clear sky conditions. The vertical column error can be further larger (about 50%) in the presence of pollution and cloud.

OMI/MLS tropospheric O₃ data (1° latitude x 1.25° longitude) are determined by subtracting MLS stratospheric column O₃ from OMI total column O₃ (Ziemke et al., 2006). The uncertainty in local TCO measurements from transient clouds using the 0.3 reflectivity criterion is around 2 DU. In this study, tropospheric columnar O₃ from OMI/MLS has been obtained from NASA archives (http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/new_ data.html). Further, OMI daily global data products (level 2G, version 3) for SO₂ (middle troposphere; OMSO₂G.003), NO₂ (OMNO₂G.003), HCHO (OMHCHOG.003), aerosol optical depths (OMAERUVG.003), UV aerosol indices and radiative cloud fraction (OMTO₃G.003) are processed and analyzed for this study. The OMI data is archived in various formats and the Giovanni interface (http://daac.gsfc.nasa.gov/giovanni/) provides one of the easiest ways to access the data.

'Measurements Of Pollution In The Troposphere' (MOPITT; Drummond et al., 2010) has been providing global measurements of CO profiles since March 2000 from NASA's Terra satellite using gas correlation radiometry. This satellite is in a polar, sun synchronous orbit (705 km altitude) with a 16 days repeat cycle and a 1030 (LT) cross over time at the equator. The instrument field of view is 22 x 22 km² with across track swath of 640 km which provides global coverage in every 3 days. The instrument senses upwelling terrestrial infrared radiation (4.7 μ m) and reflected solar radiation (2.2-2.4 μ m) by gas correlation spectroscopy to get the atmospheric profiles of CO and CO total column and CH₄ 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. For the present analysis, we have used 1°x1° monthly gridded CO data (L3, version 4) available at ftp: //l4ftl01.larc.nasa.gov/MOPITT/MOP03M.004. The data have been used widely to study the global distribution of CO and various transport phenomena in the troposphere (*Kar et al.*, 2010).

Chapter 3

Variability of trace gases over an urban site in western India

India is known to be a pre-dominantly agricultural country. However, about 32% of Indian population lives in urban areas. Although the largest population densities in India are found along the Indo-Gangetic plain and eastern coastal regions, the western part of India (Gujarat and Maharashtra) is more industrialized (ASI, 2009). Rapid industrialization has repercussions in a surging need in power, steel and other industrial products requiring burning of more and more fossil fuel like coal and petroleum, which in turn, emit primary pollutants like CO_2 , NO_x and SO_2 into the atmosphere. A part of Western India, known as the Golden corridor, contains the maximum number of large point sources (LPS) in India, mainly from power sector and sulphuric acid manufacturing. At the national level, LPS are responsible for more than 65% emissions of CO_2 as well as SO_2 (*Garg et al.*, 2002). They also contribute significantly to nitrogen oxides emissions. The average SO_2 concentrations in different regions of Gujarat state of India are shown in (Figure 3.1). It is observed that higher sources of SO_2 (> 9 ppbv) are located in the Vapi Ankleshwar belt. This region has numerous small to big industries, dominated by chemical industry plants. CPCB measurements also show high values of SO_2 in and around



Ahmedabad (a major urban region in western India).

Figure 3.1: SO_2 measurements for 2009-2010 at various places in Gujarat based on data from Gujarat Pollution Control Board. The sizes of the circles are proportional to the SO_2 concentrations and the colors represent different concentration range.

The present chapter deals with measurements of trace gases with emphasis on sulfur gases over Ahmedabad to understand the atmospheric processes contributing to their variability and the dominant emission sources impacting atmospheric composition over this rapidly growing city. Although surface measurements of O_3 over Ahmedabad date back to 1950s (*Naja and Lal*, 1996) and precursor measurements date back to 1990s (*Lal et al.*, 2000), the measurements made during the current study are aimed at investigating the trace gas variability over this region over a short time scale (May-October) with rapid changes in meteorology as well as air masses. Another aspect of these measurements was to study source signatures based on simultaneous measurements of O_3 , its precursors (CO and NO_x) along with SO₂. Further, for the first time over an Indian site *viz*. Ahmedabad, RSCs have been measured to understand the seasonal variability of these gases.

3.1 Site description and meteorology

The observational site is located in the main campus of PRL, Ahmedabad (23.03°N, 72.58°E, 49 m amsl) in the Gujarat state of India. It is situated in the western region of the Ahmedabad city (Figure 3.2). Ahmedabad is the fifth largest city of India with a population of 6.3 million, located in the western part of the country. The region has a large number of cement plants. Industry is the second largest source of SO_2 in India contributing 36% of national emissions (Garg et al., 2001). Further, a quarter of these industrial SO_2 emissions come from steel sector, 14% from fertilizer plants, 10% from cement manufacturing and 7% from refineries. The state of Gujarat has more than 13 million registered motor vehicles which accounts for 9% of the country total. Ahmedabad alone has more than 2 million registered motor vehicles which has been growing at about 10% per annum. The western part of Ahmedabad is developed as a residential area and the eastern part as an industrial area. The city has two power plants: the Sabarmati Thermal Power station (411 MW) and a Combined Cycle Dual Fuel Power Plant at Vatva (100 MW). The Sabarmati power plant is about 10 km in the north-east of the study location (Figure 3.2). Major industrial clusters of Ahmedabad are located in the east of the city and include textiles, dye, casting and forging, power driven pumps etc. In terms of SO_2 and NO_x emissions, this region is among the top 10 emitting districts in India (Garg et al., 2001).

Ahmedabad has a hot, semi-arid climate. Over the western region of India, the mean synoptic surface winds are calm and northnorth-easterly during winter (Figure 1.3). During the pre-monsoon season, the winds originate and travel from the west of Indian subcontinent. During the summer monsoon, the winds are stronger and moist and come from the marine and western regions surrounding India. The wind patterns start shifting in direction during



Figure 3.2: Left panel: The Ahmedabad city map showing industrial areas (dotted circles) to the east of the measurement site. Right panel: Map of India showing major cities and industry.

post-monsoon from southwest to northeast. The rainfall is restricted to the southwest monsoon when the city receives about 750 mm rainfall with maximum in July (average: 247 mm) and August (average: 288 mm). Among the pre-monsoon months (March-May), the climatologically hottest daytime temperature occurs during May (mean: 41.5°C). During May 2011, the maximum temperature recorded was above 43°C. Further, Ahmedabad receives maximum sunshine hours during May (>300 hours). While average RH during May and June, 2011 was below 50%, it increased to above 85% during July and August. The wind speed and direction during the study period is shown in (Figure 3.3). During pre-monsoon, surface level air masses arise mainly from Western India and the Arabian Sea. During monsoon, these air masses spend almost the entire time in the Arabian Sea before reaching the measurement locations. During post-monsoon, winds at lower altitudes mostly originate and/or pass through the northwest part of India. Further, during post-monsoon, maximum

contribution to surface concentration of trace gases is expected to come from lower altitudes (<1000 m) due to lower boundary layer height which traps the pollutants near the surface. On the other hand, during pre-monsoon and monsoon when the boundary layer height increases, air masses from higher heights may also contribute to the observed trace gas levels.



Figure 3.3: Wind rose plot for Ahmedabad for the period May-October, 2011 using hourly data from an automatic weather station near the study site.

3.2 Temporal variation of trace gases over Ahmedabad

3.2.1 Diurnal variation

Hourly average concentration data of O_3 , CO, NO_x and SO_2 during the study period are shown in (Figure 3.3) using box-and-whisker plots, where boxes represent the inter-quartile range while the lines extending vertically from the boxes (whiskers) indicate the variability outside the upper and lower quartiles. The time is given in Indian Standard Time (IST). The top panel in (Figure 3.4) shows that the diurnal variations of O_3 over Ahmedabad are characterized by a distinct noon-time peak. The peak is attributed to photochemical formation and is a characteristic of urban regions. Immediately after sunrise, O_3 concentrations start to build up due to the photo-oxidation of the precursor gases such as CO, CH₄ and NMHCs in presence of sufficient amount of NO_x. Being an urban site, NO levels over Ahmedabad are always above the threshold level (about 0.01 ppbv) for O_3 production. A typical representation for O_3 formation in the atmosphere by photo-oxidation of CO and hydrocarbons is given by reaction R6 (Chapter 1). During this process NO_x acts as a catalyst until it is permanently removed by various physical processes (e.g. surface deposition) or transformed to other NO_y compounds (NO_x + PAN + HNO₃ + NO₃ + N₂O₅ +).

Apart from photochemistry, dynamical and meteorological parameters also influence O_3 diurnal variations. Lower O_3 during night-time is attributed to absence of photochemical production, titration of O_3 by surface emissions of NO in a suppressed boundary layer and loss due to surface deposition. The diurnal amplitude in O_3 is highest for October and lowest for August (Table 3.1). Suppressed diurnal variation during August is a result of lower sunshine hours implicated by cloudy conditions. The sharp increase in diurnal amplitude in O_3 during October is attributed to changing wind pattern, resulting in higher levels of precursors over the study location. Similar increase in diurnal amplitude between August to October by more than 4 times was also observed over Ahmedabad during 1991-95 (Lal et al., 2000). Further, the maximum increase rate of O_3 between initiation phase of photochemistry (0500-0800 IST) and peak photochemical formation period (1200-1600 IST) is highest for October (Table 3.1). These rates are higher compared to the observations during 1991-95, when the increase rates observed over Ahmedabad were 1.25, 1.07, 0.77, 0.64, 1.14 and 2.76 ppbv hr⁻¹ for May, June, July, August, September



and October respectively.

Figure 3.4: Diurnal variations of surface O_3 , CO, NO_x and SO_2 over Ahmedabad during pre-monsoon, monsoon and post-monsoon of 2011. The boxes represent the inter-quartile range.

The diurnal variations of CO and NO_x during the study period are also shown in (Figure 3.4). The diurnal variation of CO and NO_x show a bimodal feature with peaks during morning and evening hours. Among these, the evening peak is always higher than the morning peak (Table 3.1). Higher evening peak could be attributed to the absence of photochemical consumption of NO_x and less dilution of vehicular emissions during evening rush hour accentuated by a lower boundary layer. Further, evening traffic could be higher

compared to morning traffic because the morning traffic is more dispersed in time. Lower values of CO and NO_x during afternoon are a result of lower emissions, higher boundary layer height (resulting in dilution) and loss due to OH chemistry. Further, in order to account for higher levels of O_3 during noon period, large amounts of precursors (like CO, NO_x , etc.) need to be consumed. Among the NO_x species, NO is mainly lost by titration with O_3 while NO_2 is mainly lost by photo-dissociation. The CO levels seem to be mainly controlled by various anthropogenic emissions, oxidations and loss due to OH. However, contribution of HCHO (which has direct emission sources over urban area along with secondary formation from VOCs) to chemical production of CO needs to be investigated. Unlike sharp peaks in case of CO and NO_x , SO_2 shows two humps during morning and evening, corresponding to traffic hours, which however, are not statistically significant. This is because the major contribution to SO_2 levels is from coal burning (in power plants and industries, which occurs throughout the day) rather than vehicular traffic. Further, there has been reduction in sulfur emissions from vehicles as a result of several regulations. The large diurnal amplitude in SO_2 during October is related to change in air masses.

3.2.2 Seasonal variation

The monthly variation of measured trace gases for the May-October period are shown in (Figure 3.5). Concentrations of O_3 gradually decrease from May $(22.1\pm9.4 \text{ ppbv})$ to August $(12.3\pm3.6 \text{ ppbv})$ and then build-up in September $(22.1\pm9.3 \text{ ppbv})$ and October $(35.0\pm20.3 \text{ ppbv})$, when precursor levels (CO and NO_x) also build-up. The build-up in precursor levels is due to change in wind direction. The sudden increase in precursor levels during September-October over Ahmedabad has also been observed during earlier studies (*Lal et al.*, 2000). Lower values of O_3 during monsoon allude to lower photochemical activity and lower levels of precursors. The average rainfall over Ahmedabad

Table 3.1: Diurnal amplitudes of O_3 , CO, NO_x and SO_2 (ppbv) during May-October, 2011. O_3 increase rate (ppbv hr⁻¹) between the night (0000-0300 IST) and day (1300-1600 IST). Difference between morning NO_x (0700-0800 IST) and afternoon NO_x (1400-1500 IST) as well as difference between evening NO_x (1900-2100 IST) and afternoon NO_x (1400-1500 IST) are also presented.

	May	Jun	Jul	Aug	Sep	Oct
O_3 inc.rate(ppbv hr ⁻¹)	1.6	1.2	1.1	0.6	1.5	3.5
O_3 amplitude	26.5	20.9	21.5	13.0	25.9	59.1
NO_x (morn. – afternoon)	4.7	2.6	2.9	3.9	6.1	18.3
NO_x (even. – afternoon)	12.9	2.8	6.4	10.0	26.4	56.5
NO_x amplitude	19.0	6.2	11.7	15.8	31.2	73.0
CO amplitude	260.9	206.0	260.6	406.0	594.0	1275.0
SO ₂ amplitude	0.8	0.5	0.3	0.9	0.5	5.6

in 2011 was 3.1, 254.2, 295.0 and 62.9 mm during June, July, August and September respectively. Thus, lowest value of O_3 during August coincides with maximum rainfall, indicating more cloudy conditions. The plot of RH with O_3 shows a strong anti-correlation (Figure 3.6). The monthly mean (sigma) of O_3 values obtained by (*Sahu and Lal*, 2006a) during 2002 over Ahmedabad are 15.9 (4), 13.2 (2), 16.8 (5), 19.0 (7), 17.9 (3) and 26 (15) ppbv for May, June, July, August, September and October respectively.

The CO levels decrease from May (248.2±47.9 ppbv) to July (224.5±46.0 ppbv) and show an enhancement from August (235.8±75.4 ppbv) to October (672.0±306.6 ppbv). The mean (sigma) CO values obtained by Sahu and Lal (2006a) during 2002 over Ahmedabad are 225 (24), 158 (21), 169 (23), 171 (19), 238 (26) and 303 (24) ppbv for May, June, July, August, September and October respectively. Considering the sigma both for this study and for Sahu and Lal (2006a), it is clear that CO values are lowest during peak monsoon months (July-August). The major contributors to NO_x are the transport and



Figure 3.5: Monthly variation of surface O_3 , CO, NO_x and SO_2 at Ahmedabad during May-October, 2011. The boxes represent the inter-quartile range. The first panel also shows monthly rainfall over Ahmedabad.

power sector, and the study location has predominant influences from both. During 2011, mean (sigma) of NO_x levels over Ahmedabad were 7.2 (3.6), 5.2 (1.0), 7.3 (1.9), 8.2 (2.9), 9.7 (7.8) and 26.0 (17.9) ppbv for May, June, July, August, September and October respectively. The seasonal variation in NO_x is very similar to the seasonal variation in CO.

The monthly average SO₂ levels are 0.85 (0.33), 0.37 (0.05), 0.46 (0.04), 0.73 (0.11), 0.98 (0.09) and 3.55 (0.52) ppbv for May, June, July, August, September and October respectively. The SO₂ values during May 2011 compare well with the reported value of 0.95 ± 0.88 ppbv over Ahmedabad during 2010 (*Mallik et al.*, 2012). Although all the trace gases measured during this study show enhancement during October over September, the SO₂ enhancement is by far

the largest (262%). This is because the major contributors to SO₂ are point sources, which are at fixed locations, and hence, the role of wind direction on SO₂ levels becomes very important (discussed in Section 3.2.3). Overall, higher variability in all the trace gases during October is attributed to large diurnal variations while the higher levels is directly/indirectly related to shift in wind regimes. A decrease in O₃ and NO_x concentrations during monsoon (compared to pre-monsoon) and a sudden rise in levels during post-monsoon (compared to monsoon) has also been observed over Hyderabad, another urban region in India (*Swamy et al.*, 2012). The low levels of SO₂ during monsoon are not only a result of dilution by marine air masses but also wet scavenging of SO₂. The washout coefficient of SO₂ due to rain is estimated to be about 2.6105 s⁻¹ times the rate of rainfall (mm hr⁻¹) (*Martin*, 1984). Thus, efficacy in wet removal processes in determining SO₂ concentrations could be significant during monsoon (*Matsuda et al.*, 2006).



Figure 3.6: Correlation of O_3 with RH over Ahmedabad during May-August, 2011. The data have been averaged into 10% RH bins for regression analysis.

3.2.3 Relationships with meteorological parameters

Variations of O_3 and CO with wind speed are shown in Figure 3.7. The primary pollutants (CO as well as NO_x and SO_2) show an inverse relationship with wind speed over Ahmedabad. Such features are characteristic of source regions. It implies that emissions of CO, NO_x and SO_2 are mostly within the city periphery and accumulation of pollutants takes place at lower wind speeds (calm conditions). Higher wind speed results in efficient dispersion of the anthropogenic emissions, causing the pollutants to be ventilated away from the measurement location. However, this explanation does not hold for O_3 , which is a secondary pollutant. In fact, O_3 shows a slight build-up at higher wind speeds. One explanation could be that O_3 values are higher during daytime (result of photochemistry) when wind speeds are also slightly high (impact of temperature). The wind speeds during sunlit hours are almost twice of the other period. Further, as evident from (Figure 3.7), the variation of O_3 with wind speed does not show any seasonal preference. As shown in the next section, destruction of O_3 takes place at very high NO_x levels over Ahmedabad. Thus, higher O_3 at higher wind speed is not a direct relationship but a result of other associated processes.

Figure 3.8 shows the variation of O_3 , CO, NO_x and SO_2 with wind speed as well as direction during the study period. It is observed that most of the data points lie between 135° and 315°. These data points mostly belong to the pre-monsoon and monsoon period (May to early September), when wind direction varies between south westerly to south-easterly (also evident from Figure 3.3). The points lying between 45°-135° mostly represent the late September-October period, when a change in prevailing winds occurs. The wind speeds are lower during this period, allowing accumulation of primary pollutants. The variation in surface O_3 is scattered in all directions because O_3 is a secondary pollutant and in-situ production of O_3 occurs on a local scale over Ahmedabad. While CO and NO_x show higher values in the 45°-



Figure 3.7: Variation of surface O_3 and CO with wind speed over Ahmedabad during May-October, 2011. The data have been averaged into 0.25 m s⁻¹ wind speed bins between 0-2.5 m s⁻¹ for regression analysis.

135° sector i.e. during October; their values are also higher in west, very close along the 45°-135° axis, indicating accumulation during calm (very low wind speed conditions) in this sector. The pattern in SO₂ is very different from the two other primary pollutants viz. CO and NO_x. The high SO₂ values are almost entirely restricted in the 30°-145° sector. It was shown in Figure 3.2 that a major thermal power plant and several industries lie in this sector. Coal burning in these industries and the power plant is likely to be responsible for the high SO₂ values observed at the study location. Further, on a finer scale, SO₂ concentrations are high irrespective of wind speed in the 45°- 90° sector. It seems that these values are mostly influenced by transport of SO₂ from the local thermal power station in the east and to some extent by the industrial cluster in Naroda, which houses several manufacturing units (Figure 3.2).

3.2.4 Correlations between trace gases

CO, NO_x and SO_2 over urban areas are supposed to be mainly impacted by anthropogenic emissions (barring influence of biomass burning for CO in some regions or volcanic emissions for SO_2 in certain areas). In general, CO is pro-



Figure 3.8: Variation of hourly averaged O_3 , CO, NO_x and SO_2 over Ahmedabad with wind direction and speed during May-October, 2011.

duced from the incomplete combustion of FF and BM/BF while NO_x is produced during high-temperature combustion. On the other hand, SO₂ is mainly produced during combustion of coal (which contains sulfur) in power plants and industries. The relationships among various trace gases measured during this study has been investigated in order to understand the processes/sources controlling their levels and variability. For regression analysis, the data was separated into two sets viz. NO_x<10 ppbv and NO_x \geq 10 ppbv, since more than 72% of data points lie below NO_x<10 ppbv. In general, we will focus more on the slopes obtained for NO_x below 10 ppbv, as this explains larger part of the data. However, as observed from (Figure 3.9), the relationship of O₃, CO and SO₂ with NO_x is similar for both the data sets.

Although the amount of O_3 produced for each molecule of NO_x consumed is controlled by a complex nonlinear chemistry (involving VOCs), the O_3 to NO_x linear relationship can be used as rough indicators for the production efficiency of O_3 . Figure 3.9 shows that O_3 concentrations decrease with increasing NO_x values for both the data sets. The negative relationship is governed by two processes, both achieving similar results. During daytime, O_3 increases due to photochemical production while NO_x decreases due to being consumed by photochemical reactions, lower emissions and also due to boundary layer dilution. Further, during evening, O_3 is slowly lost to various physical processes and inhibition of production while NO_x values are higher due to traffic emissions and inhibition of photochemical consumption. For $NO_x < 10$ ppbv, the slope is -1.04 and the intercept is 29.2 ppby. The intercept value is low due to less active photochemistry during monsoon months. Negative $\Delta O_3/\Delta NO_x$ values of -1.0 and -6.4 during monsoon and post-monsoon were obtained for Gadanki (Naja and Lal, 2002). Large negative slopes over Gadanki, a rural site, were attributed to partially processed air masses with lower O₃ production potential. Less negative slopes over Ahmedabad indicate more fresh air masses. A similar study of O_3 -NO_x relationships over Trivandrum (a coastal urban site in Southern India) also showed negative slopes, with values in the range of -2.1 to -6.8 during May-August, 2008 (David et al., 2011). Among these, the slopes were higher for morning data compared to evening data indicating production processes are faster than processes of destruction over Trivandrum. In the present study, daytime O_3 shows a positive association with night-time NO_x (slope: 1.4, $R^2 = 0.56$; Figure not shown). The relationship indicates that 1 molecule of NO_x is responsible for formation of 1.4 molecules of O_3 . The value is quite low compared to other sites in India, China and United States (Trainer et al., 1995; Cheung and Wang, 2001; David et al., 2011.

The covariance of O_3 and CO concentrations offers a valuable constraint for quantifying anthropogenic sources of O_3 (*Chin et al.*, 1994). O₃-CO relationship can be used to investigate O_3 photochemistry over polluted regions



Figure 3.9: Correlation of O_3 and CO with NO_x over Ahmedabad during May-October, 2011.

and study evolution of polluted plumes. Increasing O₃-CO ratios in a plume suggest photochemical formation of O₃. The O₃-CO relationship over East Asia was extensively studied during East Asian Regional Experiment (*Tani*moto et al., 2008). During that study, the $\Delta O_3/\Delta CO$ values at Gosan (Korea) varied between 0.03-0.07 but increased with increasing transport time due to O₃ production. For several sites in China, $\Delta O_3/\Delta CO$ values were found to be less than 0.1 (*Wang et al.*, 2010). The observed $\Delta O_3/\Delta CO$ values varied between 0.15-0.32 for various sites in northern United States during summer (*Chin et al.*, 1994 and references therein). Figure 3.10 (top panel) shows O₃-CO relationships over Ahmedabad using hourly data. It is observed that till about 500 ppbv of CO, the O₃-CO relationship shows a large scatter despite a small positive slope. It indicates that a linear relationship does not explain the variation of O_3 with CO, one of the major causes being high levels of NO_x that controls O_3 chemistry. Positive slopes (0.16 ppbv/ppbv) between O_3 and CO have been previously observed over Ahmedabad, which were however; lower than some non-urban sites (0.24-0.33 ppbv/ppbv; *Lal et al.*, 2008a). An average slope of 0.1 ppbv/ppbv was observed at Mt. Abu (a hill station in western India at an altitude of 1680 m amsl), which is a free tropospheric site where local emissions are minimum (*Naja et al.*, 2003). At very high CO concentrations (500 ppbv), the correlation becomes negative. $\Delta O_3/\Delta CO$ values were found to be negative over Hissar, a semi-urban site in India (*Lal et al.*, 2008b). Negative $\Delta O_3/\Delta CO$ values near source regions generally occur due to large short-term variability in CO emitted by the surface sources. Further, during night-time, O_3 would be gradually lost to deposition and result in a negative association with CO (*Chin et al.*, 1994).

The O₃-CO and O₃-NO_x relationships suggest that not only photochemistry but also mixing of different emissions might be responsible for the observed $\Delta O_3/\Delta CO$ values over Ahmedabad. Positive correlation is observed between daytime O₃ and daytime CO (Figure 3.10; bottom panel), suggesting O₃ production due to sufficient levels of precursors. No correlation is observed between night-time O₃ and night-time CO as they are controlled by different processes during this period and absence of photochemical reactions which link O₃ and CO. However, there seems to be an association between day-time O₃ and night-time CO, indicating the role of background CO in O₃ photochemistry. Overall, lower slope and relatively lower correlation between O₃ and CO over Ahmedabad indicate incomplete photochemical processes in the ambient air. However, due to two major complications (a. accounting for the chemical sources and sinks of CO and b. accounting for O₃ advection from outside the city), the interpretation of O₃-CO relationships must be supplemented by model studies.

Since CO and NO_x have many anthropogenic sources in common, it is of interest to investigate their relationships. The $\Delta CO/\Delta NO_x$ value in a polluted



Figure 3.10: Relationships between O_3 and CO over Ahmedabad during May-October, 2011. Top panel: Hourly data during the study period. Bottom panel: Daytime (0700-1700 IST) and night-time (1900-0600 IST) segregated data.

air parcel is impacted by (a) the ratio of the emissions of CO and $NO_{x(y)}$ (b) the levels of CO and $NO_{x(y)}$ in the background air (valid more in cases where regional transport plays substantial role) and (c) the photochemical transformation of the air parcel, which removes a different fraction of each pollutant in the time between emission and measurement (*Parrish et al.*, 1991). In general, very low slopes imply dominance of NO_x and hence vehicular emissions. On the other hand, very high slopes indicate biomass/biofuel combustions, which emit large amount of CO. High $\Delta CO/\Delta NO_x$ values obtained for Linan were attributed to biofuels (*Wang et al.*, 2002). High $\Delta CO/\Delta NO_x$ values also indicate longer transport time because with aging of an air parcel, NO_x lev-

Table 3.2: Comparison of changes in CO and SO₂ with respect to NO_x (ppbv/ppbv) obtained over Ahmedabad with other studies. s: pre-monsoon, m: monsoon, pm: post-monsoon, w: winter.

Location	Source	CO/NO_x	$\mathbf{SO}_2/\mathbf{NO}_x$	Reference
Ahmedabad	Overall	9.07	0.08	This study
	Mobile		0.026	
	Point		0.41	
Dhaka, Bangladesh	Area	12.2-14.6	0.02-0.6	Sikder
	Sources	(w,pm),	(w, pm),	et al., 2012
		19.5-22.6	0.1(s, m)	
		(s,m)		
North China	Power	0.42	1.39	Zhang
				et al., 2009
	Industry	27.49	0.99	
	Residential	82.48	1.29	
	Transport	16.16	0.02	
Linan, China	Biofuel	36-39	-	Wang
				et al., 2002
	Coal	-	0.83-1.26	
Western US	Point	1.2	1.1	Parrish
	sources			et al., 1991
	Mobile	10.2	0.05	1
	sources			

els will gradually decline due to its shorter lifetime. The $\Delta CO/\Delta NO_x$ value for Ahmedabad is very low (9.1 ppbv/ppbv with an intercept of 199.1 and $R^2 = 0.70$) indicating very fresh emissions from area sources. The slope can be interpreted as the emission ratio, assuming that CO is not produced in significant amount through oxidation of hydrocarbons and that NO_x is not removed from the atmosphere between emission and sampling. The assumption is highly valid because of nearby sources. The intercept may be interpreted as the regional background of CO.

In general, mobile sources, characterized by diesel and gasoline consumption, are rich in CO and NO_x, while point sources, mainly characterized by coal consumption, are rich in SO₂ and NO_x. Thus, mobile sources are characterized by high CO/NO_x but low SO₂/NO_x while point sources in general, exhibit higher SO₂/NO_x but lower CO/NO_x. A comparison of Δ CO/ Δ NO_x and Δ SO₂/ Δ NO_x values obtained in this study with other regions of the world is presented in Table 3.2. The emission factors provided by *Streets et al.* (2003) for coal burning in power plants are 8.4-16 g kg⁻¹ SO₂ and 4.6-11.8 g kg⁻¹ NO_x. Thus, for power plants, the SO₂/NO_x ratio can vary between 0.68 -3.49 by weight at the source. To convert into concentration ratio, we need to normalize by molecular weights i.e. (30+46)/64=1.19. This gives a volumetric SO₂/NO_x ratio of 0.81-4.15. Δ SO₂/ Δ NO_x values from INTEX-B campaign (*Zhang et al.*, 2009) for different source types is also shown in Table 3.2 (http://mic.greenresource.cn/intex-b2006).

A $\Delta SO_2/\Delta NO_x$ value of 0.39 was estimated for the University of Houstons Moody Tower supersite when air masses were arriving from a 3800 MW electrical generating unit, the largest of all fossil fuel plants in the U.S, located at 35 km southwest (*Luke et al.*, 2010). In general, the lower value of $\Delta SO_2/\Delta NO_x$ slope obtained for Ahmedabad indicates dominant impact of vehicular emissions. Further, during this study, SO₂ shows weak correlations with both CO and NO_x, suggesting that sources of SO₂ over Ahmedabad are different from sources of CO and NO_x. It is also possible that these sources have variable emission ratios of SO₂ relative to NO_x and CO. To segregate the effect of point and mobile sources in $\Delta SO_2/\Delta NO_x$ values, we segregated the hourly averaged data w.r.t. wind direction and time. To estimate impact of mobile sources, we take all the data during 1800-2100 IST when effect of mobile sources is dominant. The average NO_x and SO_2 concentrations for this dataset are 21 and 1.2 ppbv respectively. For estimating point sources, we take all data in the 0-90° sector (Figure 3.8). Further, from this subset, we select data with SO_2 concentrations greater than 1.2 ppbv to remove the impact of vehicles. This final dataset is used as an indicator of point sources. The slopes obtained for mobile and point sources from this analysis are 0.03 and 0.4 (Figure 3.11). However, it is pertinent to mention here that due to plethora of sources and mixing of air parcels, it is very difficult to entirely isolate these impacts over an urban region like Ahmedabad.



Figure 3.11: Relationships between SO_2 and NO_x over Ahmedabad during May-October, 2011.

3.3 A case study of enhanced trace gases over Ahmedabad

Long-term monitoring of trace gases over a given location also provides an opportunity to observe features which are not explained by usual causal mechanisms. Sudden drastic changes (increase or decrease) in levels of one or more trace gases in a short temporal scale, if free from instrument artefacts, can provide an opportunity to explore the relationships between causal mechanisms and their subsequent impacts in a very robust manner. An episode of simultaneous enhancement in several trace gases over Ahmedabad is explored in the present section.

3.3.1 Enhanced trace gas levels during May 2010 using in situ and satellite observations

Simultaneous measurements of various trace gases carried out during May, 2010 enabled detection of a pollution event that occurred during this period. The mean concentration of SO₂ during the study period was 0.95 ppbv with higher mixing ratios between 1800 IST to 0200 IST (1.44 ± 1.43 ppbv). However, a gradual rise in the levels of surface SO₂ was observed since the night of 17 May and the concentrations were conspicuously elevated in the night of 20 May, 2010 with values exceeding 17 ppbv (Figure 3.12). The values again returned to normal after 22 May. High values were also observed in the tropospheric columnar SO₂ from OMI which showed almost 350% increase corroborating the surface observations over an extended height regime. The columnar value of SO₂ was found to be 0.16 DU on 20 May while the average value during 14-26 May, 2010 was around 0.026 DU only. This was also the highest columnar value of SO₂ during the summer of 2010.

For most of May, night-time O_3 was below 25 ppbv. However, it increased to above 30 ppbv on the nights of 20 and 21 May. In fact, a gradual rise in the daily peaks of O_3 and NO_2 had begun since 17 May and culminated on 20 May after which these peak values started to subside (top panel in Figure 3.13). The average maximum O_3 concentration was 20.7 ppbv during 11-30 May and occurred mostly during afternoon hours. For NO_2 , the average maximum concentration was 17.9 ppbv during 1-30 May and occurred mostly around 20-



Figure 3.12: Top panel: SO_2 variations during 14-26 May, 2010 based on in-situ surface measurements over Ahmedabad and satellite based columnar values from OMI. Bottom panel: OMI values during the summer (March-May) of 2010.

21 hours IST. However, on 20 May, these concentrations were around 32 ppbv for O_3 and 46 ppbv for NO_2 . Overall, NO_2 values were around 7.4±5.2 ppbv for 1-30 May and O_3 values were around 11.2±6.4 ppbv for 11-30 May. Increased concentrations were also found to occur for trace gases like CO, C_2H_2 , C_2H_4 , C_3H_6 , C_2H_6 , C_3H_8 and i- C_4H_{10} to the extent of 78, 125, 97, 82, 102, 112 and 90 percentages above their average values during the study period.

Satellite data for aerosols, columnar water vapor and HCHO indicate that the enhancement of trace gases was not only confined to the surface but extended to higher altitudes. AOD value at 550 nm obtained from MODIS increased to 0.96 on 20 May for the Ahmedabad grid. In general, the values

were below 0.6 on other days of May. Among aerosol species, contribution of absorbing aerosols to AOD was higher on 20 May ($\sim 79\%$ increase from their average value of 0.05). Since elevated level in AOD is observed concomitantly with high concentrations of trace gases, both are likely to have a common cause. Satellite data revealed that the precipitable water vapor content (the amount of water which would be obtained if all the water vapor in a specified column of the atmosphere were condensed to liquid) within the boundary layer, the surface to 920 mb product from MODIS, was very high on 20 May. The value was 0.94 cm when compared to the average value of 0.72 cm during 14-26 May, 2010 for the Ahmedabad grid. This high amount was also seen for total precipitable water vapor content ($\sim 36\%$ increase from its average value of 2.2 cm) but not observed for the 700–300 mb retrievals. This indicates that the effect could be more confined to the lower troposphere. The HCHO column value was 27.6×10^{15} molecules cm⁻² on 20 May, the highest during the study period. This was around 114% higher when compared to its average columnar value of 12.9×10^{15} molecules cm⁻² for other days between 14-26 May. The dominant atmospheric removal mechanism for HCHO is by photolysis and oxidation by hydroxyl radicals (OH) during daylight hours, resulting in a tropospheric lifetime of approximately 0.3 days. Normally, combustion of fuels from mobile sources and process emissions from oil refineries are the largest sources of directly emitted HCHO.

While the wind speed was in general above 1.5 m s⁻¹ for all other days, it stayed below 1 m s⁻¹ since the evening of 20 May till early hours of 21 May. Thus, low wind speed could have caused stagnant/very stable conditions resulting in the inability of pollutants already present to get dispersed quickly. The local wind-direction was mainly westerly for 1-31 May, 2010. However, wind direction was distinctly different (mostly north-westerly to northerly since the evening of 20 May till early hours of 21 May) from most other days. Further, boundary layer dynamics can have substantial impacts on the buildup/removal of pollutant gases. Occasionally, a combination of meteorology



Figure 3.13: Top panel: Variations of O_3 and NO_x for surface measurements over Ahmedabad during 14-26 May, 2010. Bottom panel: AOD (550 nm) and precipitable water vapor (total column) obtained from MODIS during 14-26 May, 2010 over Ahmedabad. HCHO column and AOD (absorption) is taken from OMI.

and dynamics including wind parameters and inversion can cause pollutants to shoot up. To get an insight into the stability conditions, 0000 GMT (0530 IST) upper air data for Ahmedabad (http://weather.uwyo.edu/upperair/) were analyzed for profiles of thermodynamic variables like temperature, RH and equivalent potential temperature (e). A minimum in e was used to identify characteristic features of inversions. e is more advantageous than normal temperature because it is normalized with respect to pressure and moisture content also. A mixing ratio of ~25 g kg⁻¹ at ~970 hPa suggested a higher evaporative potential of the atmosphere during the heat wave in comparison with standard weather conditions. A very strong inversion was observed between 970-900 mb (0.3-0.9 km) at 0000 GMT (0530 IST) on 21 May, when the e value dropped from 380 K to 305 K (Figure 3.14). The time corresponded to early morning (around pre-sunrise time) of 21 May and the values are representative of the nocturnal boundary layer of 20 May. This shows that conditions were calm and stable and the inversion acted as a lid by preventing locally emitted as well as transported pollutants from escaping into the free troposphere.



Figure 3.14: Variations in equivalent potential temperature at 0000 GMT (0530 IST) during 17-22 May, 2010 over Ahmedabad. Data were not available for 18 May; hence the profile for that day is not shown.

The C₂H₂/CO value on 21 May was 0.0076, about 42% higher than its average value of 0.0053 for other days of analysis. This ratio on 21 May indicates that the ambient air was influenced by fresh emissions or it could be possible that dilution effect by more aged air mass was less because of stagnant conditions. The average C₃H₈/C₂H₆ ratio of 0.6 during the study period also points at urban sources (*Wang et al.*, 2003). The average Δ C₃H₈/ Δ CO value was 0.0068 indicating influence from fossil fuel combustion (*Baker et al.*, 2011). The CO-NO₂ ratio during the evening of 21 May (~1830 hrs IST) was 55.1, indicating influence of mobile sources. The average SO_2/NO_2 value was 0.12 during the evening hours (1830 IST) of the study period indicating contributions from mobile sources rather than point sources. However, during the event period (2000 IST on 20th May to 0100 IST on 21st May), this ratio was ~0.36 indicating other influences like transport of polluted air apart from local effects of mobile sources.

3.4 Variation of RSCs over Ahmedabad

The variations of two RSCs viz. COS and CS_2 , were measured regularly over Ahmedabad during February-October, 2013 (Figure 3.15). The mean concentrations of COS over Ahmedabad are observed to be 1.135, 1.139, 1.316, 0.793, 1.456, 0.649, 0.691 and 0.973 ppby during February, March, April, May, July, August, September and October respectively. The seasonal variation for COS showed highest values during winter $(1.076 \pm 0.657 \text{ ppbv})$, followed by postmonsoon $(0.973 \pm 0.385 \text{ ppbv})$ and pre-monsoon $(0.911 \pm 0.419 \text{ ppbv})$ with least values during monsoon $(0.711 \pm 0.335 \text{ ppbv})$. COS sources in urban areas include automobiles, automotive tire wear, coal combustion, chemical and petrochemical industries as well as cesspools (Kettle et al., 2002; Yujing et al., 2002 and reference therein). The high mixing ratio of $COS (1.338 \pm 0.718 \text{ ppbv})$ in Beijing city was attributed, mainly, to emission from cesspools (Yujing et al., 2002). The average mixing ratio of COS over Ahmedabad during the study period is found to be 0.871 ± 0.431 for about 160 data points spread over different months. The mean value is about 1.7 times higher than the tropospheric mixing ratio of COS (0.510 ppbv, with a natural variability (1s) of about 10%; Yujing et al, 2002). The high mixing ratio of COS over Ahmedabad points to the influence of anthropogenic emissions over its natural background.

However, the seasonal variation for CS_2 showed highest values during pre-



Figure 3.15: Variations of COS and CS_2 over Ahmedabad during 2013.

monsoon $(0.698 \pm 0.487 \text{ ppbv})$, followed by post-monsoon $(0.460 \pm 0.539 \text{ ppbv})$ and winter $(0.397 \pm 0.283 \text{ ppbv})$ with least values during monsoon $(0.388 \pm 0.388 \text{ ppbv})$. The mean concentrations of CS₂ were 0.407, 0.623, 0.635, 0.521, 0.989, 0.362, 0.338 and 0.460 during February, March, April, May, July, August, September and October respectively. The average mixing ratio of CS₂ during the study period was 0.517 ± 0.464 ppbv for about 160 data points, which is higher than values observed over Beijing city.

No clear diurnal pattern is exhibited by COS and CS_2 over Ahmedabad, although, elevated values have been observed during traffic hours for both COS and CS_2 during most analysis days. This indicates some vehicular influence. Further, neither COS nor CS_2 , show any association with SO₂ values over



Figure 3.16: Variation of CS_2 and CO with COS over Ahmedabad during 2013. Top inset: Relationship of COS and CS_2 for $CS_2 < 0.4$ ppbv.

Ahmedabad, indicating coal combustion also do not entirely contribute to background COS in the city. However, there seems to be a moderate correlation between COS with both CH₄ and CO. The correlations of COS with CH₄ are higher ($R^2=0.35$) during September and October. Further, both COS and CS₂ exhibit moderate correlation with CO during August ($R^2=0.36$ and 0.51 for COS and CS₂ respectively). Moreover, COS and CS₂ exhibit some linear association among themselves when CS₂ values less than 0.4 ppbv is considered (Figure 3.16). CH₄ and CO can be emitted from landfills as well as cesspools which are also sources of RSCs. Further, CO can be produced from CH₄ oxidation and COS can be produced by CS₂ oxidation. Thus, it seems that both chemical and anthropogenic sources contribute to the COS levels over Ahmedabad. Further, since Ahmedabad is located in a semi-arid region, the soil is supposed to be oxic during most part of the year, and act as a sink for COS.

3.5 Summary

In this chapter, we have investigated the surface level variation of trace gases over Ahmedabad using in-situ measurements of O_3 , its major precursors (CO and NO_x , SO_2 as well as COS and its precursor (CS₂). The diurnal variations of surface O_3 showed a daytime maximum due to photochemical production, CO and NO_x showed morning and evening peaks coinciding with traffic rush hours. In case of SO_2 , no clear diurnal variation was observed. However, SO_2 exhibited a clear seasonal variation with levels decreasing from pre-monsoon (0.85 ppbv) to monsoon (0.52 ppbv) and suddenly increasing during postmonsoon (2.26 ppbv). The sudden increase during post-monsoon is attributed to a change in wind-direction to north-easterly regime. Industries and powerplants to the north-east of the study site are found to be the major contributors of SO_2 . The seasonal variation in SO_2 is reciprocated by other primary pollutants viz. CO and NO_x , both show a sudden enhancement in levels during post-monsoon. These gases show an anti-correlation with wind-speed, indicating local sources in Ahmedabad. This is in contrast to O_3 , which does not show a decrease with increasing wind-speed, indicating that O_3 over Ahmedabad is mainly contributed by chemical processes rather than transport.

 $\Delta O_3/\Delta NO_x$ values for Ahmedabad exhibit signatures of fresh emissions. Overall, O_3 and NO_x show an inverse association resulting from competing photochemical, dynamical and physical processes in the atmosphere. Low slope and relatively lower correlation between O_3 and CO over Ahmedabad indicate incomplete photochemical processes in the ambient air. Further, the $\Delta CO/\Delta NO_x$ values varying between 9-15 ppbv/ppbv suggest major influence from vehicular emissions. The $\Delta SO_2/\Delta NO_x$ values are estimated to be 0.026 and 0.4 for mobile and point sources over Ahmedabad. An event of a sudden increase in trace gas concentrations over Ahmedabad during heat wave conditions of May, 2010, using various chemical and meteorological proxies, points to the trapping of pollutants by a strong inversion layer. This is the first time that COS measurements are being reported over Ahmedabad, and to the best of our knowledge, over an Indian site. As evident from its levels (0.871 ± 0.431 ppbv), atmospheric COS over Ahmedabad has a major anthropogenic component. Existence of moderate correlations of COS with CH₄ and CO suggests collocated sources which are likely to be cesspools, wastelands and possibly a very small vehicular component. However, COS and SO₂ are totally uncorrelated indicating that coal burning and industries may not be contributing enough COS to Ahmedabad ambient air.
Chapter 4

Impacts of dynamics and emissions on trace gas levels over the Indo-Gangetic Plain

The IGP encompasses most of the northern India (within 22-32°N range) and stretches from Pakistan in the west (68°E) to Bangladesh in the east (91°E). The IGP is spread over an area of 0.7 million km² but houses more than an eighth of the global human population. During the last decade, the IGP has been the focus of wide, scientific deliberations due to higher emissions of trace gases and aerosols occurring in this region. Rapid urbanization, changes in the land use pattern, emissions from the industries and power plants along with anthropogenic emissions from burning of fossil fuels and traditional bio-fuels by the population living there, has led to very high levels of pollutants viz. carbon monoxide (Kar et al., 2008), sulfur dioxide (*Adhikary et al.*, 2007), alkenes (*Lal et al.*, 2012), ammonia (*Clarisse et al.*, 2009) etc. Further, high aerosol loading has been reported over the Ganga basin (*Ramanathan and Ramana*, 2005). Even in case of secondary pollutants, high tropospheric ozone residual has been found along these plains throughout the year (*Fishman et al.*, 2003). These large emissions along the plains have implications to regional and global pollution, as deep convection during the summer-monsoon can efficiently lift the pollution to the upper troposphere, wherein it can then be transported to larger regions of the globe (*Lawrence and Lelieveld*, 2010). The IGP emissions are suspected to modulate local temperatures, monsoon rainfall and climate (*Ramachandran and Kedia*, 2013). Positive trends in tropospheric temperatures have been observed over urban regions in the IGP (*Mallik and Lal*, 2011) and have been linked to IGP emissions (*Gautam et al.*, 2009).

The present chapter begins with an illustration in the change of emission patterns as one moves from Western India to the IGP. The results are based on hydrocarbon measurements during a road experiment from Ahmedabad to Nainital. This is followed by an overview of seasonal patterns in SO_2 , NO_2 and CO over a few urban regions in the IGP. These urban regions are compared to other urban regions outside the IGP to detect unique characteristics (w.r.t. emission patterns) of IGP sites. Further, measurements of SO_2 over Nainital are investigated to understand the efficacy of wind-borne transport from IGP surface sites and the impact of boundary layer dynamics. Intensive sampling based observations of SO_2 , CO and hydrocarbons over Kolkata are discussed with a focus on their levels and source characteristics in the IGP outflow region. The chapter concludes with an example of free tropospheric, trans-continental transport of SO_2 from Africa over to the IGP using OMI SO_2 measurements.

4.1 Hydrocarbon variation over western India and IGP

To investigate the difference in emission characteristics between the semi-arid, industrialized western India with the densely populated IGP, air samples were collected during a road experiment from Ahmedabad to Nainital, via Agra for measurements of CO and light hydrocarbons using a Toyota Innova vehicle (Figure 4.1). During the experiment, air samples were filled to about 2.5 bar in 900 ml borosilicate glass sampling bottles using an air compressor. The distance covered during the trip was about 2400 km (2x1200 km). The onward journey started on 25 August, 2010 from Ahmedabad and ended at Nainital on 27 August, 2010. While the road trip was mainly along the National Highway, for collection of each air sample, a detour off the main route, about 1.5 km away from highway, into nearby fields, lakes or isolated parts of mountains, was taken where sample was filled after waiting for about 15 minutes ensuring no vehicle has passed during that period. The return journey from Nainital to Ahmedabad was during 30 August-01 September, 2010. About 24 sample bottles were filled at approximately, every 100 km intervals. However, results presented here are based on the analysis of 18 samples as some samples were found to be severely contaminated.



Figure 4.1: Left: Route map from Ahmedabad to Nainital during the road experiment in Aug-Sep, 2010. Right: Observed CO concentrations during the experiment. Major cities along the route are marked with squares.

In general, it was observed that CO concentrations gradually increased when we moved from western part of India to the northern plains, mainly after crossing Agra (Figure 4.1). Apart from this, CO was also found to be high near Ajmer, which is a tourist city, and hence much biofuel burning is expected. The variation of CH_4 and C_2 - C_4 NMHCs is shown in Figure 4.2. It



is observed that CH_4 does not show any significant spatial variation, probably due to its long-lived nature.

Figure 4.2: The variations of hydrocarbons during the Ahmedabad-Nainital road experiment are indicated in colour.

However, C_2H_6 , C_2H_4 , C_2H_2 and C_3H_6 concentrations are higher towards northern part of the campaign, i.e. in the Delhi-Agra-Nainital region, if Ahmedabad data point is not considered. These represent emissions from both biofuel and fossil fuel consumptions mainly. In contrast, propane and butanes (C_4H_{10}) are found to be significantly elevated in the western part of India. These represent emissions from fossil fuels mainly petrochemical units, refineries, etc (Table 1.1). Correlation analysis reveals tight correlations between C_2H_2 and CO ($R^2=0.76$), $C_2H_4-C_3H_6$ ($R^2=0.90$), $C_2H_4-C_2H_2$ ($R^2=0.74$), C_3H_8 - C_4H_{10} (R²=0.77) and between i- C_2H_4 and n- C_4H_{10} (R²=0.81). These correlations indicate influence of both biofuel and fossil fuels during the campaign. Overall, it may be inferred that western India (barring Ahmedabad, which is a major city) is more dominated by fossil fuels mainly petrochemicals while both biofuel and fossil fuel combustion dominate in the IGP region.

4.2 Trace gases over a few urban locations of India

In this section, results of measurements of SO_2 and NO_2 made by the CPCB at various locations over geographically distinct urban regions in and around the IGP viz. Delhi (central IGP), Jodhpur (west of IGP), Kolkata and Durgapur (eastern IGP), Guwahati (east of IGP) and Nagpur (south of IGP) (Figure 4.3) are used to study their tempo-spatial pattern. An effort is made to distinguish this variability in terms of in-situ emissions and transport effects by the analysis of their levels, seasonality and ratios. The results are supported by columnar SO_2 and NO_2 data (obtained from OMI archives) and the CO data (surface and columnar) obtained from MOPITT. The methodologies for these data sets have been described in Chapter 2.

4.2.1 Description of study locations

Delhi, the capital city of India with a humid subtropical climate, is characterized by intensely hot summers and cold winters. The predominant wind direction is from the north and northwest (except during the monsoon), which brings air from industrialized regions in Punjab and Haryana to Delhi. Further, the megacity itself has three coal fired power plants and many industries. The vehicular population of Delhi (5.5 million) is the highest in India. Jodhpur (600 km south-west of Delhi) is the second largest city of Rajasthan state of India. It has a hot, semi arid climate and very close (200 km) to the Thar Desert.



Figure 4.3: Study locations for the CPCB data analysis. The 2.5 arc-minutes resolution, gridded population density map for 2005 has been obtained from 'Center for International Earth Science Information Network'. http://sedac.ciesin.columbia.edu/gpw

Kolkata is a megacity located on the banks of river Hooghly, about 50 km from the Bay of Bengal, with a tropical wet and dry climate. The Kolkata metropolitan area, along with the suburbs, has a population exceeding 15 million, making it the 13th most populous urban area in the world. It also has a number of industries and very heavy vehicular traffic. Durgapur, an industrial township located 160 km north-west of Kolkata, is home to the Durgapur Steel Plant, three large power plants and several chemical and engineering industries. Guwahati, the largest city of Assam and home to a major petroleum refinery, is a rapidly growing city. It has a humid subtropical climate and experiences more than 1700 mm annual rainfall. Nagpur, located at the centre of the country, has two major thermal power stations (1920 MW) and houses the largest industrial area in Asia. Thus all the sites chosen for the study have unique geographical and climatic settings.

4.2.2 Seasonal variation

Figure 4.4 shows the average monthly variations in SO_2 and NO_2 at the surface and in total column over the different study locations for the period 2005-2009. Two conspicuous features are observed viz. a. winter maxima in both SO_2 and NO_2 surface data for all the stations barring Jodhpur. b. NO_2 levels over the IGP stations are distinctly higher compared to Guwahati (a valley region), Jodhpur (a desert region) and Nagpur (central India).

Further, the mean concentration of SO_2 is highest over Kolkata (4.1 ppbv) and is followed by Nagpur (3.6 ppbv). Both of these places are dotted with several industries including petrochemicals, chemicals, iron, steel, metallurgy, textiles, leather etc. The variability (1 sigma) is largest over Kolkata (2.8 ppbv) due to multiple sources. The seasonal minimum value for SO_2 is very high over Nagpur (2.4 ppbv) followed by Durgapur and Jodhpur (2.0 ppbv each). Among the stations studied, the SO_2 maximum is highest over Kolkata (13.6 ppbv). Modelling studies also corroborate the high background levels of SO_2 over Kolkata (*Adhikary et al.*, 2007).

The mean concentrations of NO₂ are highest over Kolkata and Durgapur (~31 ppbv each) followed by Delhi (27 ppbv). The pattern of NO₂ mean and sigma is similar to the pattern in NO₂ maxima, indicating dominant effect of stereotype sources of NO₂ over these regions rather than multiple sources (this is in contrast to SO₂). It is to be noted from *Garg et al.* (2001) that use of gasoline/diesel in transport sector and coal combustion in thermal power sector account for over 60% of NO_x emissions in India. The NO₂ minima are higher for Delhi and Durgapur (~16.7 and 16.5 ppbv) followed by Kolkata (~13.8 ppbv). The maxima peak for Delhi, Durgapur and Kolkata (>50 ppbv over each city). In India, the transport sector accounts for more than one-third of total NO_x emissions over urban regions. Thus, a disproportionate rise in the number of vehicles accompanied by heterogeneous traffic conditions can also result in higher observed concentrations for NO_2 in congested cities. The mean SO_2 and NO_2 concentrations over Guwahati are found to be 2.7 and 8.7 ppbv respectively.



Figure 4.4: Averaged monthly variations in SO_2 and NO_2 over different regions of India for the period 2005-2009. The station values (CPCB measurements) are plotted with line and points while the columnar values for the OMI grids are plotted as bars.

Surface measurements are limited in their spatial coverage while satellite data can cover large spatial domains with long periods of consistent observations. The average monthly variation of surface concentrations of SO_2 and NO_2 during 2005-2009 has been compared with the corresponding OMI columns averaged over the same temporal span (Figure 4.4). The logic behind this comparison follows the fact that if surface contributions to the column are significant, then similar features would be obtained for both surface and column. Nevertheless, a direct comparison between both is inevitably influenced by many factors, viz. vertical profiles of species, changes in boundary layer height and interferences from cloud, aerosol, etc.

Table 4.1: Study locations selected for analysis of CPCB data. The mean and 1 sigma of surface SO_2 and NO_2 values from CPCB measurements are also presented.

Stations	${ m Latitude}_{(^oN)}$	Longitude (°E)	Population (millions)	OMI grid Lat span (°N)	OMI grid Long span (°E)	${ m SO}_2 ~{ m (ppbv)}$ Mean $\pm { m sigma}$	$\mathrm{NO}_2 \; \mathrm{(ppbv)}$ Mean $\pm \mathrm{sigma}$
Jodhpur	26.7	73.0	0.87	26-27	72-73	2.5 ± 0.4	11.8 ± 1.0
Delhi	28.6	77.2	16.71	28-29	77-78	$2.9{\pm}1.0$	27.4 ± 7.0
Durgapur	23.5	87.3	0.50	23-24	86-89	3.1 ± 0.8	31.5 ± 8.8
Kolkata	22.6	88.4	11.39	22-23	88-89	4.1 ± 2.8	31.0 ± 9.3
Guwahati	26.2	91.7	0.83	26-27	91-92	2.7 ± 0.8	8.7 ± 1.9
Nagpur	21.2	79.1	2.09	21-22	78-79	3.6 ± 0.9	16.1 ± 3.8

Most of the locations studied show bimodal features with respect to columnar SO_2 and NO_2 loadings. A pronounced maxima in columnar SO_2 occurs during monsoon (June in East-Central India except Guwahati and July in North-West India) and another elevation occurs during winter. However, the winter elevations over Durgapur and Kolkata are higher than the monsoon SO_2 columns. Overall, the SO_2 columns are mostly below $3x10^{15}$ molecules cm^{-2} . It is pertinent to mention here that the highest observed monthly SO_2 columnar values over the IGP were in the range of 0.6-0.9 Dobson Units (DU) during November 2008 for Delhi, Durgapur and several IGP stations (discussed in section 4.5) due to the Dalaffilla volcanic eruption in Ethiopia (Mallik et al., 2013a). NO₂ columns vary from a low of 2×10^{15} molecules cm⁻² over Guwahati to a high of $7x10^{15}$ molecules cm⁻² over Delhi. Unlike SO₂, columnar NO₂ over Delhi, Kolkata, Durgapur and Nagpur values exhibit monsoon minima. Further, over Delhi, Durgapur and Nagpur, columnar NO_2 exhibits a pre-monsoon elevation (March and/or April) apart from the regular winter elevation. Guwahati also exhibits pre-monsoon elevation but no winter elevation. NO_2 values over Kolkata also show a winter maxima for surface as well as total column. Additionally, NO₂ columns over all stations, except Jodhpur, show monsoon minima. The winter maxima in both surface and columnar NO₂ over Kolkata (also Delhi and Durgapur) suggest significant contributions from surface emissions to columnar values (Meng et al., 2010).

The CO columnar values (MOPITT daytime retrievals) over the study regions are shown in Figure 4.5. While most of the stations over the IGP show a winter maxima in surface CO, interestingly the columnar values are highest during pre-monsoon. However, over Guwahati, both surface level and columnar CO are elevated around March. The CO values over Guwahati are also notably higher compared to other stations. Guwahati is a major metropolis in the North-East and an important hub for transportation. The city is additionally affected by emissions from refineries on the eastern sector. Further, the region is impacted by large scale biomass burning during the pre-monsoon, which is also visible in Moderate Resolution Imaging Spectroradiometer (MODIS) fire imageries. High BC (daily median values of 9-41 μ g m⁻³) over Guwahati has been observed (*Chakrabarty et al.*, 2012). Columnar NO₂ values are also found to be elevated over Guwahati during March-April (Figure 4.4). Its climate is mildly sub-tropical with warm, dry summers from April to late May, a strong monsoon from June to September and cool, dry winters from late October to March. The maximum temperatures and maximum wind speeds occur during pre-monsoon over Guwahati. An environmental impact assessment report over Guwahati found that the study region was extremely stable (F class stability) for 63% time of the year, indicating poor dispersion of pollutants. The high levels of surface and columnar CO over Guwahati along with substantial levels of SO₂ indicate additional impact of local, point sources.



Figure 4.5: Monthly variations in MOPITT derived surface and columnar CO over different urban regions of India during 2005-2009.

The amplitude of seasonal variations in surface SO_2 over Jodhpur is negligible (Figure 4.4) compared to other study locations. This suggests that

the sources and sinks of these species are relatively well-balanced and stable throughout the year at this site. Similar features have been discussed by *Meng* et al. (2010) for several locations in China. Over Kolkata, where surface SO_2 concentrations are lowest during pre-monsoon, interestingly surface NO₂ values are lowest during monsoon (Figure 4.4). This is because dry deposition, which is a major loss process for SO_2 , is operative during summer when most of the IGP is under the ambit of transport from western India and Arabian region. The elevation in surface NO_2 during winter compared to other seasons is conspicuous over Kolkata and Durgapur (Figure 4.4). Overall, surface CO is always enhanced in pre-monsoon compared to post-monsoon. Since maximum columnar loadings of SO_2 are observed over the IGP during monsoon in contrast to elevated winter concentrations at the surface, effect of transport contributing to these loadings in the free troposphere is a possibility. The surface level winds during July over the IGP stations are mainly south-westerly (Figure 1.3) which means they are traversing the highly industrialized western region of India and adding to the already significant levels of SO_2 in the IGP. Another possibility is the minimal loss of SO_2 occurring from dry deposition during monsoon. Dry deposition is believed to be the second major loss process for SO_2 after oxidation (*Faloona*, 2009). It has been observed that during the initial phase of the monsoon rainfall over the IGP, the concentration of suspended particulates are very high to neutralize the acidity of the atmosphere but in the later phase of rain events, the neutralization is not possible due to removal of particulates; which leads to increased acidity of precipitation. Seasonal changes in wind speed impact the dry seasonal deposition of particles. Also, seasonality of wind-blown dust in scavenging SO_2 during dry season corroborates this argument Adhikary et al. (2007).

4.2.3 Correlations and emission ratios

The Pearsons correlation coefficient is used to determine if there is a possible linear association between surface and columnar SO_2 , NO_2 and CO values used in this study. Surface measurements of SO_2 and NO_2 exhibit a sample statistic (correlation coefficient) above 0.5 for most of the stations studied that are statistically significant at over 95% (Guwahati and Nagpur) and over 99% (Delhi, Durgapur and Kolkata) (Figure 4.6, left). An interesting observation is that while both Durgapur and Nagpur have good correlations between columnar NO_2 and columnar CO, the columnar NO_2 over Nagpur is not well correlated with surface NO_2 , unlike Durgapur. This indicates that surface level NO_2 sources are much prevalent over Durgapur but comparatively exiguous over Nagpur. This indicates that while Nagpur is affected mainly by industrial emissions, Durgapur is affected both by industrial and vehicular sources.



Figure 4.6: Left: Correlations of SO_2 , NO_2 and CO for surface (based on CPCB data) and columnar values (based on satellite data) during the period 2005-2009. Right: Box plot showing interquartile range of SO_2 (ppbv)/NO₂ (ppbv) for the study locations.

Statistically significant correlations are obtained between surface- NO_2 and columnar- NO_2 for Delhi and Kolkata. As explained above, large scale surface emissions from these megacities would dominate columnar NO_2 values over the respective regions, thus producing good agreement between surface and columns. For most of the large cities, NO_2 and CO columns show good correlation. The correlation of MOPITT derived surface CO with surface level NO_2 concentrations are 0.72, 0.69, 0.61 and 0.49 for Kolkata, Durgapur, Guwahati, and Delhi respectively. The correlations of MOPITT derived surface CO with surface level SO₂ concentrations are 0.47 for Durgapur and 0.40 for Delhi, Guwahati and Kolkata. It must be mentioned that CO is governed more by emissions (anthropogenic; incomplete combustion of carbonaceous materials) and dynamics while SO₂ is affected by chemistry, physical loss processes, dynamics and emissions (both natural and anthropogenic). Overall, the correlations of satellite versus ground measurements vary substantially from region to region.

Emission factor for SO_2 due to coal burning in power sector varies between 8 to 16 g kg⁻¹ for the Indian region (Streets et al., 2003). Compared to coal burning, SO_2 emission factors are higher for oil (0.04 for diesel oil and 0.08 for fuel oil) (Garg et al., 2001). Emission factor for NO_2 due to oil burning in transport sector varies between 15-58 g kg⁻¹ for the Indian region (*Streets*) et al., 2003). In the present study, the mean ratios of SO_2 to NO_2 for surface measurements vary between 0.1 to 0.6 (Figure 4.6, right). For Delhi, Kolkata and Durgapur, the ratios are mostly below 0.2. The low ratios indicate dominant impacts from mobile sources (combustion of diesel/petroleum) as major contributors to the ambient air. These cities are notable for high pollution levels with prolific vehicular traffic which release more NO_2 than SO_2 at the surface level. The dominant impact of surface NO_2 over Delhi and Kolkata is also supported by the good correlations obtained between surface and columnar NO_2 over these places. SO_2 to NO_2 ratios higher than 0.3 are obtained for Guwahati and Nagpur. These cities seem to have considerable impacts from SO_2 rich point sources. Both these rapidly growing cities are characterized by pre-dominant influence from industries; mainly high SO_2 emissions from power plants, refineries, chemical industries etc.

Figure 4.6 indicates that surface concentrations can significantly impact

columnar values over high emission regions. The distribution of surface emissions over broader spatial scales (horizontal as well as vertical) is mediated by convective and advective transport processes occurring in the atmosphere. To study the possible impact of IGP emissions over larger spatial regimes, intensive measurements of trace gases were made over Nainital and Kolkata. The results have been discussed in the following sub-sections.

4.3 Role of regional transport on SO_2 levels at a high altitude site

The low-lying, topographically homogeneous IGP is bordered by the Himalayan mountain range in the north. Due to a plethora of widely scattered emission sources in the IGP, it is very difficult to find a representative site for characterizing the emissions along these plains. This is because a representative site should be remotely located and sparsely inhabited to minimize in-situ emissions. In this perspective, observations from high-altitude stations assume special significance as measurements at these places can provide a far-field picture and a sort of background against which the urban impacts can be compared. Measurements of O_3 at Nainital (29.37°N, 79.45°E; 1958 m amsl) suggest that it is an excellent regional representative site for gauging and characterizing the IGP emissions (*Kumar et al.*, 2010). Absence of daytime photochemical buildup in O_3 (typical of urban or rural sites) at Nainital, established that local emissions of precursors are not significant to affect the O_3 chemistry at the site. Trace gas measurements made over this site are expected to provide the information about background levels of these gases for the surrounding IGP.

Measurements from this site can also be used to identify the contributions from downward transport, understand free tropospheric conditions as well as influence of regional pollution and biomass burning. The present section explores the levels and variability of SO_2 over Nainital using data from continuous, in-situ measurements over a period of three years during 2009-2011. These measurements have been made with a view to decipher the emission characteristics of air masses over this region. Since emissions due to coal burning in industries and power plants release large amount of SO_2 , measurements of SO_2 along with NO_y have been used to segregate the influence of emissions from these large point sources from other emissions.

4.3.1 Site description and meteorology

The study was conducted at Manora Peak (29.37°N, 79.45°E), a pristine mountaintop located at 1958 m amsl, in Nainital (Figure 4.7). The population of Nainital is 0.95 million and the region itself is devoid of large-scale industries. The nearest megacity, Delhi, is about 225 km away to the southwest. Sharply peaking mountains are located to the north and east of the observation site while mountains, with altitudes less than 1000 m in the south and west, separate the site from the IGP. In general, air masses at this site do not arrive from the north-eastern sector in any season because of high mountains in that direction. The site is influenced by westerly winds during winter (December, January and February) and south-westerlies during monsoon (June-August). During pre-monsoon (spring, March-May), air masses are mostly north-westerly and transport pollutants from the northern Indian region and IGP to the observation site (*Kumar et al.*, 2010). Late spring (May) and early autumn (September) are the change over periods and winds mostly circulate over the Indian subcontinent. Throughout the year, except during pre-monsoon, about 10-15% of air masses influencing the observation site are from higher heights (>4000 m). During pre-monsoon, horizontal advection of air masses occurs at about 2 km amsl (Kumar et al., 2010). Overall, the wind-direction being pre-dominantly north-westerly, potentially transport the north-western IGP emissions to the study site. More than 50% of air masses originate in the 270-360° sector during January-June and about 40% during post-monsoon (September-November). However, during July-September, wind direction varies between north-westerly to south-easterly, with more than 35% air masses coming from the 90-180° and 270-360° sectors each, bringing emissions from IGP to the site.



Figure 4.7: The measurement site is located in Nainital. The major geographic divisions of India are also approximately marked in the map.

4.3.2 Diurnal variation in surface SO₂

Diurnal variations in surface SO₂ over Nainital, using hourly average data for each month during 2009-2011, is shown in Figure 4.8. The diurnal amplitude is maximum in April (300 pptv), followed by March (209 pptv) and February (136 pptv). Daytime PBL, facilitated by high solar insolation (nearly 800 W m⁻²), is highest during the pre-monsoon period (about 2250 m and 1900 m at 1130 hrs and 1730 hrs IST). This facilitates transport processes, which are further augmented by high wind speeds (>2 m s⁻¹). Further, the amplitude of wind speed is highest during March-May (increases from 2 m s⁻¹ at 0930



IST to 4 m s⁻¹ at 1830 IST). Thus, fast advection of air masses from source regions during daytime, elevates SO_2 levels at the study site.

Figure 4.8: Diurnal variations in surface SO_2 at Nainital for different months during 2009-2011.

Despite different levels of SO₂ during different months and associated variations in diurnal amplitudes, a common feature in SO₂ diurnal variations over Nainital is the existence of elevated values during daytime (except during January). Since the possibility of photochemical formation of SO₂ from RSC over Nainital is very less due to very low levels of different trace gases, the role vertical transport causing elevated daytime values becomes plausible. Diurnal changes in wind flows play significant role in the diurnal variability of trace gases over the mountains (*Kleissl et al.*, 2007). Especially after winter,

during pre-monsoon, valley walls absorb solar radiation and the air adjacent to the valley, now being warm and less dense, starts flowing upslope (valley breeze). The vertical winds at the observational site start increasing after sunrise and it is upslope (positive) during daytime, which coincides with the observed increase in SO_2 values (Sarangi et al., 2013). At Nainital, the wwind is maximum during noon hours (about 0.1 m s⁻¹), when SO₂ levels are observed to be the highest. This concurs with the explanation of transport of relatively polluted air from the low altitude areas to the mountain top. The w values show a decreasing tendency towards the evening hours and remain downslope (negative) during the night-time due to radiational cooling of valley walls (mountain breeze). This can also result in dilution of SO_2 levels with free tropospheric background air, thus resulting in lower night-time values. This feature could become very prominent during winter resulting in lowest nighttime values of SO_2 (katabatic type winds). The diurnal variation in w-wind is maximum during pre-monsoon (0.3 m s^{-1}) , which corroborates large diurnal amplitude in SO₂. During this time, the w-wind reverses from -0.2 m s^{-1} during night-time to about 0.1 m s^{-1} during daytime. Diurnal amplitude in w-wind is also substantial during winter (night-time: -0.1 m s^{-1} and daytime: 0.4 m s^{-1}) and post-monsoon (night-time: -0.17 m s^{-1} and daytime: 0.7 m s^{-1}) (Sarangi et al., 2013). However, SO_2 levels are already too low to reciprocate these effects. During monsoon, the w-wind variation is very low (night-time: -0.4 m s⁻¹ and daytime: 0.4 m s⁻¹), consequently diurnal amplitude in SO₂ is also very less.

4.3.3 Seasonal variation in surface SO₂

The monthly SO_2 concentrations averaged for the period 2009-11 are shown in Figure 4.9. It is observed that SO_2 concentrations are highest during premonsoon and lowest during winter. SO_2 concentrations start to build up from February, peak during April and come down during May-June. In particular, mean SO_2 concentrations above 500 pptv are observed during April. The SO_2 concentrations are very low during monsoon (July-August). The levels again build up during September but come down very quickly during the subsequent months. The observed seasonal variation is apparently perplexing and in sharp contrast to the seasonal SO_2 variations in nearby IGP stations as discussed in Sections 4.2.2 and later in Section 4.4.3.



Figure 4.9: Monthly averages of surface SO₂ during 2009-2011 at Nainital.

SO₂ measurements over two nearby megacities in the IGP viz. Delhi (*Datta* et al., 2010) and Kolkata as well as over Chinese sites on the opposite side of the Himalayas (*Meng et al.*, 2010) show high concentrations during winter. However, SO₂ concentrations during summer and winter were found to be comparable in regionally representative background atmospheres in China viz. Linan. *Igarashi et al.* (2006) have observed that the frequency of high SO₂ events increases during spring compared to winter at the summit of Mt. Fuzi. The observations at Nainital (Summer mean: 345 pptv; winter mean: 71 pptv) are very similar to observations at Sonnblick Observatory in Austria (Summer mean: 260 pptv; winter mean: 65 pptv; *Tscherwenka et al.* (1998). It is observed that the annual average SO₂ at Nainital (150 \pm 155 pptv) is similar to values at Mt. Sto. Tomas in Philippines (110 pptv; *Carmichael* et al. (2003). The summer values are similar to another nearby high altitude site (Mt. Waliguan) on the opposite side of Himalayas (420 pptv; *Lin* et al. (2013)). However, the winter concentrations at Nainital are far lower to those at Mt.Waliguan. Further, it is observed that many sites above 3500 m (Langtang in Nepal, Isla Redonda in Argentina and Mt. Kenya) have annual average SO₂ less than 50 pptv of SO₂ (*Carmichael et al.*, 2003). Over Mt. Fiji in Japan, higher SO₂ is observed during winter despite notable long-range transport during spring. Higher SO₂ during winter at Mt.Fuji is attributed to minimal removal of SO₂ due to cloud processes during winter while the reverse happens during spring (*Igarashi et al.*, 2006).

Seasonal variations of SO_2 can be influenced by seasonal changes in emission strengths, atmospheric circulations and depth of the boundary layer as well as the seasonal strength of removal mechanisms. Seasonal variations in anthropogenic emissions are unlikely to be substantial (Streets et al., 2003) especially for SO_2 where transport and residential sectors play a paltry role against year-long emissions from power plants and industries. Observations at Mt.Fuji also showed that seasonal changes in emissions were not responsible for observed SO_2 changes at its summit (*Igarashi et al.*, 2006). Then, the next important governing parameter for seasonal variation of SO_2 is its own transport from source regions. However, as mentioned in section 4.4.1, wind direction is mainly north-westerly both during pre-monsoon and winter, although the percentage count of wind-direction data in this sector is about 20% more in pre-monsoon than winter. However, this difference in percentage is not likely to account for the relatively high daily averages during pre-monsoon. A clinching evidence of the role of transport is demonstrated from very good correlations between observed SO_2 concentrations and wind speed. These correlations are higher during summer monsoon period (pre-monsoon + monsoon; $R^2=0.88$) compared to post-monsoon ($R^2=0.08$), indicating that transport of SO₂ from its emission sources are more effective during the summer monsoon period. The transport during pre-monsoon is also more effective because of higher wind speeds (mean >3 m s⁻¹ during March-April) and a deeper boundary layer (daytime mean>2 km) favoring horizontal advection.

The SO₂ values are lowest during winter, sometimes even below the level of detection. The monthly average RH during December-February is about 50% while it is lower during March (42%) and April (32%). The higher humidity should favor higher oxidant concentrations and thus greater SO₂ removal during winter (*Igarashi et al.*, 2006). However, the absolute RH values are still very low to account for the observed low SO₂ values. In several studies over various urban and rural sites, high SO₂ values during winter (as also for other trace gases) has been attributed to the trapping of emissions in a shallow boundary layer. However, since Nainital is a high-altitude site, local boundary layer dynamics affects this region differently as compared to the low lying plains. Figure 4.10 shows that strong association exists between SO₂ concentrations and daytime PBL heights. However, during night-time, there is almost no association with PBL heights.



Figure 4.10: Variations of surface SO_2 with planetary boundary layer (PBL) heights over the Nainital region. The correlations are based on SO_2 averages in 500 m PBL bins during daytime and 50 m bins during night-time.

Figure 4.10 further shows that night time PBLs are very low compared

to day-time values. Assuming negligible local emissions of SO_2 , this indicates that when PBL is high, import of SO_2 to the study site is more probable. Extending this argument to seasonal changes in PBL, since PBL is very low during winter, import of SO_2 to the study site is precluded. Thus, despite high SO_2 concentrations in the IGP during winter, boundary layer dynamics acts as a bottleneck in transport of IGP emissions to the study site. The average planetary boundary layer height over the region during winter is about 900 m at 1130 IST, 300 m at 1730 IST and below 50 m during night-time. This implies that the local boundary layer at the observation site should be mostly very low i.e. Manora Peak is mostly cut off from the nearby IGP emissions that are trapped within the regional boundary layer several meters below the observation site. Decent correlations ($R^2=0.41$) between PBL SO₂ and free tropospheric SO_2 during winter and post-monsoon corroborate this argument. However, columnar SO_2 does not seem to have any association with surface concentrations. It is pertinent to mention here that free troposphere refers to a region largely unaffected by the mesoscale planetary boundary layer dynamics. Low levels of SO_2 during winter at Nainital seem to represent background concentrations, though not exactly free tropospheric concentrations, for this region. These concentrations can also be modulated by cloud processes (incloud scavenging).

4.3.3.1 Sources of high SO₂ during pre-monsoon

The fact that local sources of SO_2 are not likely to be significant at Nainital, accompanied by good correlations of SO_2 with wind speed and daytime PBL substantiates the role of transport of SO_2 from outside the Nainital region. Since highest SO_2 concentrations are observed during April and May, PSCF analysis is done for these months to identify the probable source regions. These maps are based on potential source contribution function (PSCF) analysis (*Wang et al.*, 2009). PSCF analysis is widely used to identify the important geographic source areas contributing to measured concentration (*Asatar and* Nair, 2010). PSCF is defined as:

$$PSCF = \frac{m_{ij}}{n_{ij}} \tag{4.1}$$

where n_{ij} denotes the total number of trajectory segment endpoints falling in the grid cell (i,j) and m_{ij} is the number of times that the source concentration exceeded the arbitrary threshold, when the trajectories passed through the same cell. In other words, PSCF is the ratio of polluted trajectory segment endpoints falling in a grid cell to the total number of trajectory endpoints passing over that grid (*Wang et al.*, 2009). The PSCF value can be interpreted as the conditional probability that the concentrations of a given pollutant greater than the threshold level are related to the passage of air parcels through a grid cell during transport to the receptor site.



Figure 4.11: Left: Probable source regions contributing to elevated SO₂ concentrations over the study location during May. The maps are derived from Potential source contribution function analysis using TrajStat software (*Wang et al.*, 2009). Runtime: 72 hrs, cell size= $2^{\circ}x2^{\circ}$. Pollution criteria: 75 percentile of hourly variation of SO₂. The red grids are the most probable source regions, followed by pink and orange. Right: Correlation of MODIS fire pixel counts over Northern India with SO₂ concentrations measured at Nainital. The boxes represent $5^{\circ}x5^{\circ}$ grids while the circles represent $1^{\circ}x1^{\circ}$ grids.

The analysis suggests that major contributing regions are Northern India

(mainly the industrial belt of Punjab-Haryana region) and North-East Pakistan (Punjab and Khyber Pakhtunkhwa) (Figure 4.11). The probable source grids falling in Pakistan contain major refineries. The probable source grids spanning Punjab, Haryana, Northern Rajasthan and Delhi regions of India also contain several power plants. These regions have been shown to be major emission sources for SO₂ by both *Garg et al.* (2001) as well as *Streets et al.* (2003). Delhi, Chandigarh and Rupnagar, located in the northern Indian belt, are among the top 10 SO₂ emitting districts in India. Range analysis of SO₂ emissions from Indian districts indicates that the major contributing districts have more than 90% emissions due to coal combustion (*Garg et al.*, 2001). The northern Indian region is also dotted with numerous cement factories (Figure 3.2) and this industry accounts for about 10% of industrial SO₂ emissions in India (*Garg et al.*, 2001).

4.3.3.2 Influence of fires

Although emission inventories have pegged the major contribution to SO₂ levels in India to power generation (46%) and industries (36%) (*Garg et al.*, 2001), the share of biomass burning (6%) is not negligible. In general, the SO₂ emission factors for different types of biomass combustion vary between 0.6-0.8 g kg⁻¹ (*Gadi et al.*, 2003). However, SO₂ emission factors are higher for burning of wood (2.25 g kg⁻¹), agriculture residue and forest biomass (1.55 g kg⁻¹) and animal wastes (1-6 g kg⁻¹), the largest being for dung (*Venkataraman et al.*, 1999). Nevertheless, the northern Indian region has been known to be affected by biomass burning activities during pre-monsoon. These are mainly attributed to farming activities (crop residue burning) with some contribution from forest fires. Since PSCF analysis also shows air masses coming from this region to the observation site during pre-monsoon, it is likely that there could be some contribution from biomass burning activities in elevating the SO₂ levels over Nainital during pre-monsoon.

The impact of the northern Indian biomass burning has been shown in

the enhancement of O_3 levels at Nainital (Kumar et al., 2010). To investigate the impact of biomass burning on SO_2 levels over Nainital, fire data has been obtained from MODIS instrument aboard the Terra and Aqua satellites http: //modis-fire.umd.edu/AF_getdata.html. MODIS monthly fire counts over the northern Indian region (20°-38°N, 60°-95°E) is significant during April (2700 ± 1500) and maximum during May (4600 ± 1100) . To identify which are the probable source grids for fire, the fire counts are first averaged over larger grids $(5^{\circ}x5^{\circ})$. Then the temporal changes in fire pixels over these grids are correlated with SO_2 temporal changes over Nainital. Figure 4.11 shows that the grids spanning 70-80°E and $25-35^{\circ}N$ are positively associated with SO_2 measurements over Nainital during the same period. Interestingly these are the grids where a lot of biomass burning activities occur. Once the large grids are identified, grids of 1°x1° are again identified to correlate the fire pixel counts over these smaller grids with SO_2 concentrations measured at Nainital. Interestingly, it is observed that the grids that show some association with SO_2 are actually related to biomass burning. It is to be noted that most of the red and orange dots are in the Punjab-Haryana region, where lot of biomass burning occurs during pre-monsoon.

4.3.4 Source signatures from SO_2 - NO_y relationships

The relationship between SO_2 and NO_y can serve as useful indicator to the emission source types. In general, a higher SO_2/NO_x ratio (>0.5) indicates coal combustion in large point sources viz. power plants, industries etc (Table 3.2). Lower ratios indicate predominance of NO_x and are generally attributed to the transport sector (*Aneja et al.*, 2001). SO_2/NO_x ratios for different regions of the world (adopted from the EDGAR inventory of the year 2000; *Olivier and Berdowski*, 2001) are estimated to be 0.9, 0.6, 1.4 and 0.3 for Germany, Japan, Korea and Brazil respectively. These represent mostly emissions from the point sources. SO_2/NO_x values for point sources in US were in the range of 0.44 to 2.3 (Aneja et al., 2001). A $\Delta SO_2/\Delta NO_x$ value of 0.39 ± 0.77 was estimated, based on data from University of Houston's Moody Tower supersite, when air masses were arriving from 35 km southwest from a 3800 MW electrical generating unit, the largest of all fossil fuel plants in the U.S (*Luke et al.*, 2010). The $\Delta SO_2/\Delta NO_y$ value increased from 0.83 during winter nights to 1.26 during non-winter days at Linan, China indicating larger contributions from coal burning (*Wang et al.*, 2002).



Figure 4.12: SO₂ - NO_y relationships from measured surface concentrations over Nainital. The correlations are based on SO₂ averages in 100 pptv NO_y bins during winter and 250 pptv bins during pre-monsoon.

In section 4.2.3, significant correlation was observed between surface SO_2 and surface NO_2 over several major urban regions of the IGP. Over Nainital, SO_2 and NO_y seem to correlate well during pre-monsoon and monsoon. The $\Delta SO_2/\Delta NO_y$ values during this period of convective transport of industrial emissions from IGP to Nainital are about 0.57 and 0.40 during pre-monsoon and monsoon (Figure 4.12). It is possible that NO_y values have decreased faster during transport, thus increasing the slope. The $\Delta SO_2/\Delta NO_y$ value will change during transport due to different chemical conversions of SO_2 , NO_x and NO_y . Lack of correlation between SO_2 and NO_y during winter indicates the absence of IGP impact on the observation site, when due to boundary layer dynamics, Nainital is mostly cut off from the lower region. Further, OMI observations indicate that some association exists between free tropospheric SO_2 and PBL SO_2 over the Nainital grid during winter. However, no such association is observed during pre-monsoon. In the free troposphere, transport is more efficient due to reduction of surface layer drag and higher wind speeds. Thus, it can impact larger areas in a short span of time. An example of free tropospheric transport of SO_2 is presented in Section 4.5.

4.4 Transport and emission of trace gases over Kolkata

As shown in Section 4.1, the eastern part IGP is highly polluted. Despite its scientific importance, in-situ measurements of trace gases are very limited over this region. This section presents year-long measurements of SO₂, CO, CH₄ and C₂-C₅ NMHCs during March 2012 - February 2013 over Kolkata, a megacity in the eastern IGP, with a focus on processes impacting their levels. Being a major urban region in tropical South Asia, Kolkata can significantly influence the regional chemistry. The outflow of IGP pollution into the BoB occurs over this region as the winds turn towards south instead of going further east. Thus, it is apt to describe Kolkata as the gateway for air pollutants from the IGP to the BoB during winter and post-monsoon and vice-versa during monsoon and pre-monsoon.

4.4.1 Site description and meteorology

Kolkata (formerly Calcutta; 22.55°N, 88.50°E; 6 m amsl), a megacity in Eastern India, is spread over an area of 2000 sq. km with a population of about 15.7 millions. Kolkata is the capital city of the West Bengal state of India (Figure 4.13). Haldia is a major port city, about 120 km south-west of Kolkata with a major refinery. Durgapur and Asansol are two other major industrial townships about 170 and 210 km to the north-west of Kolkata. Huge power plants lie within a few hundred kilometers in the north-west of Kolkata. The study site is located in the campus of Jadavpur University at Salt Lake, a planned township in East Kolkata, with mostly office and residential buildings.



Figure 4.13: The study location in 1. Kolkata (city map on the right). Major power plants a. Farakka (2100 MW) b.Menjia (2340 MW) c. Bakreshwar (1050 MW). Industrial areas: 2. Haldia (petrochemicals), 3. Durgapur (steel industry), 4. Asansol (steel, locomotives), 5. Raniganj (coal fields). Industrial areas in Kolkata:
6. Kasba, Tangra (leather, polymer); 7. Behala, Majerhat (engineering, pharmaceuticals, food); 8. Garden Reach (ship builders).

The city itself has a few small-scale industries mostly located in the southwest of the study location. Dhapa, located south of the study location, is a major landfill site for dumping solid wastes of Kolkata. Excluding two-wheelers (0.18 million) and cars (0.19 million), the city has about 0.45 million registered motor vehicles constituted by trucks (20%), buses (6%), taxi (45%) and autorickshaws (28%). Most of these vehicles run on diesel, auto-rickshaws run on compressed natural gas (CNG) while two-wheelers and cars run on petrol (gasoline).



Figure 4.14: Seasonal patterns of prevailing winds over Kolkata at 200 m amsl. 120 hr backward trajectory data from HYSPLIT are grouped into three major regimes representing pre-monsoon, monsoon and post-monsoon + winter. The altitude of these trajectory groups is shown by the colour bar. Size and colour of the circles (representing thermal power plants) are scaled according to the capacity of the power plants. e.g. The Mudra Thermal power station in western Gujarat has an installed capacity of 4620 MW.

The prevailing wind patterns over Kolkata during the study period are shown in Figure 4.14. Based on their spatial coverage, the air masses may be divided into three major types. During pre-monsoon (March, April, May), Kolkata is influenced by low-level southerly air masses from the Bay of Bengal and coastal India. These air masses spend about 75% time below 500 m and about 15% time between 500-1000 m. During monsoon (June, July, August and early September), the wind regime shifts to south-westerly and brings air parcels from southern peninsular India. These air parcels spend about 64% time below 500 m, 18% time between 500-1000 m and 15% time between 1000-2000 m. A complete reversal of winds takes place during late September. During the post-monsoon (late September, October, November), wind is mostly north-westerly over the study location. During this period, air masses reside about 37% time below 500 m, 21% time between 500-1000 m and 35% time between 1000-3000 m. During winter (December, January, February), the prevailing wind-pattern is same as during post-monsoon, bringing in air-masses from the IGP. The residence times during winter are 37% below 500 m, 31% between 500-1000 m and 28% between 1000-3000 m. Reversal of winds again takes place in March. During pre-monsoon, the trajectories reside 89% time over oceans whereas during monsoon, this value reduces to 43%.

4.4.2 Diurnal variation in surface SO₂

Figure 4.15 shows the diurnal variation of SO_2 over Kolkata during different seasons. A very slight enhancement in daytime SO_2 is observed during premonsoon. The daytime enhancement becomes more conspicuous during monsoon. Elevated daytime values in SO_2 during premonsoon and monsoon are related to southerly winds. Daytime enhancement in SO_2 envisages impacts of photochemistry. It was shown in Figure 4.13 that vast landfill regions exist to the exact south of the study location within 5 km distance. Thus, oxidation of RSCs (which have major sources in landfill sites) may be surmised. There could also be other anthropogenic sources of SO_2 but their emissions will occur both during day and night. Early morning enhancements are observed during post-monsoon. The daytime values are lower due to boundary layer dilution but build-up from evening into the night. Daytime dip in SO_2 concentrations also occur during winter. A gradual increase in SO_2 concentrations from midnight to early morning during winter seems to be a clear effect of decreasing MLD. Absence of evening peaks during winter asserts that vehicular traffic does not significantly impact SO_2 concentrations over this region.



Figure 4.15: Diurnal variations in surface SO_2 at Kolkata for different months during March 2012 to February 2013.

4.4.3 Seasonal variation in surface SO₂

The variation in observed hourly average SO_2 concentrations as a function of wind direction is shown in Figure 4.16. It is clearly observed that the hourly SO_2 concentrations during post-monsoon (mean=4.1 ppbv) and winter (mean=6.7 ppbv) are far higher than those during pre-monsoon (mean=1.4 ppbv) and monsoon (mean=1.6 ppbv). From the figure, there seems to be a dominant effect of prevailing wind regimes, resulting in different catchment areas for SO₂ during the different periods. During post-monsoon and winter, sources are mainly in north and north-west (also Figure 4.17). Decent correlations between daily means of SO₂ and zonal wind (\mathbb{R}^2 =0.22 and 0.30 during winter and post-monsoon; n=90 for each season) and a skewed distribution of SO₂ with wind direction indicate a regional influence. Further, a sudden change in SO₂ levels is observed towards the end of September, along with a concurrent change in wind regime.



Figure 4.16: Variation of hourly SO_2 (ppbv) with wind direction over Kolkata during the study period.

The regional sources potentially contributing to higher SO_2 concentrations during January and July are shown in Figure 4.17. The left panel shows that SO_2 concentrations greater than 75 percentile of January values are related to air masses passing over two towns with steel industries (Bokaro and Durgapur), coal mining regions of Jharia and Raniganj, apart from numerous other industrial townships and polluted areas in West Bengal, Jharkhand, Bihar and Uttar Pradesh. These air masses also intersect with numerous power plants including Menjia (2340 MW), Farakka (2100 MW) and Bakreshwar (1050 MW) (Figure 4.14). Modelling studies have also shown these regions as hotspots for SO₂ emissions (*Adhikary et al.*, 2007). Coal combustion in power plants and steel industries are major contributors to regional SO₂. The right panel shows that SO₂ concentrations greater than 75 percentile of July values are related to air masses coming from the industrial townships of Haldia and Paradeep.



Figure 4.17: Probable source regions contributing to elevated SO₂ concentrations over the study location during a. January b. July. The maps are derived from Potential source contribution function analysis using TrajStat software (Wang et al., 2009). Runtime: 120 hrs, cell size= $2^{\circ}x2^{\circ}$. Pollution criteria: 75 percentile of monthly variation of SO₂. The red grids are the most probable source regions, followed by pink and orange. MTPA: million tonnes per annum.

The average SO₂ concentration during March-August is about 1.5 ppbv, which is about 28% of the average concentration during September-February (5.4 ppbv). This is because the air masses during winter pass over more polluted regions of the IGP. Although numerous power plants lie in the catchment area for SO₂ during March-August (Figure 4.14), dilution effect is larger during this period. *Meng et al.* (2010) attributed lower SO₂ concentrations during summer at several Chinese sites to vertical mixing and removal mechanisms (precipitation, photochemical). Dilution effects can be measured from VC, obtained by multiplying wind speed with MLD. In source regions such as megacities, VC represents the rate by which pollutants will be blown out of the mixed layer over a particular location. MLD values over the study location are generally below 500 m during winter and post-monsoon but extend to 2000 m and above during pre-monsoon and monsoon. Further, wind speeds are higher over Kolkata during monsoon and pre-monsoon (mean= 3.4 m s^{-1}) accentuating the VC values during these periods. Thus higher VC during premonsoon results in dilution of local emissions while lower VC during winter and post-monsoon results in stronger trapping of air parcels transported from other source regions as well as local emissions. Apart from the effect of source contributions, removal mechanisms play a vital role in governing ambient SO_2 levels. The columnar dust AOD at 550 nm over Kolkata during summer is 0.36, which is about 45% higher than winter average (0.25) and could result in higher heterogeneous losses of SO_2 . Adhikary et al. (2007) have discussed the importance of heterogeneous pathways in conversion of SO_2 to sulfate over the Indian region, especially during the dry season. Guttikunda et al. (2001) have also estimated high sulfur deposition over the Indian region during summer.

4.4.4 Source signatures from inter-species relationships

Air samples were collected at 3 hour intervals during daytime on a biweekly basis during the study period. These samples were analysed at PRL for CO, CH_4 and C_2 - C_5 hydrocarbons. The daytime patterns in hydrocarbons during winter revealed high values during morning and evening. The morning values seem to be related to atmospheric stability conditions rather than traffic activity (which should have peaked between 0900-1100 IST). Intense fog, observed almost daily during November to February over the study region, corroborate presence of strong inversions during morning hours. Higher values of C_3H_8 and C_4H_{10} during summer indicate impacts of petrochemical industries. One source region could be Haldia refinery towards south of the study location. Among the measured hydrocarbons, C_4H_{10} contributes about 29% to the C_2 - C_5 total, followed by C_3H_8 (25%).

Excellent correlations are observed for butane isomers over Kolkata (Figure 4.18). The slope matches the values (0.34-0.52) obtained over several sites in UK which was attributed to evaporative emissions from petrol station refuelling and refinery operations (*Derwent et al.*, 2000). C_4H_{10} also shows good correlations with C_3H_8 , alluding to LPG emissions (Table 1.1). Good correlation of n- C_4H_{10} with C_2H_2 confirms impact of vehicular emissions. Overall, strong correlations among C_3H_8 , C_4H_{10} and C_2H_2 suggest impacts of local vehicular emissions as well as influence of LPG. Associations between C_2H_4 and C_3H_8 suggest additional co-emissions from combustion sources. Strong correlations between CH_4 , C_2H_6 and C_2H_4 during winter compared to pre-monsoon also indicate influence of combustion sources (BM/BF).



Figure 4.18: Correlations between CO, CH_4 and NMHCs (C2-C5) over Kolkata during 2012-13.

CO is strongly correlated to CH_4 , C_2H_6 , C_2H_4 , C_2H_2 and C_4H_{10} during
winter indicating impacts of BM/BF burning (Figure 4.18). Since not much biomass burning occurs during this period, it is more likely that biofuel burning along the east IGP is the major source of CO (Table 1.1). The $\Delta C_2 H_6 / \Delta CO$ value obtained in this study (0.0076 ppbv/ppbv) is very close to the values obtained for Ahmedabad (0.008; Sahu and Lal, 2006a and Hissar (0.01; Lal et al., 2012 as well as East Asia (Wang et al., 2004b). Further, $\Delta C_2 H_4 / \Delta CO$ value of 0.02 and $\Delta C_2 H_4 / \Delta C_3 H_6$ of 1.4 obtained by (Lal et al., 2012) are close to winter values obtained in this study (Figure 4.18) indicating impacts of biofuel on CO values. However, there are bound to be significant impacts of fossil fuel combustions to CO levels in the IGP as suggested by low $\Delta C_2 H_6 / \Delta C_3 H_8$ $(slope=0.2, R^2=0.6)$ during winter. Good correlations also exist between CO, C_3H_8 and $n-C_4H_{10}$ during winter, corroborating co-emissions from petrochemical industries/LPG sources (Table 1.1). Further, correlations of CO with hydrocarbons are very poor during pre-monsoon. Efficient mixing of various emissions from various collocated sources accompanied by boundary later dilution results in weak source signatures during pre-monsoon. Hence measurements of specific tracers like 3-methyl pentane (gasoline marker) or CH_3CN (biomass burning indicator) are desirable.

The unique combination of SO₂, CO and NMHC measurements allows to establish that SO₂ is more likely to be impacted by regional anthropogenic sources (power plants, industries and refineries) rather than local emissions (transport, residential) (Figure 4.19). This is because SO₂ is more strongly associated with CO and C₂H₆ and exhibits poorer correlations with gases emitted locally (C₃H₈, n-C₄H₁₀ and C₂H₂) during winter. This is corroborated by PSCF analysis and weekday/weekend ratios. Nevertheless, being a major urban region, there would still be local emissions of SO₂ impacting its background concentrations. The observed Δ SO₂/ Δ CO value during winter is lower than an estimate of 0.045 over China, which was attributed to coal burning (*Wang et al.*, 2004b). This could be due to lower sulfur content of Indian coals.



Figure 4.19: Correlations between SO₂, CO, CH_4 , C_2H_6 and C_3H_8 over Kolkata during 2012-13.

4.4.4.1 Positive matrix factorization

Positive matrix factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into matrices that facilitates grouping of sources based on observations at the receptor site. PMF v3.0 was utilized in this study using 10 gaseous species and 70 samples. Details regarding this method can be found in *Ling et al.* (2011) and references therein. The analysis resulted in 6 major factors (Figure 4.20). Factor 1, dominated by i-C5H10, is identified as gasoline evaporation (Table 1.1). Factor 2 and 4, dominated by C_2H_2 and C_2H_4 , seem to be related to traffic emissions, mainly diesel (*Ling et al.*, 2011). However, factor 4 also has substantial influences from C_2H_6 , CH_4 and CO, and thus seems to be a mixture of both biofuel and fossil fuel. Factor 3 is dominated by SO_2 and related to coal combustions (power plants and industries). Factor 5 is dominated by C_3H_8 and C_4H_{10} and connotes influence of LPG (Table 1.1). Factor 6 is dominated by CH_4 and CO (and some C_2H_6) and seems to be related to biomass/ biofuel combustion (mainly biofuel).



Figure 4.20: Analysis of source profiles (percentage of species total) resolved with PMF.

4.5 Trans-continental transport of volcanic SO₂

Combustion of fossil fuels (coal and petroleum products) constitutes a continuous source of anthropogenic SO_2 into the atmosphere. However, natural sources like volcanoes can also inject copious amounts of SO_2 directly into the troposphere and sometimes even into the stratosphere. These event based volcanic eruptions provide solitary opportunities to study transport and transformation of atmospheric constituents. In this section, an episode of high SO_2 concentration over the Northern India and IGP, as a result of long-range transport from Africa, is explored using multiple satellite observations. Though, volcanic SO_2 plumes have been extensively studied over many parts of Asia, Europe and USA, analysis of such events for the IGP region is being reported for the first time.

4.5.1 Enhanced SO₂ over IGP

Monthly OMI columnar SO₂ and NO₂ during 2005-2010 over different geographically and climatologically distinct regions in India are shown in Figure 4.21. While SO₂ values are generally less than 0.3 DU during the entire period of six years, conspicuously elevated columnar SO₂ are observed over multiple stations in the IGP (Ludhiana, Delhi, Kanpur, Durgapur, and Kolkata) during November, 2008. The observed SO₂ columnar values are 0.75 DU and 0.9 DU over Delhi (28-29°N, 77-78°E) and Durgapur (23-24°N, 86-89°E) regions respectively. Noticeably, this feature is not observed for stations in north-eastern (Guwahati: 25-26°N, 91-92°E), western (Ahmedabad: 22-24°N, 72-73°E), central (Nagpur: 20-21°N, 78-79°E) and southern (Chennai: 12-13°N, 79-80°E) regions of India. It is also noticed that the elevated concentrations during this period are only for SO₂ and are neither educed for trace gases like NO₂ (Figure 4.21) which originate from fossil fuel combustion nor from CO which is produced mainly from biomass burning as well as fossil fuel combustion.

Further analysis of the daily data of SO_2 columns during November, 2008



Figure 4.21: Time series of monthly column concentrations based on OMI data during 2005-2010 for various regions over India. Latitude and longitude of lower left of each grid over a station is shown within braces adjacent to the respective station name. The top and bottom panels are for SO_2 (in DU) and NO_2 (in molecules per square centimeter), respectively.

revealed elevated columnar burdens during November 5-7 over several regions in the IGP (Ludhiana, Delhi, Kanpur, Durgapur, and Kolkata). While SO_2 levels in Ludhiana region were the highest (2.2 DU) on November 5, rest of the places showed elevated values on November 6. Highest SO_2 level was about 6.2 DU over Durgapur on November 6, 2008. This was followed by columnar SO_2 of about 4.7 DU, 3.6 DU and 2.9 DU over Delhi, Kolkata and Kanpur. It is to be noted that this was a transient phenomenon i.e. the values peaked and receded in a span of 2-3 days. However, the loadings of SO_2 during November 5-6 were copious enough to affect the monthly average of November, 2008. Further, the feature was reciprocated by several locations in the IGP, giving it a regional perspective.



Figure 4.22: Spatial averaged SO₂ columns (DU) during November 4-7, 2008 based on OMI data.

The columnar OMI SO₂ imageries over the 0-50°N and 20-100°E region during November 4-7, 2008 are shown in Figure 4.22. The top panel shows a strong source of SO₂ over the 'Red Sea' on November 4, 2008 (Figure 4.22a). The source gave rise to a SO₂ plume that travelled over Iran, Pakistan and North-West India on November 5 (Figure 4.22b). The plume had encompassed the entire IGP region on November 6 leading to high columnar loadings over Delhi, Kanpur, Durgapur etc (Figure 4.22c). These satellite imageries are also in agreement with the higher columnar SO₂ values observed over Ludhiana (Punjab province) on November 5 as the plume entered the Indian region from its northwest boundaries on November 5. Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) observations were used to perceive the vertical distribution of aerosols over this region. Though there was heavy aerosol loading from surface to 3 km (mixing layer) from local sources, a distinct thin layer of aerosols at 4-5 km was observed over this region on November 6 most likely as a result of transport from this volcanic emission (Figure 4.23). The SO₂ plume travelled further towards the Bay of Bengal where it got dissipated around November 7 (Figure 4.22d).

4.5.2 The Dalaffila eruption

Further investigations revealed that the emissions of elevated SO₂ occurred from the Dalaffilla volcanic emission (Volcano number 0201-07) (http://www. volcano.si.edu/) on November 4, 2008. Dalaffilla (13.8°N, 40.5°E, summit elevation 613 m) is located in the Afar region of Ethiopia. It is one of the 6 volcances in the Erta Ale Range rising to an altitude of 300 m above the surrounding terrain. The eruption of lava (which began on November 3, 2008 at 1350 UTC) from Alu-Dalaffilla in November, 2008 was the largest eruption in Ethiopia in historical times (*Wunderman et al.*, 2008). This eruption generated a large cloud of SO₂. A total of 0.1-0.2 Tg of SO₂ had been measured in the eruption cloud by OMI at 1100 GMT on November 4, by which time the SO₂ cloud had reached Southern Iran (*Wunderman et al.*, 2008). As detected by OMI and the Atmospheric Infrared Sounder (AIRS), the cloud initially drifted east over the Arabian Peninsula. The plume top was estimated to be between 13 to 15 km from Meteosat IR data.

The wind flow was from the Arabian Peninsula into the Northern India in the free troposphere (500-200 mb) during November 4-6, 2008. To confirm the source location and plume path, air mass back-trajectories were analyzed using the HYSPLIT model, which is based on National Centers for Environmental Prediction (NCEP) reanalysis data (*Draxler and Hess*, 1998). Figure 4.23 shows 72 hours back-trajectories originating at 8 GMT on November 6, 2008 from the Ludhiana region (30°N, 75°E), the Nainital region (29°N, 79°E) and the Kolkata region (23°N, 88°E). The back-trajectories over each of these locations are calculated for the altitudes of 3, 5 and 8 km and point the plume coming from the Dalaffilla region of Ethiopia.

The radiosonde data available over a few locations along the plume track (Abha, Abu Dhabi, New Delhi and Kolkata) were examined to deduce the atmospheric structure. The virtual potential temperature profile, which takes into account the pressure reduction with height as well as influence of water content on density of air, is a direct indicator of static stability of the atmosphere. Positive gradients in virtual potential temperature with altitude over all the 4 locations indicated a stable atmosphere with minimal vertical mixing during this period (also evident in the CALIPSO retrieval, Figure 4.23). This implies that the SO₂ emitted into the upper troposphere was advected over to downwind regions along with the wind-streams (Figure 4.23) over to the Indian subcontinent.



Figure 4.23: Left– Night-time profiles of 532 nm attenuated backscatter return signal (sr⁻¹ km⁻¹) from the CALIPSO lidar showing the vertical distribution of aerosols on November 6, 2008. Notice the aerosol layer at 4-5 km (encircled) which is well separated from the boundary layer (aerosols below 3 km). The top-right inserted-panel is CALIPSO track over India. Right– Three days back-trajectories originating at 8 GMT on November 6, 2008 from some of the selected locations [Ludhiana ($30^{\circ}N$, $75^{\circ}E$), Nainital ($29^{\circ}N$, $79^{\circ}E$) and Kolkata ($23^{\circ}N$, $88^{\circ}E$) regions] over India.

The presence of a strong anti-cyclone in the extreme east of the IGP as

revealed by vertical winds (omega) of the order of 0.2 Pascal s⁻¹ on November 7 hindered the plume from travelling further east. The downward vertical motion brought down the plume to lower heights where it got mixed up due to convective activity. The Severe WEAther Threat index (SWEAT), which combines wind parameters including shear as well as many other thermodynamic variables including dew point temperature, was very high over Kolkata on November 7. A moist lower atmosphere would have a high scavenging potential for any SO₂ that would cross into this region (*Rai et al.*, 2010). By the time the plume has completely dissipated on November 7, the convective available potential energy was over 1000 J kg⁻¹ (Figure 4.24).



Figure 4.24: T- Φ gram for Kolkata at November 7, 2008 (12 GMT). Dry adiabats are lines are of equal potential temperature (K), saturated adiabats refer to saturation over ice for temperatures less than 0°C, saturation mixing ratio or dew point lines describe the pressure and temperature conditions in which given amounts of water vapor will just saturate 1 kg of dry air. The light pink colored region shows the CAPE.

Considering an average enhancement of 4.7 DU for the Delhi region (28-29°N, 78-79°E); the estimated amount of injected SO₂ by this event of long-

range transport was calculated to be about 1.4 Gg. The annual anthropogenic emissions over this region is around 5.8 Gg SO₂ (estimated from the EDGAR 32FT2000 emission inventory; *Olivier et al.*, 2005). Therefore, the amount of SO₂ injected naturally in a short time was 25% of the annual anthropogenic emissions over this region. Since volcanic eruptions inject SO₂ directly into the free troposphere, where its lifetime is longer, it has greater potential to perturb atmospheric chemical and radiative properties. On the other hand, even though the surface emissions are larger and continuous, considerable amount is lost due to deposition and transformation processes.

4.6 Summary

In this chapter, the variation of atmospheric trace gases over the IGP is investigated in terms of diurnal and seasonal variability, emission characteristics and dynamical processes governing their horizontal and vertical distributions. Hydrocarbon measurements during a road campaign from Ahmedabad to Nainital indicate that western India (except major cities like Ahmedabad) is more dominated by fossil fuels (mainly petrochemicals) while both biofuel and fossil fuel combustions dominate in the IGP region. Measurements made by the CPCB (India) clearly show that surface concentrations of SO_2 and NO_2 over urban regions in the IGP viz. Delhi, Durgapur, Kolkata and Guwahati are highest during winter. Using a combination of surface measurements and satellite retrievals, it has been shown that surface emissions of NO₂ significantly impact its columnar levels over major urban regions in the IGP where secondary production of NO_2 from fossil fuel combustion is substantial. Very low mean SO_2 to NO_2 ratios (<0.2), over Delhi, Kolkata and Durgapur indicate emissions from vehicular traffic as major contributors to the ambient air. Ratios higher than 0.3 are obtained for Guwahati and Nagpur and indicate dominant influence of point sources. OMI retrievals show that SO_2 columnar levels over the Indian region are significantly elevated during monsoon. This feature calls for further investigation and evaluation of the role dry and wet deposition processes for SO_2 removal over the Indian region.

Measurements of SO_2 and NO_y over Nainital during 2009-2011 have provided useful information on the transport of IGP emissions over to this pristine background location. Daytime elevations in SO_2 were also observed at Nainital throughout the year. However, these elevations were caused by transport due to valley winds. The seasonal variation of SO_2 show high values during pre-monsoon and low values (sometimes below the detection limit of the instrument) during winter. The high values during pre-monsoon are attributed to effective transport of air masses (favored by a high PBL) from the IGP and Northern Indian plains to the study location. Again, the sources of SO_2 are several high capacity thermal power plants and industries where coal is used. Low levels of SO_2 over Nainital during monsoon are attributed to oxidation losses, wet scavenging and dilution of IGP pollution by monsoon winds. Despite high SO₂ concentrations in the IGP, boundary layer dynamics prevents transport of IGP emissions to the observation site at Nainital during winter. This leads to very low SO_2 levels over Nainital which lies several hundred meters above the regional boundary layer during winter.

A year-long study of SO₂, CO and hydrocarbons over Kolkata, a megacity in the region of IGP outflow to the BoB, during 2012-13 enabled interpretation of emission characteristics for the first time over this South Asian megacity. Interspecies correlations showed the dominant influence of LPG leakage and petrochemical industries to local air quality during winter apart from vehicular traffic. Correlation analysis showed that CO is dominated by biofuel combustions. High levels of SO₂ during winter (>6 ppbv) over Kolkata are attributed to regional emissions from coal burning (in industrial areas and power plants) in the eastern IGP and subsequent trapping of these air masses favoured by a stable atmosphere with low ventilation coefficient.

High levels of SO_2 over several regions of the IGP during November, 2008 were attributed to the long-range transport from a volcanic emission in Africa. Although the Dalaffilla volcanic eruption that occurred in Ethiopia on 4 November (2008) was not a major one, yet it released significant amount of SO_2 to increase columnar levels over IGP sites to above 6 DU, which was far above the monthly background concentrations of <0.3 DU, observed during 2005-2010. As SO_2 and its bi-products (particulates matter) have potential environmental and climatic implications, specifically over a polluted region like IGP; such long-range transport events could also be used as a tracer to evaluate the regional and global models.

Chapter 5

Role of transport and chemistry on distribution of trace gases over the Bay of Bengal

The marine environments of the Earth serve as the source and sink of several atmospheric trace gases and aerosol particles. The Bay of Bengal (BoB), the largest bay in the world, is a region of active chemical cycling driven by photochemistry and transport (advection, convection and entrainment) and offers a unique natural laboratory to probe these processes. While the BoB occupies only 0.6% of global oceans, the importance of this marine region lies in the virtue of its location in the north-eastern part of the Indian Ocean. Not only does it serve as a corridor for one of the most important monsoonal systems of the world (the Indian Monsoon), it also lies downwind to the most populated and polluted regions of the globe viz. India and South-East Asia. Specifically, during post-monsoon and winter months, pollutants are transported from different source regions in Asia into the BoB via strong low-level winds. This transport of pollutants from the Asian region is popularly known as 'Southern Asia outflow'. These plumes are fed by emissions comprising combustion of fossil fuels and traditional bio-fuels as well as biomass burning. These plumes are also domains of chemical and photochemical reactions leading to transport, genesis and transformation of O_3 and its precursors. Further, presence of convection during summer-monsoon causes some of these gases to be lifted higher up into the atmosphere and distributed over a larger region of the globe. Consequently, the region assumes global significance. Thus, simultaneous measurements of O_3 and its precursors are highly desirable over this marine region to better understand the short and long-range transport of pollution, en-route photochemical transformations within the MABL.

5.1 A brief background of trace gas studies over the BoB

During the 'Indian Ocean Experiment (INDOEX)', O_3 levels over the BoB sometimes exceeded the levels in nearby coastal cities, highlighting the complexity of chemistry and dynamics over this region (Mühle et al., 2002; Lelieveld et al., 2001). The INDOEX-99 revealed two major pathways for South Asian pollutants to the Indian Ocean: first one from the IGP via the BoB and second one from South-West Asia via the Arabian Sea. Detailed chemical study of BoB air masses was first attempted through the 'Bay of Bengal Experiment' (BOBEX I) when measurements of O₃, CH₄, CO and sulfur-hexafluoride were made during February-March, 2001 (Lal et al., 2006). High levels of O_3 (>60 ppbv), observed over the central BoB (10-14°N) during BOBEX I, were traced to Bangladesh and Myanmar regions. Measurements of NMHCs over the BoB were initiated during the 'Bay of Bengal Process Studies (BOBPS)' in September-October 2002 (Sahu et al., 2006). Subsequent measurements, made during February 2003 (BOBEX II; Lal et al., 2007), enabled characterization of air masses using trace gas ratios. Strong correlations of C_2H_6 and C_2H_2 with CO provided chemical evidence of transport of anthropogenic emissions into the MABL. The spatio-temporal heterogeneity and effects of continental

transport on the distributions of trace gases over the BoB were investigated further during the 'Integrated Campaign for Aerosols, gases and Radiation Budget' (ICARB) during March-May, 2006 (Srivastava et al., 2012b). Further, surface measurements of O_3 , CO and NO_2 were investigated during the winter phase of ICARB (W-ICARB) during December 2008 to January 2009 (Asatar and Nair, 2010; David et al., 2011). While there have already been a few campaigns to study trace gas variability over the BoB, measurements had been lacking during monsoon (June, July and August) and later half of post-monsoon (October and November) periods. The current campaign was conducted to reduce this temporal gap through reporting of extensive measurements of O_3 along with its several precursors during October-November, 2010. During this period, sudden increase in pollution levels (due to changing wind regimes) are supposed to affect the air over the BoB, which has been cleansed by the preceding monsoon circulation. In the present chapter, we explore the behaviour of O_3 and its precursors over different regions of the BoB in terms of transport and chemistry.

5.2 Details of the experiments aboard the cruise

5.2.1 The cruise track

The annual wind pattern at 10 m above mean sea level (AMSL) is shown in Figure 5.1. The three panels show 7 day backward-trajectories at 3 different latitudes (a. 8°N representing South BoB, b. 13°N representing Central BoB and c. 18°N representing North BoB) along the 90°E longitude. Figure 5.1 shows that during winter (represented by January), the BoB is under the ambit of continental air from the IGP, Pakistan and Arabian peninsula, transporting pollutants and dust from these far off regions. However, during summer (represented by April), the surface level winds are mostly of local marine origin. During monsoon (represented by July), winds are from the south representing pristine, marine air masses of the South Indian Ocean. The post-monsoon season is generally a transition period and as elucidated in Figure 5.1, wind regimes change as one move across latitudes along a longitude (influences of Indian Ocean, South-East Asia and Indian subcontinent over south, mid and north BoB respectively). This campaign was conducted to access air masses originating from these different source regions.



Figure 5.1: The three panels show 7 day backward trajectories originating at 10 m AMSL at 3 different latitudes (a. 8°N, b. 13°N and c. 18°N) along the 90°E longitude during 2010. Trajectories in different colours represent different seasons [Dark green: January (winter); Light green: April (summer); Blue: (monsoon) and Pink: November (post-monsoon)]. Trajectories are based on NOAA reanalysis data and plotted using TrajStat software (*Wang et al.*, 2009).

The cruise track of the campaign aboard the Ocean Research Vessel Sagar Kanya (SK-277) is shown in Figure 5.2. The ship sailed off the Chennai port (13.1°N, 80.6°E) on 28 October, 2010 at 0320 IST (IST= GMT + 5.5 hrs) and headed in a south-east direction till about 8°N, 89°E on 31 October, 2010. The ship docked back at the Chennai port on 17 November, 2010 at 1930 IST. There were several halts in between of varying time periods, ranging from a few minutes to more than a day, for other scientific activities (it was a multi-disciplinary cruise).

5.2.2 Measurement details

Trace gases aboard the cruise were monitored by on-line analyzers. Atmospheric air was drawn from the bow of the ship at 10 m above the sea level



Figure 5.2: The cruise track of ORV Sagar Kanya (SK-277) is shown by the green line. The cruise started from Chennai port on 28 October, 2010 and returned to the same place on 17 November, 2010. The (Lat-Long) circles mark the position of SK-277 at 00 hrs of each day. The cross symbols denote the positions where air samples were collected. The arrow marks indicate the travel path during the campaign.

through a 50 m long, 10 mm ID PFA Teflon tubing with an inverted Teflon funnel at the input side to minimize smoke-stack contamination and ingress of water from high waves. A suite of trace gas and aerosol instruments were connected to the other end of the tube via a manifold. The total flow through the 50 m tube resulting from suction generated by this suite of instruments was around 33 liters per minute. At this flow rate, the total air volume in tube (4 litres) would be drawn in about 8 s. Hence, it is assumed that residence time effects in the sample line would be negligible. While the O₃ instrument drew sample air directly from the manifold, the CO and NO_x analyzers drew the same air from the manifold through an additional peltier based moisture removal unit. The laboratory temperature, where analyzers were placed, was maintained around 26°C. A common exhaust from all the analyzers was vented out through the back side of the ship. Calibration checks (zero and span tests) were done on a daily basis during the cruise.

Air samples were collected regularly during the cruise from the top of a bow tower (10 m height) on the deck of the ship at every 4-hour intervals during days and nights when the ship was in motion with a speed of at least 6 knots (kt) or more. These samples were later analyzed in the laboratory at Ahmedabad for CH₄, CO and light NMHCs (C₂-C₄) within two months of the cruise to minimize storage problems (Figure 2.12). The CO values obtained during the cruise from two independent measurements viz. using online analyzer and via GC analysis of air samples showed a good correlation (R²=0.85), confirming the representativeness of the collected samples.

Meteorological parameters were measured by sensors placed on an automatic weather station (AWS; Komoline Electronics Pvt. Ltd., India) in the upper deck of the ship. Temperature was measured by a 'precision resistance temperature detector' with an accuracy of $\pm 0.1^{\circ}$ C. RH was measured by a capacitive element with an accuracy of $\pm 2\%$. Wind speed and direction were measured with accuracy of ± 2 m s⁻¹ and ± 2 degrees respectively. Solar radiation was measured with an accuracy of ± 5 W m⁻². The speed of the ship was calculated from the latitude and longitude values obtained using the GPS. Since the AWS was fixed to the ship and the ship was in motion, the wind direction measured by the wind direction sensor would be a relative value. This measured wind direction was corrected using Equation 5.1, and values recorded independently by the AWS compass and another hand-held compass.

True wind direction = measured wind direction +
compass direction (recorded in data-logger) –
angle between compass and wind pointers
$$(5.1)$$

The angle between compass pointer and the wind pointer was independently measured at 82° both before and after the cruise. If the value of true wind direction comes out to be negative, 360 is added to the output value.

Data analysis involved removing data till 10 minutes after zeroing of the NO_x and CO analyzers (allowing sufficient time for reaction chambers to be flushed by ambient air). Similarly, data up to 15 minutes after completion of span calibration were filtered out to allow the reaction chamber (of the respective analyzers) to measure ambient values. Data were also checked for contamination when the ship speed was less than 6 kt. Further, data contaminated due to ship exhausts and/or emissions from trawlers passing in vicinity of the ship were identified and filtered.

5.3 Air masses over the BoB

While ambient air temperatures during the cruise showed clear diurnal variations, there were several instances of large fluctuations. Some of the largest fluctuations in temperature e.g. large decrease on 7 November coincided with a simultaneous increase in RH above 90%. The daytime maximum in solar radiation on the same day was also below 500 W m⁻² resulting in a drop of air temperatures near the surface and representing cloudy/rainy conditions. Similar conditions were encountered on 3 and 15 November also. A drop in RH values below 60% was observed on 10 November, when the ship was stationary at the northern part of the transect (18°N). The daytime maximum solar radiation was observed to be higher than 700 W m⁻² on most of the days, while 3, 7 and 15 November were found to be significantly cloudy. Heavy rainfall was observed on 30-31 October, 7 and 15 November. In general, wind speeds were below 10 m s⁻¹ until 4 November. However, higher wind speeds (over 13 m s⁻¹) were observed during 4-6 November, when cyclone Jal was pervading over the BoB. Wind speeds decreased steadily after 6 November. The wind speeds started increasing since 14 November and another maximum above 13 m s⁻¹ was observed on 15 November.

5.3.1 Air mass types

Backward trajectory analysis for the cruise days was used to group the air masses into various transport regimes. The trajectories were calculated based on ensembles at 500 m above the receptor locations of the moving ship, originating 5 days back in time, using the HYSPLIT model driven by NCEP reanalysis data with model vertical velocity to compute vertical motions. The model was run to calculate ensemble trajectories at 8 hour intervals i.e. 0230, 1030 and 1830 IST for each day. For grouping the air masses, simultaneous averaging of latitude as well as longitude was carried out. To achieve this, trajectories leading to similar air masses and continuous in time were bunched together. Then, the trajectory data was averaged for mean latitude (λ) with 1 sigma at different time intervals. Similar averaging was done for longitudes (ϕ). Further, these values along with their error bars were averaged by transforming from Cartesian to polar co-ordinates (angle θ and radius ρ) to get the spread in latitude and longitude (Equation 5.2).

$$[\theta, \rho] = \text{Cartesian to polar} \left[\phi \left(\text{mean} \pm \sigma\right), \lambda \left(\text{mean} \mp \sigma\right)\right]$$
(5.2)

The values in $[\theta, \rho]$ in polar co-ordinates were converted back into Cartesian coordinates to get the actual mean and sigma of latitudes and longitudes at different temporal points up to 120 hours backwards. This kind of averaging gives a better representation of air masses in contrast to only latitudinal or only longitudinal averaging which could be biased in favor of air masses arriving from a particular direction. The resultant grouping of air masses shows four distinct types (Figure 5.3) viz.

a. Marine air from the Indian Ocean (IO)

b. Continental air from South China (Macao and Hong Kong), Vietnam, South Myanmar and over the East Bay of Bengal (NE-BoB)

 c. Air masses from North Bay of Bengal, eastern Indo-Gangetic Plain, Bangladesh and Myanmar (N-BoB).



d. Air masses from East Bay of Bengal, South Myanmar, Cambodia and coastal Thailand (E-BoB).

Figure 5.3: Air mass groups encountered aboard ORV Sagar Kanya during 28 October - 17 November, 2010. The altitude variations of these air masses are shown using different colours. The colored lines represent the spread of the trajectory group about the mean trajectory.

The IO group was observed during 28 October (1830 IST) to 2 November (0230 IST) and was predominantly marine. The NE-BoB air mass represents long-range transport during 3 November (1830 IST) to 8 November (1030 IST). While the NE-BoB represents SE-Asian air masses, the N-BoB is constituted by air masses from nearby northern land-masses over the IGP, Bangladesh and some portion of Myanmar as well as the marine regions over North BoB during 8 November (1830 IST) to 14 November (0230 IST). The E-BoB air masses were encountered during 14 November (1030 IST) to 16 November (1030 IST) and resembled the NE-BoB air masses in terms of their spatial coverage with a few distinct differences. The most copious difference is that the NE-BoB air masses represent long range transport i.e. originate further east considering the 5 days temporal span. Further, the NE-BoB air masses spent greater time above 3 km altitude while E-BoB had large marine influence (Figure 5.4).

5.3.2 Residence time of air masses

Residence time analysis is used to classify the air masses into different horizontal and vertical regimes. The residence times were computed using back air trajectories generated by HYSPLIT model for the ship's locations at every 8 hour intervals during the cruise (Figure 5.4). To compute residence times over continental and marine regions separately, a proxy method was used. In this method, images were generated such that 5 day back-trajectories were plotted over maps with the continental regions in black, oceanic regions in white and every hourly latitude-longitude values of trajectories as red points. Next, these images were analyzed to identify a red dot surrounded by black dots. The total number of such red dots gives the number of points falling over continents. Similarly, number of points falling over oceanic regions was computed from the number of pixels that had a colour difference from neighbouring pixels equivalent to difference between red and white. For red points which have both black and white as neighbours i.e. for coastal locations, more weight is given to continents if there are more black points as neighbours and vice versa. There would still be some error in this method if a trajectory crosses itself at some point of time, but we consider this negligible. Thus, this analysis provides a robust, efficient and fully automated way of segregating the trajectory points into continental and oceanic types. The analysis showed that IO air mass had spent almost 97% time over oceanic regions (Figure 5.4), and hence correctly represents marine signature. In contrast, the NE-BoB air mass had spent only 41% time over oceanic regions and 59% over continental South Myanmar, Vietnam and Hong-Kong region of China. The N-BoB air mass had spent 58% time over North BoB and 42% over North-West Myanmar, East Bangladesh and North-East India). The E-BoB air mass had a large marine influence (78% time over East BoB) but considerable continental influence as well (22% time over Myanmar, Thailand and Vietnam).

Residence times were also computed for different altitude ranges (Figure



Figure 5.4: Variations of residence time of air parcels encountering the cruise during 28 October - 17 November, 2010 over the Bay of Bengal; Top: different altitude bins; Middle: % residence times over continental and marine regions.

5.4). The trajectories belonging to IO group spent 81% of their time below 750 m and 19% time between 750-1500 m altitudes. Trajectories in NE-BoB air mass spent 17% time above 3000 m, 28% between 1501-3000 m, 26% between 701-1500 m and 28% below 750 m altitude. Similarly, trajectories in N-BoB air mass spent 7% time above 3000 m, 38% between 1501-3000 m, 35% between 701-1500 m and 20% below 750 m altitude. The trajectories E-BoB spent 45% time between 701-1500 m and 55% below 750 m altitude. Thus, these trajectories spent most of their time in lower altitudes, unlike the NE-BoB air

masses. It must be noted that while the altitudinal distributions of the IO and E-BoB air masses are fairly similar, their spatial coverage is entirely different as explained in the preceding section.

The MABL for the IO air masses varied mostly between 250-750 m. These MABL values were calculated from HYSPLIT model using NCEP meteorological data. MABL values were highest in the NE-BoB air mass on 4 November. The average MABL gradually decreased from 4-11 November as the ship moved towards northern latitudes. The night-time MABL value around 10 November was about 600 m. During the return leg, the MABL values again continued to increase and were around 1000 m on the mid-day of 16 November. The average MABLs (mean of 0600, 0900, 1200, 1500, 1800 and 2100 IST) in the IO, NE-BoB, N-BoB and E-BoB air masses were 475, 1140, 706 and 820 m respectively.

5.4 Variability of trace gases over the BoB

5.4.1 Variations in O_3 , CO and NO_x

Variations in O_3 , CO and NO_x during the cruise are shown in Figure 5.5. Both O_3 and CO gradually increased during 2 to 6 November when the ship was moving towards the northern BoB i.e. from about 8°N to 18°N. During 7-10 November, the ship did not change its location much (Figure 5.2), however, O_3 as well as CO showed slight decrease in the levels. Interestingly, during 14-17 November, although the ship was approaching towards coastal Indian region (Chennai), O_3 and CO (as also CH₄, C₂H₆ and C₂H₂, shown later in Figure 5.9) values showed a decreasing tendency. This was because the air-masses encountered were not coming from the Indian sub-continent, but were influenced by marine regions over the East BoB. During the complete cruise, a wide range of O_3 concentrations were encountered from as low as 11 ppbv in the open ocean (29 October) to over 60 ppbv in the North BoB

(6 and 11 November). O_3 values of 28 ppbv were measured off the Chennai coast both at the beginning and end of the cruise. CO mixing ratios varied from a low (45 ppbv on 30 October) to about 260 ppbv (7 November). The lowest CO values were observed coinciding with the very low O_3 values (30 October) but the highest CO values did not coincide with the highest O_3 values. NO_x levels varied from 0.2 ppbv (28 October and 15 November) to 1.2 ppbv (2 November). Lowest NO_x values (0.2 ppbv) were encountered on 28 October and 15 November in the open ocean. However, the NO_x levels seemed to increase during 29 October - 2 November period, when the ship moved southwards towards lower latitudes into the open ocean. A decrease in NO_x levels was observed during 11-15 November during the return leg of the cruise.

Species	ΙΟ	NE-BoB	N-BoB	E-BoB
O ₃	20.1 ± 3.5	46.9 ± 6.1	45.9 ± 9.7	32.9 ± 4.6
CO	73.4 ± 13.7	234.9 ± 23.1	198.0 ± 27.1	200.2 ± 39.9
NO _x	0.60 ± 0.18	0.71 ± 0.16	0.59 ± 0.13	0.39 ± 0.12
C_2H_6	0.49 ± 0.08	1.64 ± 0.18	1.73 ± 0.15	2.58 ± 1.25
C_2H_4	0.10 ± 0.04	0.18 ± 0.05	0.13 ± 0.05	0.10 ± 0.05
C_3H_8	0.05 ± 0.02	0.21 ± 0.12	0.17 ± 0.20	0.14 ± 0.10
C_3H_6	0.06 ± 0.04	0.06 ± 0.03	0.07 ± 0.03	0.07 ± 0.02
$i-C_4H_10$	0.05	0.06 ± 0.01	0.10 ± 0.07	0.10 ± 0.09
$n-C_4H_10$	0.04 ± 0.01	0.07 ± 0.02	0.12 ± 0.08	0.09 ± 0.09
C_2H_2	0.09 ± 0.05	0.65 ± 0.11	0.65 ± 0.24	0.44 ± 0.17

Table 5.1: Trace gas levels in different air masses (units in ppbv) during 28 October17 November, 2010.

The mean concentrations of different trace gases measured in different air masses during the cruise are shown in Table 5.1. It is observed that mean O_3 ,

CO and NO_x levels were highest in the NE-BoB air mass, indicating anthropogenic contributions. In general, O₃ and CO values were high when wind direction was between 30-90° (Eastern sector) and wind-speed was above 12 m s⁻¹ (Figure 5.6). These conditions were encountered during 4-6 November. It must be noted that O₃ and particularly CO values were high when ventilation coefficient (VC) was greater than 8000 m² s⁻¹. VC was obtained by multiplying wind speed (m s⁻¹) with the marine atmospheric boundary layer height (MABL; m). In sink regions such as oceans, VC represents the rate by which pollutants will be blown into the mixed layer over a particular location. Particularly for the NE-BoB air mass, wherein wind speeds were consistently high (mean=9.6 m s⁻¹) and MABLs were also very high, a high VC allowed for the long-range transport of continental emissions into the MABL, resulting in higher levels of several trace gases (Table 5.1).

Nevertheless, NO_x levels were conspicuously high (0.60 ± 0.18) in the IO air mass, which is supposed to be have a pristine marine characteristic. It is possible that the IO air mass, which is sourced to southern marine regions, could be affected by NO_x emissions from international shipping lanes along Yemen - Sri Lanka - (Malayasia - Sumatra) corridor.

Figure 5.5 shows sudden enhancement in O_3 and CO values around 2 November and these values were constantly increasing during 3-6 November. While the general increase in trace gas concentrations after this period occurred due to transport from China and South-East Asia, the sudden increase is suggested to be associated with the cyclone 'Jal', over the Bay of Bengal during this period. It has been shown that the presence of Cyclone Jal had led to a low pressure system along with very peak wind speeds of over 100 km h⁻¹ (Figure 5.7). Such strong winds could have resulted in the faster transport of continental air masses into the Bay of Bengal. However, the cyclone did not directly intercept our cruise track as the ship was heading towards North BoB when the cyclone was moving towards Chennai.

Two episodes of high CO (>250 ppbv) occur during 6 and 14 November.



Figure 5.5: Variations of O_3 , CO and NO_x along the cruise track during 28 October - 17 November, 2010. The mean (black) and sigma (grey) are shown for every 30 minutes. The time axis is divided to represent different air masses encountered during the cruise.

PSCF analysis was used to identify the geographic source regions possibly contributing to these enhanced levels. PSCF analysis was carried out for the receptor regions (16°N, 89°E and 12°N, 87°E) where CO values were over 250 ppbv during 6-7 November and 14-15 November respectively. The analysis was based on CO gridded daily averages from MOPITT. The threshold value was taken at 75 percentile of the data available over the grid. The analysis indicates Myanmar, Thailand and southern tip off Guangdong (China) as most potential contributors of CO to the air parcels encountered on during 6-7 November. The potential contributor regions to enhanced CO during 14-15



Figure 5.6: Variation of wind speed (m/s) and wind direction along with concentrations of O₃ (ppbv) (Left panel) and CO (ppbv) (Right panel).

November are found to be the south of Myanmar (Kayin) and Thailand (TAK region) (Figure 5.8). The 'Moderate Resolution Imaging Spectroradiometer' (MODIS) fire maps indicated that these regions were actually influenced by fire activities during this period.

A composite of the observations of O_3 and CO made during 7 ship campaigns conducted over the BoB are compiled in Table 5.2 to understand the seasonal variability of these gases. O_3 levels over the BoB are observed to be the highest during winter months (36 ± 8 to 54 ± 17 ppbv) and lower during spring (22 ± 1 to 28 ± 14 ppbv). O_3 levels exhibit a secondary enhancement during November (41 ± 9 ppbv). Similar to O_3 variability, CO levels are also highest during winter (155 ± 43 to 228 ppbv) suggesting that the BoB is most polluted during winter season which is mainly attributed to the strong continental outflow. CO levels also discern a secondary enhancement during November (197 ± 44 ppbv) similar to O_3 . In contrast to O_3 , CO levels are moderately higher during spring (145 ± 38 to 162 ± 3 ppbv). Notably, despite of numerous efforts by several groups (Table 5.2), measurements of O_3 during May to August are still lacking. Measurements of O_3 precursors are even more lacking and therefore highly desirable to better understand the chemical and



Figure 5.7: Left panel: Track of cyclone 'Jal'. 7 days backward trajectories encountering the cruise track during 2 and 3 November are also shown. Altitude variations of the backward trajectories are shown in the bottom panel. Right panel: Wind streamlines and Omega at 850 hPa.

dynamical processes over the BoB.

5.4.2 Variations in CH₄ and NMHCs

Variations in CH₄, CO and C₂-C₄ NMHCs measured during the cruise are shown in Figure 5.9. The mean values for different air masses are also presented in Table 5.1. CH₄ values varied between 1.6-1.9 ppbv for most of the samples. CH₄ values were highest around 10 November. The variation of C₂H₆ was very similar to the variation of CO (R²=0.68) indicating co-located sources. The average C₃H₈ for all the air samples collected during the cruise was 0.142 ppbv with a sigma of 0.105 ppbv. Similar variation in C₃H₈ values ($\sigma > 60\%$) were also observed during the Trace-P measurements (*Wang et al.*, 2003). Highest C₃H₈ value (>0.3 ppbv) was observed on 5 November in the NE-BoB air mass.

During the BOBPS campaign over the BoB (Sahu et al., 2006), C_2H_6 and C_3H_8 values for oceanic air masses were 0.598 ± 0.140 and 0.192 ± 0.060 ppbv



Figure 5.8: Left: Potential source contribution function (PSCF) maps for the receptor region 12°N, 87°E during 14 November at 100 m AGL. The colour axis represents the probability of a grid as potential contributor to the receptor region. Right: Satellite imageries of MODIS fires during 7-16 November, 2010. The MODIS fire maps accumulate the locations of the fires detected by MODIS on board the Terra and Aqua satellites over a 10-day period. Each colored dot indicates a location where MODIS detected at least one fire during the compositing period.

respectively. The C₂H₆ values during this cruise for the pristine, marine air (Table 5.1) are close to the *Sahu et al.* (2006) oceanic values while C₃H₈ values for this air mass are very low compared to those values. However, our C₃H₈ measurements in IO air mass compare very well with INDOEX BoB plume results of 0.050 ± 0.036 ppbv C₃H₈ (*Mühle et al.*, 2002). C₃H₈ values less than 0.025 ppbv were detected south of 16oN over BoB during INDOEX. It is also pertinent to mention here that the air masses encountered by *Sahu et al.* (2006) were coming either from southern oceanic regions or from the Indian landmass. In our case, the air masses originated from southern marine regions during the first few days only. The air masses during major part of the present campaign were directed from North and North-East marine regions and adjoining continental regions, as explained in Section 5.3.1. The average C₃H₈ values for the NE-BoB, N-BoB and E-BoB air masses (Table 5.1), as

Month	Year/ Cam-	Region	Ove	erall	Reference
	paign				
			O ₃	CO	
Jan	Dec 2008 - Jan	8-21°N	48 ± 8	228	David et al., 2011,
	2009 Winter-				Asatar and Nair, 2010
	ICARB				
Feb	Feb 2001	13-20°N	42 ± 12	217 ± 31	Lal et al., 2006
	BOBEX1				
Mar	Mar-Apr 2006	$5-20^{\circ}$ N	12 ± 27	145 ± 38	Nair et al., 2011
Apr	ICARB				
Sep	Sep-Oct 2002	7-20°N	27 ± 6	143 ± 23	Sahu et al., 2006
	BOBPS				
Nov	Nov 2010	8-18°N	41 ± 9	197 ± 44	This work

Table 5.2: O_3 and CO values in ppbv reported over the Bay of Bengal in different months during different campaigns.

well as the total average C_3H_8 (0.142 ppbv) are somewhat close to Sahu et al. (2006) values (which were also affected by transport from continental regions).

The C₂H₂ values were below 0.2 ppbv in marine air masses encountered till 2 November (Table 5.1). After this, the values are observed to be clearly increasing, indicating transport from continental sources (Figure 5.9). This is corroborated by good correlation between C₂H₂ and O₃ (R=0.86). Both n-C₄H₁₀ and i-C₄H₁₀ were below 0.1 ppbv for most of the samples. In a few cases, n-C₄H₁₀ values were around 0.3 ppbv. The values of double-bonded hydrocarbons: C₂H₄ and C₃H₆ were below 0.4 and 0.1 ppbv respectively; however, their patterns do not bear resemblance to C₂H₆ or C₃H₈. The levels of C₂H₄ were higher in continental air masses (NE-BoB and N-BoB) compared to marine air masses (IO). However, this differentiation is not so clear for C₃H₆ (Table 5.1), indicating that these could represent background oceanic values for this time of the year. The average C₂H₄ and C₃H₆ values obtained during the cruise for all air samples were 0.125 ± 0.065 and 0.062 ± 0.028 ppbv respectively. These



Figure 5.9: Variations of CH_4 , CO and C_2 - C_4 NMHCs along the cruise track during 28 October - 17 November, 2010. The time axis is divided to represent different air masses encountered during the cruise. The missing points mostly indicate that these species were not detected in samples.

values are in the range $(0.299 \pm 0.170 \text{ and } 0.129 \pm 0.050 \text{ ppbv}$ for C_2H_4 and C_3H_6) obtained during post-monsoon of 2002 by *Sahu et al.* (2006), if sigma is also considered.

5.4.3 Latitudinal variation of O_3 and CO

Latitudinal gradients in O_3 and CO were computed by binning the observed concentrations into 0.25° bins for 8-18°N latitudes. Though steep gradients were observed for both O_3 and CO, their patterns are very different (Figure 5.10). During the onward journey towards higher latitudes, O_3 and CO showed positive latitudinal gradients but this did not occur during the return leg. While O_3 values were steadily decreasing since 13 November when the ship was moving towards lower latitudes (away from northern landmasses), the CO values were on the rise. Figure 5.10 shows that the gradients were sharper at some places and flat at others. This is because the ship did not move directly across latitudes. Rather, there was substantial longitudinal coverage as well e.g. during 28 October to 2 November and between 14-17 November, the longitudinal variation of 10° (80-90°E) was more compared to latitudinal variation of 5° (8-13°E). This resulted in flatter gradients in both O_3 and COat 8-11°N compared to 13-18°N (Figure 5.10). The spread was different in different latitudinal bins because the ship had spent greater time in some latitudinal bands compared to others. Further, there are bound to be other effects e.g. effect of diurnal features embedded in this estimated slope. The overall variation of O_3 was 3.95 ppbv per degree change in latitude, with increasing concentrations towards northern continental landmasses. CO values showed a latitudinal gradient of 16.56 ppbv/degree, increasing towards northern latitudes. The positive gradients in the concentrations of air pollutants towards the northern BoB is mainly attributed to the relatively higher influences of the continental outflow over the northern part of BoB as compared with the marine air in the southern part. It is pertinent to mention here that the southern BoB is marked by absence of large, continental regions and hence, devoid of strong anthropogenic sources of O_3 and CO.

The O_3 and CO gradients obtained in this study have been compared with previously reported values over the BoB during different seasons and years in Table 5.3. The observed latitudinal gradient in O_3 (3.95 ppbv/degree) as well as CO (16.56 ppbv/degree) is significantly higher as compared with previous surface observations (1.3 to 2.1 ppbv/degree for O_3 and 4.2 to 15 ppbv/degree for CO) over the BoB. The larger gradients obtained in this study may be attributed to the spatial heterogeneity in trace gas concentrations in the N-BoB and S-BoB, which are under the influence of different transport regimes in



Figure 5.10: Latitudinal variation of O_3 (Left panel) and CO (Right panel) during 28 October-17 November, 2010. Half-hourly concentration data is used for these plots.

November i.e. the N-BoB is affected by emissions over the Asian region while the S-BoB is still cleaner. Large scale biomass burning during this period could also contribute to these gradients. Further, the relatively larger gradient in O_3 compared to CO is a result of their lifetime i.e. shorter lifetime of O_3 results in larger gradients between source (continents) and sink (marine) regions.

The dynamic lifetime of a trace gas is represented by its e-fold distance (De) i.e. the distance after which a given initial concentration decreases to 1/e of its value. The e-fold distance for O₃ is calculated using the Equation 5.3.

$$O_3(D) = O_3(D_0) \exp(-D/D_0)$$
 (5.3)

Using an exponential fit to the O₃-latitude data (figure not shown), we obtain a $R^2=0.62$. Assuming 58 ppbv as the maximum concentration of O₃ obtained at 17.0°N, an e-fold concentration of 21 ppbv is found at 9°N. This gives an e-fold distance of about 900 km. A median wind speed of 4.47 m s⁻¹ during the cruise leads to an estimate of the time taken to cover De to about 2.3 days. This is in agreement with the estimated lifetime of O₃ in the remote MABL of less than a week (*Liu et al.*, 1983). *Chand et al.* (2003) reported an e-fold time of 4.8 days over the BoB. However, their spatial and temporal regimes were different. In our case, a lower e-fold time indicates a higher O₃

Period	$O_3(ppbv/^o)$	$CO(ppbv/^{o})$	Reference
Feb 2003	1.4	10.0	Lal et al., 2007
Feb-Mar 2001	1.45	15.0	Lal et al., 2006
Mar-Apr 2006	1.3	9.0	Nair et al., 2011
Sep-Oct 2002	1.3	4.2	Sahu et al., 2006
Oct-Nov 2010	3.95	16.56	This study
Dec'08 -Jan 2009	2.1	-	David et al., 2011

Table 5.3: Latitudinal gradients in O_3 (ppbv/degree) and CO (ppbv/degree) reported over the Bay of Bengal.

destruction potential and/or less efficient production over the BoB region.

5.5 Characterization of air masses

5.5.1 Emission characteristics

The relationship among CO and VOCs measured during this campaign was explored to get an insight into their sources. For East Asia, the major sources of C₂H₆ are combustion of biofuel (BF, 45%) followed by industry (19%), and biomass (BM, 16%) with minor sources in transport (10%) and residential coal combustion (10%) (*Streets et al.*, 2003). Unlike C₂H₆, the major sources of butanes are the transport sector (58%), followed by industry (31%) (*Streets et al.*, 2003). C₂H₂ has sources in BF (45%), transport (26%), industry (12%), residential coal combustion (9%) and BM (8%) (*Streets et al.*, 2003). Higher C₄H₁₀ values in the N-BoB air mass (Table 5.1) had indicated the influence of FF combustion in this air mass. The value of Δi -C₄H₁₀/ Δn -C₄H₁₀ of 0.62 (R²=0.85) in the N-BoB air mass indicates the influence of urban/industrial sources. The observed ratio is also higher than reported literature values of 0.33 for BF burning (*Andreae and Merlet*, 2001) and of 0.37–0.55 for urban



measurements (*Derwent et al.*, 2000). Thus the N-BoB air mass seems to be influenced by a mixture of BF and FF but dominated by the latter.

Figure 5.11: Variation of CH_4 and NMHCs with CO in various air masses during the cruise. Four different colours represent different air masses viz. IO (black), NE-BoB (blue), N-BoB (red) and E-BoB (green). The fit lines in the diagram are based on robust regression.

The inter-relationships among different NMHCs and CO in the E-BoB air mass indicate influence of BM/BF (Figure 5.11). Negative value of 0.29 (R²=0.66) for $\Delta C_3 H_8 / \Delta C_2 H_6$ in E-BoB indicates greater impact of BM/BF (C₂H₆) in these air masses rather than FF (C₃H₈). Low $\Delta C_2 H_2 / \Delta CO$ value of 0.003 ppbv/ppbv (R²=0.64) in this air mass is closer to the Asian outflow value (0.0044 ppbv/ppbv) and bears signatures of biomass burning (0.0046 ppbv/ppbv; Wang et al., 2003). $\Delta CH_4 / \Delta CO$ value of 0.1 ppbv/ppbv (R²=0.48) and $\Delta C_2 H_2 / \Delta C_2 H_6$ value of 0.3 (R²=0.64) for E-BoB air mass also indicate dominance of combustion products viz. C₂H₆ and CO. Decreasing $\Delta C_3 H_8 / \Delta CO$ ratio, as in E-BoB plume, was observed by Kurata et al. (2004) for biomass burning regions. Further, $\Delta C_2 H_6 / \Delta CO$ of 0.01 (R²=0.8) for E-BoB compares well with a value of 0.01 for a semi-urban region in India (Hissar; Lal
et al., 2012), which was attributed to BM/BF burning effects. Moreover, $\Delta C_2 H_6/\Delta CO$ values of 0.0108 for BM burning and 0.0143 for BF burning were obtained by Andreae and Merlet (2001). Widespread BM and BF burning emissions are presumed to occur in suburban and rural areas (Baker et al., 2011). Further, trajectory analysis revealed that no major urban region was traversed by the E-BoB air mass. Negative associations between i-C₄H₁₀ with CO with (R²=0.49) in the E-BoB with a slope of 0.001 corroborates this fact.

Thus, multiple chemical evidences indicate that the E-BoB air mass was influenced by BM/BF emissions. However, given the spread in data and the limited number of species measured, it is not possible to categorize our measurements into BM and BF types. Measurement of tracers such as CH_3CN and CH_3Cl would have helped to segregate the actual contributions of BM and BF in the continental plumes. Nevertheless, model studies using results from the 1999 INDOEX campaign show that between 60-90% of CO can be attributed to BM/BF burning, and that the burning of biofuels in particular represents a large fraction of total biomass burning (*Lelieveld et al.*, 2001). Nevertheless, the R² values for different slopes in NE-BoB and E-BoB air masses indicate that the E-BoB was more strongly influenced by BM/BF.

Alkenes (C_2H_4 and C_3H_6) are short-lived compounds and can have significant local sources in surface ocean waters related to biological activity. C_3H_6 and C_2H_4 correlate very well in the IO air mass with a slope of 0.66 ppbv/ppbv ($R^2=0.98$) (Figure 5.11) indicating local oceanic emissions.

5.5.2 Relationships among O_3 , NO_x and CO

Although the amount of O_3 produced for each molecule of NO_x consumed is controlled by complex nonlinear chemistry (Section 1.2), the O_3 to NO_x slopes can be used as rough indicators for the production efficiency of O_3 . Positive slopes for the NE-BoB, N-BoB and E-BoB air masses are comparable to similar features observed over many rural and maritime locations downwind of major urban and industrial sources of the world. O_3 has been found to be strongly correlated with NO_z (NO_y - NO_x) for air masses with all degrees of photochemical processing (*Trainer et al.*, 1993). However, in absence of NO_{y} measurements during the present campaign, we have to rely on $\Delta O_3/\Delta NO_x$ values to study the ozone production efficiency. It must be mentioned here that the O_3 production from NO_x over low NO_x regions like oceans will be limited by availability of NO_x . During the present campaign, the O_3 to NO_x slopes show different rates of O_3 production in different air masses including a net negative value in air mass from Indian Ocean (Figure 5.12). The $\Delta O_3 / \Delta NO_x$ values are -2.17, 12.89, 38.75 and 13.34 ppbv/ppbv for the IO, NE-BoB, N-BoB and E-BoB air masses respectively. However, the \mathbb{R}^2 values are very low (<0.1) indicating local perturbations and inhomogeneous transport effects. The $\Delta O_3/\Delta NO_x$ values are observed to be similar for both NE-BoB and E-BoB air masses, indicating similar O_3 -NO_x chemistry in these air masses which share common source regions. The large observed slopes in continental air masses accompanied by very low NO_x levels over the BoB indicate that transport from continental regions plays the dominant role in maintaining the O_3 levels over the BoB rather than in-situ local production.

However, $\Delta O_3/\Delta NO_x$ values are supposed to be more meaningful near polluted plumes due to shorter lifetime of NO_x. On the other hand, $\Delta O_3/\Delta CO$ ratios have previously been used to estimate the amount of O₃ exported over large distances (*Parrish et al.*, 1998). Wang et al. (2004b) attributed a positive $\Delta O_3/\Delta CO$ to production of O₃ in aged air masses that had reduced CO levels. As an air parcel ages, the O₃ and CO levels in the parcel are modified during transport, primarily by dilution with background free tropospheric air and O₃ production resulting from the NO_x-VOC photochemistry. The $\Delta O_3/\Delta CO$ for a polluted air parcel decreases as it ages and is transported further from the CO and O₃ source. Further, in the remote tropical MABL, where NO_x levels are supposed to be low coupled with intense solar radiation and water vapor, photochemical processing will simultaneously remove both O₃ and CO. The



Figure 5.12: Top panel: O_3 -NO_x relationships in the four different air masses viz. IO (black), NE-BoB (blue), N-BoB (red) and E-BoB (green). Bottom panel: O_3 -CO relationships in these air masses. The fit lines in the diagram are based on robust regression (*Mallik et al.*, 2013b).

 $\Delta O_3/\Delta CO$ are 0.09, 0.37, 0.20 and 0.11 (R²= 0.5, 0.9, 0.7 and 0.9 respectively) for the IO, NE-BoB, N-BoB and E-BoB air masses respectively (Figure 5.12). The lower slopes in IO and E-BoB are indicative of aged tropical marine air which is expected to be more depleted in O₃ than CO because of the shorter lifetime of O₃.

The $\Delta O_3/\Delta CO$ ratio in the N-BoB compares well to a value of 0.16 obtained for Kaashidhoo (5°N, 73.5°E) in the Indian Ocean. This ratio was estimated at 0.14 during INDOEX 1999 (*Stehr et al.*, 2002). The lower $\Delta O_3/\Delta CO$ value over the Asian region was attributed to the photo-chemically less efficient O_3 production over the Indian region compared to the mid-latitudes (*Naja and Lal*, 2002). The $\Delta O_3/\Delta CO$ value of 0.11 for the E-BoB air mass compares well with a $\Delta O_3/\Delta CO$ of 0.1 obtained in emission plumes transported from Asia across the Pacific Ocean observed during the Intercontinental Transport and Chemical Transformation experiment in 2002 (*Nowak et al.*, 2004). A smaller slope (0.18) in Hong-Kong outflow compared to around 0.40 in pollution outflow from United States is attributed to a reduced efficiency in photochemical production and/or to a larger emission ratio of CO to NO_x in China (*Wang et al.*, 2004b).

5.5.3 Principle component analysis

Extensive measurements of O_3 , NO_x , CO, CH_4 , NMHCs and meteorological parameters over the BoB during the post-monsoon period of 2010 allowed application of principal component analysis (PCA, a multivariate statistical technique) (Jackson, 2005) to elucidate underlying relationships among the various chemical and dynamical parameters. The main idea of this method (of data reduction) is to form a smaller set of representative variables [uncorrelated or orthogonal principle components (PC), each containing a linear combination of some of the variables from a large number of variables. The number of explanatory variables is reduced while retaining most of the original information by grouping the variables with similar characteristics into factors. The first PC is oriented to explain most of the data. The second PC is orthogonal to the first and explains the next largest variation in the data. To carry out PCA, we interpolated all the data into 4 hour intervals. The values for each component were then standardized by subtracting mean and dividing by the standard deviation, to ensure that some variables do not become unduly important because of scale effects.

A 'Kaiser-Meyer-Olkin Measure of Sampling Adequacy' (KMO represents

Variables	Components				
	1	2	3		
O ₃	0.882	-0.092	0.079		
СО	0.893	0.066	-0.017		
C_2H_4	0.588	0.366	0.355		
CH ₄	0.743	-0.036	0.318		
RT (Ocean)	-0.823	-0.211	-0.130		
RT (Land)	0.871	0.313	0.084		
R Hours	-0.778	0.091	-0.128		
MABL depth	0.610	0.696	0.015		
NO _x	-0.263	-0.489	0.435		
Wind speed	0.250	0.717	-0.090		
Wind dir.	0.099	-0.686	-0.064		
Temperature	0.405	0.196	0.704		
Humidity	-0.520	0.155	-0.703		
Sol. Radiation	-0.031	-0.044	0.730		

Table 5.4: Structure matrix for variables analyzed by the method of PrincipalComponents. The major components are shown in bold.

the strength of connection between variables) of 0.73 indicated appropriateness of factor analysis to these variables. In general, KMO values greater than 0.5 indicate that pattern of correlations are relatively compact leading to distinct and reliable factors. The correlation coefficients showed that none of the coefficient was larger than 0.9, thus problems arising from singularity (perfect correlations) in data are not expected in this analysis. It is to be noted that C_2H_6 and C_2H_2 were removed from the analysis after initial runs, as the correlation between C_2H_2 with O_3 was 0.86 while that between C_2H_6 and CO was 0.88. Further, the Bartletts test was highly significant (p <0.001) indicating that the R-Matrix is not an identity matrix; therefore the variables used in this analysis are not totally uncorrelated. From the initial eigen values, it was seen that factors 1, 2, 3 and 4 explained 40.2, 13.5, 12.1 and 8.6% of variances respectively. The scree plot (figure not shown) indicated that approximately 3 factors could be retained.

The component matrix showed three major components and the first three components are retained after rotation (Oblimin with Kaiser normalization) as well. The structure matrix (Table 5.4) shows the correlation between each variable in the analysis and its component. The first component contained most of the trace gases (O_3, CO, CH_4, C_2H_4) as well as % residence hours over land). This indicates that transport from continental source regions played a major role in the variability of these trace gases during the campaign. Further, the residence hours over ocean and in the 1-750 m altitude are negatively loaded on to the first component. Thus, PCA independently confirms that transport from continental source regions would be less effective when residence time of air parcels is more at lower altitudes or over oceans. The second factor contained NO_x , wind direction (-ve) and wind speed. This indicates that there could be significant source of NO_x over the BoB (probably emitted from various ships, trawlers etc), which could be picked up by low altitude air masses with significant wind speed. Further, wind direction being negatively loaded with NO_x in the second component indicates that some of the NO_x could be of local origin. Further, since wind parameters (measured locally) are not loaded along with O_3 and CO, this means that these gases were generally not governed by very local sources.

5.6 Simulations of O₃ diurnal patterns

To get an insight into the balance between chemical production and loss processes over the marine environment of BoB, observed diurnal patterns in surface O_3 concentrations during selected days are simulated with a chemical box model National Center for Atmospheric Research Master Mechanism (NCAR-MM) http://cprm.acd.ucar.edu/Models/MasterMech/index.shtml. The NCAR-MM (*Madronich*, 2006) consists of highly detailed gas phase chemistry (about 2000 species participating in about 5000 reactions) and this includes about 306 photolysis reactions. The model can simulate the time evolution of an air parcel initialized with measured concentrations of trace gases. However, it is not sensitive to further dilution, emissions and transport. Photolysis rate coefficients i.e. j-values are estimated using the Tropospheric Ultraviolet Visible (TUV) radiative transfer model (*Madronich and Flocke*, 1999). More details of the model can be seen elsewhere (*Madronich*, 2006). In the present study, the model has been initialized with measured concentrations of O_3 , H_2O , NO, NO_2 , CO, CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , i- C_4H_{10} and n- C_4H_{10} while N_2 , O_2 and photons are hard-wired into the model. MABL heights and dilution are also added as inputs to the model.

The model was operated for four different scenarios:

1. When the ship was encountering mostly clean, marine air (IO air mass) near the southern-most part of its transect (2 November)

2. When the ship was close to Port Blair under regime of NE-BoB air mass (4 November).

3. When the ship was heading towards the North BoB and was under influence from South-East Asia (6 November).

4. When the ship was returning from the North BoB and was under influence of the N-BoB air mass (12 November).

The comparison between the observations and model simulations is shown in Figure 5.13. Here, instead of showing the absolute levels, change in O_3 (ΔO_3) is shown. ΔO_3 for box model simulations is the difference between the hourly data with the mean daily concentration. ΔO_3 for observations represents the difference between measured O_3 and predicted O_3 using a linear fit for the day. Overall, the model-simulated diurnal patterns as well as the variability agree well with the observations.



Figure 5.13: Left panel: Comparison of observed diurnal variations of O_3 with simulations from the box model. Right panel: Sensitivity of the Box Model to changes in various input parameters (for 2 November, 2010 over the BoB).

The O_3 values were on the lower side i.e. 25-35 ppbv on 2 November and entrainment did not seem to play a major role on this day. The diurnal feature was that of a clean, marine region characterized by day-time loss. The day was marked by conspicuous O_3 destruction during daytime which may be attributed to photochemistry. O_3 loss in MABL is attributed to photolysis due to excited oxygen atoms $O(^1D)$, followed by reaction with water vapour, odd hydrogen radicals (HO_x) and surface deposition. Further, reactive halogen species released into the atmosphere over oceans may also contribute to O_3 destruction in the MABL.

However, the model was not exactly able to simulate the large daytime loss on 4 November and the sudden increase in O_3 values after 1700 IST. The sudden increase may be attributed to transport effects as surface wind speed was over 13 m s⁻¹ on 4 November. The MABL was highest on 4 November (>1400 m) resulting in higher VC. However, the model was still able to simulate amplitude of about 7.8 ppbv of O₃. Incorporation of halogen chemistry might have accounted for the daytime loss processes better on this occasion, however, reliable measurements of halogens are still lacking for the BoB.

The diurnal variation on 6 November was characterized by higher O_3 levels (45-60 ppbv) and dominated by transport effects. The 6 November pattern is most perturbed with several instances of O_3 build-up on a basic pattern marked by daytime destruction and night-time advection (import). However, the model was able to simulate the day-time loss which might be dominated by chemistry. Since CO values did not rise as sharply as O_3 during these nights, advection alone seems incompetent to explain the night time recovery. The preferential enhancement of O_3 w.r.t. CO on this day indicates exchange between the O_3 -rich free troposphere and the O_3 -poor boundary layer. The exchange process is supposed to be more important during the night than during the day, allowing O_3 night-time recovery (*Bremaud et al.*, 1998). Initially, the box model was not able to closely match the high O_3 values between 2000-2400 IST. However using different entrainment rates during day (1 mm s⁻¹) and night (25 mm s⁻¹) (*Bremaud et al.*, 1998), the model was able to produce the night-time recovery.

The diurnal variation of O_3 on 12 November was conspicuous by the occurrence of high O_3 values after sunrise. The enhancement occurred in two steps, once after 0300 IST and the other after 0600 IST. The first enhancement may be attributed to advection of O_3 and precursor rich air into the MABL. *Donahue and Prinn* (1990) have observed a sudden MABL deepening at dawn allowing influx of O_3 rich air. The second one may be attributed to photochemistry. This photochemical production can occur under optimum levels of precursor gases. It must be noted that CO and NO_x levels on this day had also showed early morning enhancement. Model simulation confirms the daytime O_3 production suggesting that the amount of precursors was sufficient to result in net O_3 production on this day (Figure 5.14). This high O_3 is then slowly acted on by photochemical loss processes during the day. However, model simulation somewhat underestimates the O_3 production. The difference in model and observation could be associated with transport of O_3 rich air along with the precursors which is not considered in the box model.

5.6.1 O_3 production and loss rates

In remote MABL, O_3 mixing ratios generally show "virtually no diurnal variations" (Liu et al., 1983). Further, it is suggested that the general balance of O_3 in the MABL is governed by the competition between two processes: a. entrainment of O_3 rich air from higher altitudes and large-scale horizontal advection from source regions b. net photochemical destruction throughout the day along with continuous deposition to the ocean. The box model can also be used to partly account for the sensitivity of O_3 variations due to these competitive processes viz. chemistry $(NO_x, CO \text{ and } NMHCs)$ and dynamical parameters (e.g. boundary layer height, entrainment etc). In our case, the box model was found to be very sensitive to various background levels of O_3 , indicating the role of entrainment processes (Figure 5.13). This is corroborated by the fact that the model was sensitive to dilution effects as well. The model was also highly sensitive to NO_2 values and it is seen from Figure 5.13 that background NO_2 regimes can determine whether O_3 is produced or lost during daytime. Further, Monks et al. (2000) had observed that a 10% drop in water levels would lead to a 6% drop in radical levels.

The O_3 formation $F(O_3)(R7$ in Section 1.2) and O_3 destruction $D(O_3)(R5, R11, R12$ in Section 1.2) rates may be represented by the following equations [Davis et al., 1996]:

$$F(O_3) = k_1 [NO] [HO_2] + \sum k_i [NO] [RiO_2]$$
 (5.4)

$$D(O_3) = k_4 [O^1D] [H_2O] + k_5 [HO_2] [O_3] + k_6 [OH] [O_3]$$
(5.5)

The balance between $F(O_3)$ and $D(O_3)$ gives the O_3 net production potential $P(O_3)$. The O_3 production and loss rates were calculated using concentrations of peroxy species, OH, HO₂ etc from the box model for 2 and 12 November. 2 November (which showed conspicuous daytime O_3 loss) was selected because the influence of transport e.g. night-time advection was minimum on that day. In contrast, 12 November is marked by daytime O_3 production. Sum of CH₃O₂ and C₂H₅O₂ has been used here to represent levels of peroxy radicals considering them as the major contributing species to this group.

The daytime variation in estimated O_3 production and loss rates is shown in Figure 5.14. On 2 November, the chemical loss of O_3 loss was found to dominate O_3 production throughout the day as also indicated by the observed net O_3 destruction over the BoB. Maximum production occurred from the reaction of CH_3O_2 with NO and was almost closely matched by the reaction of HO_2 with NO. The major contributor to the O_3 chemical loss was the reaction of O^1D with H₂O during the daytime. Liu et al. (1983) have found a net O_3 photochemical loss rate of 2 ppbv day⁻¹, with roughly 70% of the loss coming from the reaction of excited oxygen, $O(^{1}D)$, with water vapor to form OH and 30% coming from reaction of O_3 with HO_2 . The maximum production occurred around 0900 IST and while the maximum loss occurred around 1100 IST on 2 November (Figure 5.14). On 12 November, maximum O_3 production is observed at 0900 IST. As the day progresses, the photochemical loss processes start to pick up (Figure 5.14). However, on this day, the losses are never sufficient to generate a net negative $P(O_3)$. Apart from these photochemical production and loss processes, there could be significant contributions of advection and entrainment processes towards O_3 build-up and physical processes in O_3 loss.



Figure 5.14: Calculated daytime variation of formation $F(O_3)$, destruction $D(O_3)$ and net production $P(O_3)$ rates for O_3 on Left panel: 2 November and Right panel: 12 November, 2010 over the BoB.

5.7 Summary

This chapter presents the results from ship-based observations of O_3 and its precursors over the BoB during 28 October - 17 November, 2010. Measurements made during this period, are likely to reflect direct impact of air masses originating from different source regions in South Asia over a cleaner BoB. So far, measurements of O_3 precursors viz. NO_x , were not available for these post-monsoon months over this marine region. Simultaneous measurements of O_3 , CO and NO_x , CH₄ and C_2 -C₄ NMHCs were achieved for the first time during this campaign. A wide range of O_3 concentrations were encountered during the cruise from as low as 11 ppbv in the open ocean to over 60 ppbv in the North BoB. During the present campaign, four distinct types of airmasses characterized by heavy pollution from nearby source regions (N-BoB; 42% time over North-West Myanmar, East Bangladesh and North-East India), mixed type (E-BoB; 22% time over SE Asia and 75% time over East BoB), affected by long-range transport of pollutants (NE-BoB; 59% time over continental SE Asia), and pristine marine type (IO; 97% time over oceanic regions) were identified. Among these, the continental air masses were fresher

compared to marine air masses.

Both O_3 and CO showed sharp latitudinal gradients of 3.95 ppbv/degree and 16.56 ppbv/degree respectively, increasing towards northern continental landmasses. These latitudinal gradients were higher than previous studies over the BoB, which were conducted during other seasons. Higher latitudinal gradients confirm the large spatial heterogeneity in O_3 and CO levels due to unique transport patterns over the north and south BoB during post-monsoon. Principle component analysis indicated that transport from continental source regions played a major role in determining the chemical composition of the air masses during the campaign and presence of regional sources of NO_x . These regional sources of NO_x , apart from transport from nearby land masses, could also be due to emissions from large number of ships and trawlers operating over the BoB, especially the international shipping lanes along Yemen - Sri Lanka - (Malayasia - Sumatra) corridor.

Highest O_3 and CO levels were observed in air masses coming from South-East Asia. Signatures of BM/BF burning were detected in these air masses (NE-BoB and E-BoB) using correlations of C_2H_2 , C_3H_8 and C_2H_6 with CO. Potential Source Contribution Function analysis indicated the fire impacted South East Asian regions as potential contributors to high levels of CO measured on 14 November. C_4H_{10} and C_2H_2 were very high in air masses arriving from the North BoB and nearby land regions indicating influences of urban/industrial sources over Bangladesh, India and North-West Myanmar.

Diurnal variations of surface O_3 revealed effects of advection, entrainment and photochemistry. This was corroborated by box model simulations. The model simulated diurnal variations were found to be highly sensitive to background NO₂ and background O₃ levels as well as dilution. The model was able to simulate the observed daytime O₃ reduction in pristine oceanic air masses and photochemical buildup in polluted air masses. The model results were in good agreement with observations when transport effects were more homogeneous. Indirectly, the model enabled us to assess if the diurnal variations were sensitive to transport or chemistry.

Chapter 6

Summary, conclusions and future scope

The Asian region is developing very fast. This is leading to uncontrolled emissions of pollutants into the atmosphere. The increased emissions of several gaseous species are resulting in the perturbation of the chemical and radiative balance over the region and leads to deleterious impacts on human health, crops and on the environment at large. Further, trace gases emitted over South-East Asia and India have been strongly linked to regional and global climate change. The present study is aimed at understanding the temporal and spatial variability of atmospheric trace gases over environmentally and climatically distinct regions of India using in-situ measurements (Section 1.7). The study locations were selected such that each site was unique with respect to emission sources, geographical setting w.r.t. source regions and transport patterns. The measured temporal and spatial variability of trace gases over these selected locations provided an insight to the role of chemical, dynamical and meteorological processes in influencing the observed trace gas levels. A summary of this thesis work and the future directions are discussed in this chapter.

6.1 Highlights of the present study

6.1.1 Summary of important results

As discussed in Chapter 3, trace gas measurements made over Ahmedabad, an urban site in western India, revealed clear influence of different local sources for different trace gases. While CO and NO_x concentrations over Ahmedabad were significantly modulated by vehicular traffic, SO₂ levels were influenced mainly by emissions from a power plant in the north-east of the study location and a few industries in the east as corroborated by $\Delta SO_2/\Delta NO_x$ value of 0.41(ppbv/ppbv). Ozone on the other hand, was mainly attributed to local photochemical processes. Further, we have been able to document the levels of atmospheric COS and CS₂ for the first time over an Indian location using a new GC setup (Section 2.3) in our laboratory at Ahmedabad.

The impacts of emission sources and dynamical processes on trace gas levels over the IGP have been discussed in Chapter 4. Surface measurements of SO₂, NO₂ and CO in conjunction with satellite estimations of the columnar levels of these gases over a few urban locations showed that over regions of strong surface emissions, columnar levels are significantly impacted by surface emissions. Measurements of SO₂ and NO_y made over Nainital clearly revealed signatures of IGP emissions transported to Nainital. This was corroborated by higher correlations of SO₂ with wind speed (R²=0.88) during the summer monsoon period and between SO₂ and NO_y during the same period (slope=0.57 ppbv/ppbv; R²=0.94). Simultaneous measurements of SO₂ and hydrocarbons made over Kolkata revealed that despite being a megacity with strong local emissions, regional transport from the IGP plays a major role in enhanced SO₂ levels over Kolkata during winter (6.7 ppbv) and post-monsoon (4.1 ppbv). These measurements also enabled interpretation of the contribution of various emission sources to the ambient air of Kolkata megacity.

As discussed in Chapter 5, ship-borne measurements of O_3 and precursors

over BoB during a post-monsoon campaign identified various emission signatures from different regions of Asia. Large latitudinal gradients in O_3 and CO over BoB were attributed to transport processes while high levels of NO_x in the South BoB were attributed to local emissions from ships and trawlers. The importance of chemical and dynamical processes in determining the diurnal variation of O_3 over different parts of the BoB was illustrated using chemical box model simulations. Overall, atmospheric trace gas measurements conducted over Ahmedabad, Nainital, Kolkata and the BoB have highlighted the impacts of different processes governing trace gas levels over these sites which represent different emission environments.

6.1.2 Levels and diurnal variability of atmospheric SO₂

Till recently, studies of atmospheric SO₂ over the Indian region were based on wet chemical methods. These methods are not suitable for high resolution measurements. Further, the scope of these methods is limited because of poor detection limits (>1 ppbv) associated with them. Recent techniques based on UV fluorescence have allowed SO₂ concentrations as low as 50 pptv to be measured with a time resolution of few minutes. During the present study, SO₂ measurements, based on UV fluorescence, have been reported for Ahmedabad, Kolkata and Nainital. The SO₂ levels measured over different regions of India is compared to previous measurements over India and other parts of the world in Table 6.1. It has been observed that SO₂ emissions over the Indian region are showing a positive trend (largely due to increasing emissions from thermal power plants) while levels are going down over united States, Europe and nearly stabilized over China (Lu et al., 2011). However, the levels of SO₂ observed over the Indian sites are generally lower than its values in China and South East Asia.

A comparative representation of diurnal variation of SO_2 during October over Ahmedabad, Kolkata and Nainital is presented in Figure 6.1. October

Station	Year	\mathbf{SO}_2	Reference		
Ahmedabad	2011	1.3	This study		
Kolkata	2012-13	3.4	This study		
Nainital	2009-11	0.15	This study		
Delhi	2008	1.76	Datta et al., 2010		
Agra	1999-2001	1.35	Kumar et al., 2004		
Mumbai	1997-2000	3-19	Gupta et al., 2003		
Hong-Kong	2002-03	6.2	Guo et al., 2007		
Linan (China)	2007-08	12.3	Meng et al., 2010		
Seoul	1998-2003	7.9	Nguyen and Kim, 2006		
Beirut (Lebanon)	2004-05	7.1	Saliba et al., 2006		
East Europe	2000	0.5	Hanke et al., 2003		

Table 6.1: Average concentrations of SO_2 (ppbv) over different regions in India and the world.

month has been used here to depict these variations as it is during this time of the year that the influence of monsoon winds over the Indian subcontinent recedes and the impact of continental sources over a cleaner background is observed. The SO₂ levels observed over Ahmedabad, Nainital and Kolkata clearly identify them to be respectively impacted by moderate, weak and strong sources of SO₂. Nainital, being a pristine high altitude site, with no significant in-situ emissions, has extremely low levels of SO₂. On the other hand, SO₂ levels in Kolkata are impacted by both local emissions as well as transport from the IGP. Further, the diurnal variations during October over Ahmedabad and Kolkata reveal impacts of boundary layer variations leading to dilution of SO₂ during daytime and build up during evening and early night. On the other hand, Nainital shows elevated daytime values due to transport of SO₂ from lower altitudes by upslope winds. Further, strong correlations were observed between SO_2 levels over Nainital during day-time (1130 and 1730 IST) and corresponding PBL heights (Figure 4.10). The diurnal variations during other months also highlight the role of different transport processes as has been discussed in Chapters 3-5 of this thesis. Overall, in-situ measurements of atmospheric SO_2 over different regions of India during this study have generated a representative database for modeling investigations of the sulfur cycle over the Indian region, which is yet to be reliably deciphered.



Figure 6.1: Average diurnal pattern of SO_2 over Ahmedabad, Nainital and Kolkata during October month. The Nainital data has been scaled by a factor of 10 to make the pattern comparable to the other sites.

6.1.3 Seasonal changes and effects of transport on trace gas distribution

The change in SO_2 levels under the influence of different wind regimes is shown in Figure 6.2. For comparison, SO_2 levels over Delhi (based on *Datta et al.*, 2010) are also shown in the plot. The measurements at Delhi were conducted at the campus of National Physical Laboratory (NPL) during January to December, 2008 using a UV florescence monitor. The other measurements are from this thesis work. The SO₂ levels over Ahmedabad, Delhi, Nainital and Kolkata are found to be 0.69, 1.36, 0.20 and 1.50 ppbv respectively during premonsoon and monsoon period. However, during the post-monsoon and winter period, SO₂ levels over Ahmedabad, Delhi, Nainital and Kolkata are observed to be 2.26. 2.55, 0.07 and 5.40 ppbv respectively. Thus, while Nainital levels show a decrease during the winter, all other sites show an increase.



Figure 6.2: Seasonal changes in levels of SO_2 over Ahmedabad, Delhi, Nainital and Kolkata. The Delhi data is based on *Datta et al.* (2010). The scale for the bar plots is shown in the right e.g. the grey bar for Kolkata is 5.4 ppbv.

The seasonal changes in SO_2 levels are associated with changes in air masses, thus connoting the influence of different source regions. The magnitude

of these seasonal changes in SO_2 levels are 230, 87 and 260% respectively from pre-monsoon to winter over Ahmedabad, Delhi, and Kolkata and 330% from winter to pre-monsoon over Nainital. The changes over Kolkata (Nainital) represent the impact of IGP emissions during winter (pre-monsoon) as well as boundary layer influences. As described in Section 4.4, particularly high levels of SO_2 during winter (>6 ppbv) over Kolkata megacity are attributed to regional emissions from coal burning (in industrial areas and power plants) in the eastern IGP and subsequent trapping of these air masses favoured by a stable atmosphere with low ventilation coefficient. The change is notably less over Delhi (87%) as it is impacted by IGP emissions throughout the year to various extents. On the other hand, Nainital is cut off from IGP during winter as the site lies above the regional boundary layer for most of the season. Similarly, air masses over Kolkata are impacted by BoB and eastern coast of India during pre-monsoon and monsoon respectively (Figure 4.14). Likewise, Ahmedabad is flushed by marine air masses during the monsoon and impact of continental source regions becomes pronounced during post-monsoon and through the winter. Thus seasonal variations in SO_2 levels over different strate-

gically chosen sites have provided an idea of the magnitude of the effects of transport processes, which vary from region to region.

6.1.4 Impact of emission sources on trace gas levels

The seasonal variation of columnar levels of SO_2 , NO_2 and CO (based on OMI and MOPITT data) exhibit very different features compared to surface levels. In general, SO_2 columnar concentrations are found to be elevated both during monsoon as well as winter. Columnar NO_2 is elevated during winter while columnar CO is high during winter and pre-monsoon. NO_2 columnar levels are found to be higher over strong emission source regions like megacities, exhibiting strong, statistically significant correlations between surface and columnar values over a six year period (2005-2010) (Section 4.2). The pre-monsoon elevation in CO levels suggests the impacts of biomass burning and the role of convective transport lifting surface emissions to higher levels. The high levels of columnar SO₂ during monsoon compared to pre-monsoon merits further investigation and could be related to various chemical and physical loss processes during other seasons. The SO₂-NO₂ ratios are found to be lower than 0.2 over regions with significant vehicular traffic viz. Kolkata and Delhi (Figure 4.6). However, over regions dominated by point sources viz. power plants and industries, these ratios are found to be higher than 0.3 (Figure 4.6). The influence of point and mobile sources are clearly identified from the slopes of SO₂ w.r.t. NO_x over Ahmedabad (Figure 3.11). Here, vehicular emissions resulted in Δ SO₂/ Δ NO_x value of 0.026 while the emissions from coal burning in a thermal power plant and a few industries resulted in an enhanced slope of 0.41. Such features have also been observed over other parts of the world (Table 3.2).

Further, $\Delta SO_2/\Delta NO_y$ of 0.57 during pre-monsoon over Nainital not only indicate impacts of coal burning in this pristine location, but also established that emissions from these coal burnings were sourced to thermal power plants and industries in the IGP (Section 4.3). This was corroborated by absence of any correlation between SO_2 and NO_y over Nainital during winter, when the site is cut off from IGP emissions due to boundary layer dynamics. Further, the relationships between SO₂ and hydrocarbons over Kolkata megacity indicate that substantial portion of the SO_2 over Kolkata is contributed by regional transport (Section 4.4). This is evinced from the fact that several anthropogenic NMHCs emitted locally over Kolkata viz. C_2H_2 , C_3H_8 and C_4H_{10} were not correlated to SO_2 . Further, over this city, where multiple emissions release multiple trace gases, PMF analysis allowed to identify various emission sources and roughly established their percentage contributions to a particular chemical species. Inter-species correlations from ship borne measurements established that over BoB, SE-Asian air masses are dominated by biofuel emissions while air masses from IGP and Bangladesh were pre-dominantly impacted by fossil fuel combustion (Section 5.5). The spatial variation of $\Delta C_2 H_6/\Delta CO$ and $\Delta C_2 H_2/\Delta CO$ from various studies over the Indian region show that not much variation occurs in $\Delta C_2 H_2/\Delta CO$ as this slope is mainly influenced by vehicular emissions which have similar emission characteristics over the Indian region (Figure 6.3). However, large variation in $\Delta C_2 H_6/\Delta CO$ is observed along the IGP showing a gradual decrease from Northern India to Eastern India to BoB (Figure 6.3). Further, these values are found to be higher for the SE-Asian plume indicating BM/BF burning.



Figure 6.3: Variation of C_2H_6/CO and C_2H_2/CO over different regions of India using values from current study as well as previous studies. Values for Hissar (29.14°N, 75.7°E) and Kanpur (26.43°N, 80.33°E) are taken from *Lal et al.* (2012). The arrows indicate that air masses over the BoB are coming from continental source regions in India and SE Asia.

Levels of CO and C_2 - C_5 hydrocarbons over different cities of India and other countries are shown in Table 6.2. Hydrocarbon measurements made during a road experiment from Ahmedabad to Nainital showed that the levels of CO, CH₄ and C_2H_6 increased towards IGP while C_3H_8 and C_4H_{10} were higher in western India (Section 4.1). These results connote that western India is more dominated by fossil fuels mainly petrochemicals while both biofuel and fossil fuel combustions dominate in the IGP region. It is further observed that trace gas levels over Ahmedabad are comparable to levels in Hong-Kong (Table 6.2), a major urban region in South East Asia. Higher values of C_2H_6 but lower values of C_4H_{10} over Northern India (Hissar) indicate dominance of biofuel combustions. Kolkata, being a megacity at the IGP outflow region has elevated levels of C_2 - C_5 hydrocarbons compared to Ahmedabad. It is observed that CO and C_2H_6 levels over Kolkata are comparable to several Chinese sites while C_3H_8 and C_4H_{10} are substantially higher over the study region. However, C_2H_6 levels over Kolkata are still lower than Hissar.

Table 6.2: CO, CH_4 and NMHCs (ppbv) over different regions in India and the world.

Station	Ahmed-	Hissar	Kolkata	Hyder-	Kara-	Hong-	NE-	Mexi-	Lon-
	abad			abad	chi	Kong	China	со	don
								City	
Year	2002	2004	2012-13	2010	1998-	2002-	2007	2006	2002
					99	03			
CO	385 ± 200	553 ± 292	677 ± 194		1600	511	645	1862	530
CH_4	1880 ± 400		$2259{\pm}210$		6300	2024		2880	
C_2H_6	3.7 ± 3.7	7.9 ± 3.6	3.9 ± 3.4	28.3	93	2.1	3.0	13.9	7.1
C_2H_4	2.9 ± 2.6	7.9 ± 3.6	4.5 ± 2.9	3.1	19	2.7	2.8	13.9	2.4
C_2H_2	2.0 ± 1.9	7.5 ± 5.5	3.7 ± 2.5	2.6	18	2.9	4.0	16.3	1.3
$\mathrm{C_{3}H_{8}}$	3.1 ± 2.0	7.9 ± 3.6	8.4 ± 5.6	3.5	41	2.5	1.9	78.3	2.7
C_3H_6	1.0 ± 0.9	2.3 ± 1.9	1.8 ± 1.7		5.5	0.6	1.1	4.0	0.7
$i-C_4H_{10}$	1.9 ± 1.5	1.6 ± 1.5	4.0 ± 3.6		11.0	1.5	0.9	11.7	1.2
$n-C_4H_{10}$	2.8 ± 2.4	2.1 ± 1.9	6.3 ± 5.0	2.4	19.8	2.6	1.0	2.0	2.0
$i-C_5H_{12}$	1.9 ± 2.4	1.1 ± 2.1	3.2 ± 3.2	7.7	12.1	1.1	1.2	9.2	1.6
	Sahu and Lal, 2006a	Lal et al., 2012	This study	Swamy et al., 2012	Barletta et al., 2002	Guo et al., 2007	$Xue \ et \ al.$, 2011	$Apel \ et \ al., 2010$	Schneidemesser et al., 2010

Overall, the levels of hydrocarbons observed over the Indian cities are lower than the levels observed over Karachi and Mexico City, which are highly polluted regions in the world. However, levels are comparable to the values observed over several Chinese stations. Nevertheless, hydrocarbon measurements made during this study over different locations in the Indian subcontinent and the BoB have not only helped in interpretation of emission sources but have

also provided a reliable database for future modeling investigations and development of emission inventories over this data sparse region.

6.1.5 COS measurements in the global perspective

The average mixing ratio of COS over Ahmedabad during the January-October, 2013 is found to be 0.87 ± 0.43 ppbv. The mean value is about 1.7 times higher than the global, tropospheric mixing ratio of COS (0.51 ppbv, with a natural variability (1s) of about 10%). The annual mean Northern Hemisphere mixing ratio of COS estimated from measurements at seven surface sites in America and Europe during 2000–2005 was 0.48 ppby (Montzka et al., 2007). The observed COS mixing ratios over Ahmedabad are found to be lower than in Beijing city $(1.34 \pm 0.72 \text{ ppbv})$. High levels of COS over Beijing are attributed, mainly, to emissions from cesspools but also central heaters and domestic stoves (Yujing et al., 2002). COS measurements over Brazil showed that its concentration varied between 0.5 and 1.0 ppby over areas dominated by biogenic sources while values were as high as 8 ppbv near petrochemical complexes (Nunes et al., 2005). Over India, levels of COS are likely to be different over different regions not only because of the presence of various anthropogenic sources, but also due to various soil types (both oxic and anoxic), marshlands, large water bodies etc. Because of the importance of COS in the global environment, its sources, sinks, atmospheric budget, and particularly the effect of human activities on global sulfur cycle are of special interest and merit further research starting with quantitative estimation over different parts of India.

6.2 Future scope

While the current thesis work has given information on the temporal variability of trace gases in different environments, understanding the role of dynamical processes and identification of emission sources (as outlined in Section 1.7), it has also laid open a few avenues to be pursued in future. Measurements of surface O_3 are now available over several locations in India. However, measurements of O_3 precursors were lacking and only during the last few years, reliable measurements of NO_x have become available over a few sites. Further, simultaneous measurements of CO and hydrocarbons are available only over Ahmedabad, Nainital, Hissar and Kanpur. The data over the latter two sites are based on campaign measurements over a short period of time. During this study, a database of CO and hydrocarbons over Kolkata (eastern part of India) has been generated and it would be useful to model their impacts over the Indian region. Likewise, simultaneous measurements of O_3 , NO_x , CO and hydrocarbons over the BoB will now allow for detailed modeling estimations of the budgets of these species. Measurements of HO_x radicals and NO_y species have now become highly desirable for the Indian subcontinent and its surrounding marine regions to have deeper understanding of the atmospheric chemistry over this region of high emissions, which are lifted up by deep convection and transported to larger regions of the globe. Further, these measurement can facilitate budget closures for O_3 and related species. Moreover, apart from surface measurements, vertical profiles of trace gases using balloon and aircraft platforms are needed to estimate the impacts of deep convection and other dynamical processes on trace gas distributions over the Indian region particularly along the IGP and over the BoB. As highlighted in Chapter 5, measurements of trace gases over the BoB are lacking for the monsoon period. These prospective measurements will help in gaining a deeper insight into the impacts of convective transport on trace gas chemistry.

Despite estimates of increasing SO_2 emissions over the Indian region (Lu

et al., 2011), the low levels of SO_2 observed over India compared to regions in China and South-East Asia indicate that either emissions are actually low or scavenging processes (oxidative as well as deposition losses) are highly efficient over the Indian region. Further, as evident from the present study, the surface SO_2 levels over India are found to be very low during monsoon but the columnar levels are found to be elevated during this period. Similar to SO_2 , SO_4^{2-} concentrations over Ahmedabad are also found to be much higher during postmonsoon compared to monsoon and pre-monsoon (Rastogi and Sarin, 2009). Further, SO_4^{2-} concentrations are found to be higher during August compared to June-July. Guttikunda et al. (2001) have estimated higher sulfur deposition over the Indian region during summer-monsoon period. These facts merit further research to understand the levels, seasonal cycle and budgets of SO_2 , RSCs and sulfate over the Indian region with respect to emissions as well as physical and dynamical processes. Since these gases are intrinsically related to climate studies, their fluxes over the Indian region need to be systematically determined.

Further, Notholt et al. (2003) have observed COS mixing ratios to be 20– 50% larger than are assumed in models and suggest that biomass-burning emissions transported upward by deep convection could be the source of the enhanced COS in the upper tropical troposphere. Thus, tropical regions like India and South East Asia could be strong sources of COS and hence actual measurements of this species over representative locations are essential for understand the sulfur cycle and estimate the stratospheric sulfur species over this region. Due to important role of sulfur gases in climate regulation, measurements of SO₂, COS, DMS and SO₄^{2–} are highly desirable at various sites in India and South-East Asia to have a reliable database for further modeling studies.

The simultaneous measurements of several trace gases made during this study have enabled interpretation of emission sources contributing to the chemical composition ambient air over Ahmedabad, Kolkata, Nainital as well as the BoB. However, interpretation of sources needs to be scaled up to grids by conducting such simultaneous measurements over more representative locations in India so that a good database can be generated to compare measurements and inventories which ultimately drive chemical transport models and finally global climate models. Moreover, emission inventories need to be validated with recent measurements and modified accordingly for this part of the world. Further, the rapidly changing economy of the Asian region engenders changing surface emission scenarios and has implications to changes in regional chemistry and climate.

Long-term measurements of atmospheric trace constituents (including trace gases, aerosols and radicals) along with meteorological and dynamical parameters (RH, wind speed, wind direction, boundary layer height etc) and radiation parameters over different locations in India are necessary to forecast changes in atmospheric chemistry as well as climate change over this very important tropical region of the Earth.

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Variability in ozone and its precursors over the Bay of Bengal during post monsoon: Transport and emission effects

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[1] Simultaneous measurements of O₃, CO, NO_x, CH₄, and light nonmethane hydrocarbons were made over the Bay of Bengal (BoB) during 28 October to 17 November 2010 to study the role of chemistry and dynamics. The measurements revealed large variability in O_3 (11 to 60 ppbv) and CO (45 to 260 ppbv). Estimated south to north latitudinal gradients in O₃ (3.95 ppbv/°) and CO (16.56 ppbv/°) were significantly higher than those observed during earlier campaigns. Hybrid Single-Particle Lagrangian Integrated Trajectory simulated back air trajectories were used to classify these measurements into pollution plumes from nearby sources (India-Bangladesh region and Southeast Asia), influenced by long-range transport and pristine marine air from the Indian Ocean. Interspecies correlations were used to identify emission signatures in these air masses, e.g., chemical proxies suggested influence of biofuel/biomass burning in NE-BoB and E-BoB air masses. Principle component analysis indicated contributions of ship emissions to NO_x levels over the BoB. Influences of fire from the Myanmar and Thailand regions are shown to be the potential contributor to enhanced CO levels (>250 ppbv) over the BoB during 14-15 November. Diurnal variations in surface O₃ revealed effects of advection, entrainment, and photochemistry. A chemical box model simulated the photochemical buildup in O_3 in polluted air masses and daytime destruction in pristine oceanic air masses.

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1. Introduction

[2] The marine atmospheric boundary layer (MABL) that envelops 70% of the Earth's surface is a region of active physical and chemical exchanges between the ocean and the atmosphere. It also serves as the source and sink of several atmospheric trace gases and aerosol particles [Johnson et al., 1990]. The Bay of Bengal (BoB), the largest bay in the world, is a region of active chemical cycling driven by photochemistry and transport (advection, convection, and entrainment) and offers a unique natural laboratory to probe these processes. While the BoB occupies only 0.6% of global oceans, the importance of this marine region lies in the virtue of its location in the northeastern part of the Indian Ocean. Not only does it serve as a corridor for one of the most important monsoonal systems of the world (the Indian Monsoon), it also lies downwind to the most populated and

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polluted regions of the globe, namely, India, and Southeast Asia. According to Lawrence and Lelieveld [2010, p. 1], this is 'probably the only place in the world where an intense source of continental aerosols, anthropogenic trace species and their reaction products (e.g., sulfates and ozone) from the SAARC and ASEAN economic blocks is directly connected to the pristine air of the Southern Indian Ocean. Specifically, during post monsoon and winter months, pollutants are transported from their source regions into the BoB via strong low-level winds, the composite phenomenon is now known by the popular adage of "Southern Asia outflow." These plumes are fed by emissions comprising combustions of fossil fuels and traditional biofuels as well as biomass burning. These plumes are also domains of chemical and photochemical reactions leading to transport, genesis, and transformation of ozone (O₃) and its precursors. Further, presence of convection during summer-monsoon causes some of these gases to be lifted higher up into the atmosphere and distributed over a larger region of the globe. Consequently, the region assumes global significance. Thus, simultaneous measurements of O3 and its precursors are highly desirable over this marine region [Naja et al., 2004; Lal et al., 2007] to better understand the short and long-range transport of pollution, en route photochemical transformations and photochemistry within the MABL as well as the potential impact on a larger scale.

[3] Interest in trace gas measurements over the BoB have ensued since the "Indian Ocean Experiment" (INDOEX)

Additional supporting information may be found in the online version of this article.

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Figure 1. The three panels show 7 day backward trajectories originating at 10 m AMSL at three different latitudes ((a) 8°N, (b) 13°N, and (c) 18°N) along the 90°E longitude during 2010. Trajectories in different colors represent different seasons (Dark green, January (winter); Light green, April (summer); Blue, (monsoon); and Pink, November (post monsoon)).

[Lelieveld et al., 2001; Muhle et al., 2002]. During INDOEX, O₃ levels over the BoB sometimes exceeded the levels in nearby coastal cities, highlighting the complexity of chemistry and dynamics over this region. The INDOEX-99 revealed two major pathways for South Asian pollutants to the Indian Ocean: first one from the Indo-Gangetic Plain (IGP) via the BoB and second one from Southwest Asia via the Arabian Sea [Ramanathan et al., 1996]. Higher levels of pollution over the BoB compared to the Arabian Sea highlighted the importance of this marine region in influencing the tropical chemistry. Detailed chemical study of BoB air masses was first attempted through the "Bay of Bengal Experiment" (BOBEX I) when measurements of O_3 , methane (CH₄), carbon monoxide (CO), and sulfur hexafluoride were made during February-March 2001 [Lal et al., 2006]. High levels of O₃ (>60 ppbv), observed over the central BoB (10°N-14°N) during BOBEX I, were traced to Bangladesh and Myanmar regions. Measurements of nonmethane hydrocarbons (NMHCs) over the BoB were initiated during the "Bay of Bengal Process Studies" (BOBPS) in September-October 2002 [Sahu et al., 2006]. Subsequent measurements, made during February 2003 (BOBEX II) [Lal et al., 2007], enabled characterization of air masses using trace gas ratios. Strong correlations of ethane and acetylene with carbon monoxide (CO) provided chemical evidence of transport of anthropogenic emissions into the MABL. The spatiotemporal heterogeneity and effects of continental transport on the surface and vertical distributions of trace gases over the BoB were investigated further during the "Integrated Campaign for Aerosols, gases and Radiation Budget" (ICARB) during March-May 2006 [Srivastava et al., 2011; Srivastava et al., 2012]. The ICARB results were useful to actually quantify the impacts of various source regions on O₃ distributions over the BoB. Further, surface measurements of O₃, CO, and nitrogen dioxide (NO₂) were accompanied by airborne measurements of O₃ and NMHCs during the winter phase of ICARB (W-ICARB) during December 2008 to January 2009 [Asatar and Nair, 2010; David and Nair, 2011]. While there have already been a few campaigns to study trace gas variability over the BoB, measurements had been lacking during monsoon (June, July, and August) and later half of post monsoon (October and November) periods. The present study is aimed at reducing this temporal gap through reporting of extensive measurements of O₃ along with its several precursors during October-November 2010. During this period, sudden increase in pollution levels (due to changing wind regimes) are supposed to be observed over the BoB, which has been cleansed by the preceding monsoon circulation. The choice of this period finds support in *Barret et al.* [2011] which states that during this period, "South Asia" is characterized by heavy pollution and by fast and large-scale variability of the tropospheric circulation potentially impacting the tropospheric O₃ distribution in this region. Thus, unlike winter months, measurements during November provide an opportunity to study trace gas levels due to heterogeneous transport patterns over different sectors of the BoB. In the present paper, we explore the behavior of O₃ and its precursors over these sectors in terms of transport and chemistry.

2. Experimental Details

2.1. The Cruise

[4] The fate of wind-borne transport of reactive pollutants in sink regions depends primarily on speed and direction of low-level prevailing winds. The annual wind pattern at 10 m above mean sea level (AMSL) is shown in Figure 1. The three panels show 7 day backward trajectories at three different latitudes ((a) 8°N representing South BoB, (b) 13°N representing Central BoB, and (c) 18°N representing North BoB) along the 90°E longitude. Trajectory data are taken from reanalysis archives (ftp://arlftp.arlhq.noaa.gov/pub/archives/ reanalysis) and plotted using TrajStat software (http://ready. arl.noaa.gov/HYSPLIT.php) [Wang et al., 2009]. Figure 1 shows that during winter (represented by January), the Bay of Bengal is under the ambit of continental air from the IGP, Pakistan, and Arabian peninsula, transporting pollutants and dust from these far off regions. However, during summer (represented by April), the surface level winds are mostly of local marine origin. During monsoon (represented here by July), winds are from the south representing pristine, marine air masses of the South Indian Ocean. The post monsoon season is generally a transition period, and as elucidated in Figure 1, wind regimes change as we move across latitudes along a longitude (influences of Indian Ocean, Southeast Asia, and Indian subcontinent over south, mid, and north BoB, respectively). This campaign was conducted to access air masses originating from these different source regions.

[5] The cruise track of the campaign aboard the Ocean Research Vessel Sagar Kanya (SK-277) is shown in Figure 2. The ship sailed off the Chennai port (13.1°N, 80.6°E) on



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Figure 2. The cruise track of ORV Sagar Kanya (SK-277) is shown by the green line. The cruise started from Chennai port on 28 October 2010 and returned to the same place on 17 November 2010. The (Lat-Long) circles mark the position of SK-277 at 00 h of each day. The cross symbols denote the positions where air samples were collected. The arrow marks indicate the travel path during the campaign.

28 October 2010 at 0320 IST (Indian standard time (IST) = GMT + 5.5 h) and headed in a southeast direction until about 08°N, 89°E on 31 October 2010. Then it moved in a northeast direction until 12°N, 90°E (on 3 November) and headed north until it reached 18°N, 89.5°E on 7 November. Later, it moved southwest until it reached 16.5°N, 88°E on 11 November, then southeast to reach the 15°N, 90°E on 12 November. The ship sailed back to reach 12°N, 90°E on 13 November and then sailed across longitudes in a mostly westward direction to dock back at the Chennai port on 17 November 2010 at 1930 IST. There were several halts in between of varying time periods, ranging from a few minutes to more than a day, for other scientific activities (it was a multidisciplinary cruise).

2.2. Trace Gas Measurements

[6] Trace gases were monitored by online analyzers from Thermo Scientific (O₃ (49i), CO (48i-TLE), and NO_x (42i-TL)). The ultraviolet photometric O₃ gas analyzer works on the standard principle of absorption of radiation at 254.7 nm by atmospheric O₃. The lower detection limit of the instrument is 0.5 ppbv with a response time of $20\,s$ and measurement precision of ~1 ppbv. The zero noise of the instrument is 0.25 ppbv at 60s averaging time. The CO analyzer is based on gas filter correlation technology and operates on the principle of infrared absorption at 4.67 µm vibration-rotation band of CO [Nedelec et al., 2003]. It has lower detection limit of 40 ppbv and a 60 s response time. The zero noise of the instrument is 20 ppbv root-mean-square (RMS) at 30 s averaging time. The NO_x analyzer is based on the detection of chemiluminescence produced by the oxidation of nitric oxide (NO) by O3 molecules, which peaks at 630 nm radiation [Navas et al., 1997]. The method is specific to NO only. NO2 is measured by converting it into NO using a molybdenum convertor and then measuring total NO_x as NO. Unfortunately, the reduction of NO₂ to NO is not specific for NO₂, and other nitrogen species are also reduced to NO and act as interferences in the NO₂ measurement [Wendel et al., 1983]. The instrument has a lower detection limit of 0.05 ppbv and a response time of 60 s. Zero noise of the instrument is 0.025 ppbv RMS at 120 s averaging time.

[7] Atmospheric air was drawn from the bow of the ship at 10 m above the sea level through a 50 m long, 10 mm inside diameter, perfluoroalkox (PFA) Teflon tubing with an inverted Teflon funnel at the input side to minimize smokestack contamination and ingress of water from high waves. A suite of trace gas and aerosol instruments were connected to the other end of the tube via a manifold. The total flow through the 50 m tube resulting from suction generated by this suite of instruments was around 33 L per minute. At this flow rate, the total air volume in tube (4 L) would be drawn in about 8 s. Hence, it is assumed that residence time effects in the sample line would be negligible. While the O3 instrument drew sample air directly from the manifold, the CO and NO_{x} analyzers drew the same air from the manifold through an additional Peltier-based moisture removal unit. PTFE (Polytetrafluoroethylene) filters (5 µ; Sartorius AG, Germany), placed in the filter housings at the inlet of each analyzer, were replaced regularly. The laboratory temperature, where analyzers were placed, was maintained around 26°C. A common exhaust from all the analyzers was vented out through the back side of the ship.

[8] The O₃ instrument was calibrated with a traceable O₃ generator (Sonimix 3001, LN Industries, Geneva, Switzerland) before and after the cruise. The CO and NO_x instruments were calibrated for background concentrations with a zero air generator (PAG 003, Ecophysics), both before and after the cruise. For daily background check of the NO_x instrument, a zero air cylinder was used (cross checked with the PAG 003 before the cruise). The zero drift of the CO instrument was checked with the same zero air cylinder and the internal scrubber. The span calibration checks were carried out everyday using calibration mixtures (507 ppbv±5% NO in N₂, 510 ppbv±5% NO₂ in N₂, and 1995 ppbv CO in N₂) from Intergas, UK and traceable to National Physical Laboratory, UK. Multipoint calibrations were done prior to and at the end of the cruise.



Figure 3. Variations of meteorological parameters along the cruise track during 28 October to 17 November 2010. The black circles (except wind direction) represent the mean for every 30 min. In case of wind speed, 1-sigma spread in 30 min data is also shown. The 30 min median wind direction is shown by black circles.

[9] Air samples were collected in 900 mL borosilicate glass sampling bottles at every 4 h intervals during days and nights when the ship was in motion with a speed of at least 6 knots (kt) or more. Air samples were collected from the top of a bow tower (10 m height) on the deck of the ship using an oil-free air compressor (MB-158-E, Metal Bellow, USA). Air was drawn through a PFA Teflon tube (4 mm ID) into preevacuated Vensil glass sampling bottles that were flushed with ambient air 3–4 times before finally filling to a

pressure of around 2.5 bar leading to sample sizes of 2.25 L (standard temperature and pressure) each. These samples were analyzed in the laboratory at Ahmedabad for CH₄, CO, and light NMHCs (C_2 – C_4), using methods given in *Sahu et al.* [2006], within 2 months of the cruise to minimize storage problems [*Boissard*, 1992]. The stability tests regarding storage of these hydrocarbons showed variations of the order of 4%–5% with respect to the mean for a 2 month period. Ethane (C_2H_6), ethene (C_2H_4), propane (C_3H_8),

propene (C₃H₆), acetylene (C₂H₂), n-butane (n-C₄H₁₀), and ibutane (i-C₄H₁₀) were measured by gas chromatography using a capillary column and a flame ionization detector with an overall detection limit of 5–10 pptv for a 1 L sample and an accuracy of 3%–10% [*Sahu et al.*, 2006]. The CO values obtained during the cruise from two independent measurements namely, using online analyzer and via gas chromatographic analysis of air samples showed a good correlation (R^2 =0.85), confirming the representativeness of the collected samples.

2.3. Measurements of Meteorological Parameters

[10] An automatic weather station (AWS; Komoline Electronics Pvt. Ltd., India) was placed in the upper deck of the ship for measurement of meteorological parameters. Air temperature and humidity were measured using KDS-011, which is a single-substrate integration of temperature and humidity sensors, allowing computation of dew point. Temperature was measured by a "precision resistance temperature detector" with an accuracy of $\pm 0.1^{\circ}$ C. Relative humidity (RH) was measured by a capacitive element with an accuracy of $\pm 2\%$. Atmospheric pressure was measured by a KDS-021 sensor with accuracy of ± 0.2 hPa. Wind speed and direction were measured with accuracy of $\pm 2 \text{ m s}^{-1}$ and $\pm 2^{\circ}$, respectively. Solar radiation was measured with an accuracy of ± 5 W m⁻². Data were continuously stored in a data logger at every 10 s interval, along with position information from a built-in Global Positioning System (GPS).

[11] Data analysis involved removing data until 10 min after zeroing of the NO_x and CO analyzers (allowing sufficient time for reaction chambers to be flushed by ambient air). Similarly, data up to 15 min after completion of span calibration were filtered out to allow the reaction chamber (of the respective analyzers) to measure ambient values. Data were also checked for contamination when the ship speed was less than 6 kt. Further, data contaminated due to ship exhausts and/or emissions from trawlers passing in vicinity of the ship were identified and filtered. The data removed during halts and conditions when the ship was moving very slowly accounted for 35% of the data.

[12] The speed of the ship was calculated from the latitude and longitude values obtained using the GPS in the AWS fixed on the ship deck. Since the AWS was fixed to the ship and the ship was in motion, the wind direction measured by the wind direction sensor would be a relative value. This measured wind direction was corrected using equation (1) and values recorded independently by the AWS compass and another handheld compass.

True wind direction = measured wind direction

- (by the wind direction sensor)
- +compass direction(recorded in data logger) -angle between compass pointer and wind pointer (1)

pointer and wind pointer (1)

[13] The angle between compass pointer and the wind pointer was independently measured at 82° both before and after the cruise. If the value of true wind direction comes out to be negative, 360 is added to the output value.

3. Meteorology

[14] The various meteorological parameters observed during the cruise are shown in Figure 3. The mean temperatures varied between 26°C and 28°C until 2 November, when the ship was moving toward southeast direction. Thereafter, the mean temperatures were found to increase above 28°C as the ship moved toward higher latitudes. While ambient air temperatures showed clear diurnal variation, there were several instances of large fluctuations. Some of the largest fluctuations in temperature, e.g., large decrease on 7 November, coincided with a simultaneous increase in RH above 90%. The daytime maximum in solar radiation on the same day was also below 500 Wm⁻² resulting in a drop of air temperatures near the surface and representing cloudy/ rainy conditions,. Similar conditions were encountered on 3 and 15 November also. Temperatures above 30°C and RH below 70% were encountered on 1 November when the ship was mostly stationary in the southern part of the transect (8°N). On this day, the ship encountered mostly calm winds from the northwest. A drop in RH values below 60% was observed on 10 November, when the ship was stationary at the northern part of the transect (18°N). The daytime maximum solar radiation was observed to be higher than 700 $\mathrm{Wm^{-2}}$ on most of the days, while 3, 7, and 15 November were found to be significantly cloudy. Heavy rainfall was observed on 30-31 October and 7 and 15 November. In general, wind speeds were below 10 m s⁻¹ until 4 November. However, higher wind speeds (over 13 m s^{-1}) were observed during 4–6 November, when cyclone "Jal" was pervading over the BoB. Wind speeds decreased steadily after 6 November. The wind speeds started increasing since 14 November and another maximum above $13 \,\mathrm{m\,s^{-1}}$ was observed on 15 November.

3.1. Air Mass Grouping

[15] Backward trajectory analysis for the cruise days has been used to group the air masses into various transport regimes. The trajectories are calculated based on ensembles at 500 m above the receptor locations of the moving ship, originating 5 days back in time, using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [*Draxler and Hess*, 1997] (http://ready.arl.noaa. gov/ HYSPLIT.php). It is driven by National Centers for Environmental Prediction (NCEP) reanalysis data with model vertical velocity to compute vertical motions. The model was run to calculate ensemble trajectories at 8 h intervals, i.e., 0230, 1030, and 1830 IST for each day.

[16] For grouping the air masses, we have used simultaneous averaging of latitude as well as longitude. To achieve this, trajectories leading to similar air masses and continuous in time were bunched together. Then, the trajectory data were averaged for mean latitude (λ) with 1 sigma at different time intervals. Similar averaging was done for longitudes (φ). Further, these values along with their error bars were averaged by transforming from Cartesian to polar coordinates (angle θ and radius ρ) to get the spread in latitude and longitude (equation (2)).

$$[\theta, \rho] =$$
Cartesian to polar $[\phi(\text{mean} + / - \text{sigma}))$ (2)
 $,\lambda(\text{mean} - / + \text{sigma})]$



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Figure 4. Air mass groups encountered aboard ORV Sagar Kanya during 28 October to 17 November 2010. The altitude variations of these air masses are shown using different colors. The colored lines represent the spread of the trajectory group about the mean trajectory.

[17] The values in $[\theta, \rho]$ in polar coordinates were converted back into Cartesian coordinates to get the actual mean and sigma of latitudes and longitudes at different temporal points up to 120 h backward. This kind of averaging gives a better representation of air masses in contrast to only latitudinal or only longitudinal averaging which could be biased in favor of air masses arriving from a particular direction. The resultant grouping of air masses shows four distinct types (Figure 4) namely, (1) marine air from the Indian Ocean (IO), (2) continental air from South China (Macao and Hong Kong), Vietnam, South Myanmar. and over the East Bay of Bengal, eastern Indo-Gangetic Plain, Bangladesh. and Myanmar (N-BoB), and (4) air masses from East Bay of Bengal, South Myanmar, Cambodia, and coastal Thailand (E-BoB).

[18] The IO group was observed during 28 October (1830 IST) to 2 November (0230 IST) and was predominantly marine. The NE-BoB air mass represents long-range transport during 3 November (1830 IST) to 8 November (1030 IST). While the NE-BoB represents SE Asian air masses, the N-BoB is constituted by air masses from nearby northern landmasses over the IGP, Bangladesh, and some portion of Myanmar as well as the marine regions over North BoB during 8 November (1830 IST) to 14 November (0230 IST). The E-BoB air masses were encountered during 14 November (1030 IST) to 16 November (1030 IST) and resembled the NE-BoB air masses in terms of their spatial coverage with a few distinct differences. The most copious difference is that the NE-BoB air masses represent long range transport, i.e., originate further east considering the 5 days temporal span. Further, the NE-BoB air masses spent greater time above 3 km altitude while E-BoB had large marine influence (see color bars in Figure 5).

3.2. Residence Time of Air Masses

[19] Residence time analysis is used to classify the air masses into different horizontal and vertical regimes. The

residence times were computed using back air trajectories generated by HYSPLIT model for the ship's locations at every 8 h intervals during the cruise (Figure 5). To compute residence times over continental and marine regions separately, a proxy method was used. In this method, images were generated such that 5 day back trajectories were plotted over maps with the continental regions in black, oceanic regions in white, and every hourly latitude-longitude values of trajectories as red points. Next, these images were analyzed to identify a red dot surrounded by black dots. The total number of such red dots gives the number of points falling over continents. Similarly, number of points falling over oceanic regions was computed from the number of pixels that had a color difference from neighboring pixels equivalent to difference between red and white. For red points which have both black and white as neighbors, i.e., for coastal locations, more weight is given to continents if there are more black points as neighbors and vice versa. There would still be some error in this method if a trajectory crosses itself at some point of time, but we consider this negligible. Thus, this analysis provides a robust, efficient, and fully automated way of segregating the trajectory points into continental and oceanic types. The analysis showed that IO air mass had spent almost 97% time over oceanic regions (Figure 5) and hence correctly represents marine signature. In contrast, the NE-BoB air mass had spent only 41% time over oceanic regions and 59% over continental South Myanmar, Vietnam, and Hong Kong region of China. The N-BoB air mass had spent 58% time over North BoB and 42% over Northwest Myanmar, East Bangladesh, and Northeast India. The E-BoB air mass had a large marine influence (78% time over East BoB) but considerable continental influence as well (22% time over Myanmar, Thailand, and Vietnam).

[20] Residence times were also computed for different altitude ranges (Figure 5). The trajectories belonging to IO group spent 81% of their time below 750 m and 19% time between 750 and 1500 m altitudes. Trajectories in NE-BoB air mass spent 17% time above 3000 m, 28% between 1501



Figure 5. Variations of residence time of air parcels encountering the cruise during 28 October to 17 November 2010 over the Bay of Bengal. (top) Different altitude bins. (middle) % residence times over continental and marine regions.

and 3000 m, 26% between 701 and 1500 m, and 28% below 750 m altitude. Similarly, trajectories in N-BoB air mass spent 7% time above 3000 m, 38% between 1501 and 3000 m, 35% between 701 and 1500 m, and 20% below 750 m altitude. The trajectories E-BoB spent 45% time between 701 and 1500 m and 55% below 750 m altitude. Thus, these trajectories spent most of their time in lower altitudes, unlike the NE-BoB air masses. It must be noted that while the altitudinal distributions of the IO and E-BoB air masses are fairly similar, their spatial coverage is entirely different as explained in the preceding section.

[21] The MABL for the IO air masses varied mostly between 250 and 750 m. These MABL values were calculated from HYSPLIT model using NCEP meteorological data (http://ready.arl.noaa.gov/ HYSPLIT.php). MABL values were highest in the NE-BoB air mass on 4 November. The average MABL gradually decreased from 4 to 11 November as the ship moved toward northern latitudes. The nighttime MABL values around 10 November were about 600 m. During the return leg, the MABL values again continued to increase and were around 1000 m on the midday of 16 November. The average MABLs (mean of 0600, 0900, 1200, 1500, 1800, and 2100 IST) in the IO, NE-BoB, N-BoB, and E-BoB air masses were 475, 1140, 706, and 820 m, respectively.

4. Levels and Variability of Trace Gases

4.1. Variations in O₃, CO, and NO_x

[22] Variations in O₃, CO, and NO_x during the cruise are shown in Figure 6. Both O3 and CO gradually increase during 2 to 6 November when the ship was moving toward the northern BoB, i.e., from about 8°N to 18°N. During 7-10 November, the ship did not change its location much (Figure 2); however, O₃ as well as CO showed slight decrease in the levels. Interestingly, during 14-17 November, although the ship was approaching toward coastal Indian region (Chennai), O3 and CO (as also CH4, C2H6, and C₂H₂, shown later in Figure 9) values showed a decreasing tendency. This was because the air masses encountered were not coming from the Indian subcontinent but were influenced by marine regions over the East BoB. During the complete cruise, a wide range of O₃ concentrations were encountered from as low as 11 ppbv in the open ocean (29 October) to over 60 ppbv in the North BoB (6 and 11 November). O₃ values of 28 ppbv were measured off the Chennai coast both at the beginning and end of the cruise. CO mixing ratios varied from a low (45 ppbv on 30 October) to about 260 ppbv (7 November). The lowest CO values were observed coinciding with the very low O₃ values (30 October), but the highest CO values did not coincide with the highest O₃



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Figure 6. Variations of O_3 , CO, and NO_x along the cruise track during 28 October to 17 November 2010. The mean (black) and sigma (grey) are shown for every 30 min. The time axis is divided to represent different air masses encountered during the cruise. The shaded portion represents measurements when cyclone "Jal" was pervading over BoB.

values. NO_x levels varied from 0.2 ppbv (28 October and 15 November) to 1.2 ppbv (2 November). Lowest NO_x values (0.2 ppbv) were encountered on 28 October and 15 November in the open ocean. However, the NO_x levels seemed to increase during 29 October to 2 November period, when the ship moved southward toward lower latitudes into the open ocean. A decrease in NO_x levels was observed during 11–15 November during the return leg of the cruise.

[23] The mean concentrations of different trace gases measured in different air masses during the cruise are shown in Table 1. It is observed that mean O_3 , CO, and NO_x levels were highest in the NE-BoB air mass, indicating anthropogenic contributions. In general, O_3 and CO values were high when wind direction was between 30° and 90° (Eastern sector) and wind speed was above 12 m s^{-1} (Figure 7). These conditions were encountered during 4–6 November. It must be noted that O_3 and particularly CO values were high when ventilation coefficient (VC) was greater than $8000 \text{ m}^2 \text{ s}^{-1}$. VC was obtained by multiplying wind speed

(m/s) with MABL (m). In sink regions such as oceans, VC represents the rate by which pollutants will be blown into the mixed layer over a particular location [*Krishnan and Kunhikrishnan*, 2004]. Particularly for the NE-BoB air mass,

Table 1. Trace Gas Levels in Different Air Masses (Units in ppbv)During 28 October to 17 November 2010

Species	IO	NE-BoB	N-BoB	E-BoB
O ₃₃ CO NO _{xx}	$\begin{array}{c} 20.1 \pm 3.5 \\ 73.4 \pm 13.7 \\ 0.60 \pm 0.18 \end{array}$	$\begin{array}{c} 46.9 \pm 6.1 \\ 234.9 \pm 23.1 \\ 0.71 \pm 0.16 \end{array}$	$\begin{array}{c} 45.9 \pm 9.7 \\ 198.0 \pm 27.1 \\ 0.59 \pm 0.13 \end{array}$	$\begin{array}{r} 32.9 \pm 4.6 \\ 200.2 \pm 39.9 \\ 0.39 \pm 0.12 \end{array}$
$C_{2}H_{6}$ $C_{2}H_{4}$ $C_{3}H_{8}$ $C_{3}H_{6}$	$\begin{array}{c} 0.487 \pm 0.077 \\ 0.100 \pm 0.041 \\ 0.048 \pm 0.016 \\ 0.059 \pm 0.036 \end{array}$	$\begin{array}{c} 1.640 \pm 0.179 \\ 0.178 \pm 0.055 \\ 0.206 \pm 0.119 \\ 0.062 \pm 0.035 \end{array}$	$\begin{array}{c} 1.734 \pm 0.146 \\ 0.129 \pm 0.055 \\ 0.170 \pm 0.204 \\ 0.071 \pm 0.032 \end{array}$	$\begin{array}{c} 2.579 \pm 1.254 \\ 0.098 \pm 0.055 \\ 0.143 \pm 0.095 \\ 0.067 \pm 0.016 \end{array}$
$i-C_4H_{10}$ $n-C_4H_{10}$ C_2H_2	$\begin{array}{c} 0.047 \\ 0.044 \pm 0.009 \\ 0.093 \pm 0.046 \end{array}$	$\begin{array}{c} 0.056 \pm 0.007 \\ 0.068 \pm 0.022 \\ 0.646 \pm 0.109 \end{array}$	$\begin{array}{c} 0.104 \pm 0.070 \\ 0.118 \pm 0.084 \\ 0.655 \pm 0.241 \end{array}$	$\begin{array}{c} 0.104 \pm 0.088 \\ 0.089 \pm 0.088 \\ 0.440 \pm 0.166 \end{array}$



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Figure 7. Variation of wind speed (m/s) and wind direction along with concentrations of O₃ (ppbv) (Left panel) and CO (ppbv) (Right panel).

wherein wind speeds were consistently high (mean = 9.6 m) s^{-1}) and MABLs were also very high, a high VC allowed for the long-range transport of continental emissions into the MABL, resulting in higher levels of several trace gases (Table 1).

[24] Nevertheless, NOx levels were conspicuously high (0.60 ± 0.18) in the IO air mass, which is supposed to have a pristine marine characteristic. It is possible that the IO air mass, which is sourced to southern marine regions, could be affected by NO_x emissions from international shipping lanes along Yemen-Sri Lanka-(Malaysia-Sumatra) corridor.

[25] Figure 6 (shaded region) shows sudden enhancement in O₃ and CO values around 2 November, and these values were constantly increasing during 3-6 November. While the general increase in trace gas concentrations after this period occurred due to transport from China and Southeast Asia, the sudden increase is suggested to be associated with the cyclone Jal, over the Bay of Bengal during this period. It has been shown that the presence of Cyclone Jal [Chandrasekar and Balaji, 2012] (http://en.wikipedia.org/ wiki/Cyclone Jal) had led to a low-pressure system along with very high wind speeds over 100 km h^{-1} (Figure 3). Such strong winds could have resulted in the faster transport of continental air masses into the Bay of Bengal. However, the cyclone did not directly intercept our cruise track as the ship was heading toward North BoB when the cyclone was moving toward Chennai.

[26] Two episodes of high CO (>250 ppbv) occur during 6 and 14 November. "Potential source contribution function" (PSCF) analysis [Asatar and Nair, 2010; Mallik et al., 2012] was used to identify the geographic source regions possibly contributing to these enhanced levels. PSCF is the ratio of polluted trajectory segment endpoints falling in a grid cell to the total number of trajectory endpoints passing over that grid. The PSCF value can be interpreted as the conditional probability that the concentrations of a given pollutant sample greater than the threshold level are related to the passage of air parcels through a grid cell during transport to the receptor site. PSCF analysis was carried out for the receptor regions (16°N, 89°E and 12°N, 87°E) where CO values were over 250 ppbv during 6-7 November and 14-15 November, respectively. The analysis was performed using CO gridded daily averages from "Measurements of Pollution in the Troposphere" (http://eosweb.larc.nasa.gov/ PRODOCS/mopitt/table mopitt.html) using TrajStat software [Wang et al., 2009]. The threshold value was taken at 75 percentile of the data available over the grid. The analysis indicates Myanmar, Thailand, and southern tip off Guangdong (China) as potential contributors of CO to the air parcels encountered during 6-7 November. The potential contributor regions to enhanced CO during 14-15 November are found to be the south of Myanmar (Kayin) and Thailand (TAK region) (Figure 8). The Moderate Resolution Imaging Spec-troradiometer (MODIS) fire maps [Davies et al., 2004] (http://rapidfire.sci.gsfc.nasa.gov/cgi-bin/imagery/firemaps.cgi) indicated that these regions were influenced by fire activities during this period.

[27] A composite of the observations of O₃ and CO made during seven ship campaigns conducted over the BoB are compiled in Table 2 to understand the seasonal variability of these gases. O3 levels over the BoB are observed to be the highest during winter months $(36\pm 8 \text{ to } 54\pm 17 \text{ ppbv})$

Table 2. O3 and CO Values in ppbv Reported Over the Bay of Bengal in Different Months During Different Campaigns

Month		Region	Overall		
	Year/Campaign		O_3	СО	Reference
January	Dec 2008–Jan 2009 W-ICARB	8°N–21°N	48 ± 8	228	David and Nair [2011] Asatar and Nair [2010]
February	Feb 2001 BOBEX I	13°N-20°N	42 ± 12	217 ± 31	Lal et al. [2006]
March-April	Mar-Apr 2006 ICARB	5°N–20°N	12	145 ± 38	Nair et al. [2011] Srivastava et al. [2011]
September	Sep-Oct 2002 BOBPS	7°N–20°N	27 ± 6	143 ± 23	Sahu et al. [2006]
November	Nov 2010	8°N–18°N	41 ± 9	197 ± 44	This Study
December			-	-	-



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Figure 8. (left) Potential source contribution function (PSCF) maps for the receptor region 12°N, 87°E during 14 November at 100 m above ground level. The color axis represents the probability of a grid as potential contributor to the receptor region. (right) Satellite imageries of Moderate Resolution Imaging Spectroradiometer (MODIS) fires during 7–16 November 2010. The MODIS fire maps accumulate the locations of the fires detected by MODIS on board the Terra and Aqua satellites over a 10 day period. Each colored dot indicates a location where MODIS detected at least one fire during the compositing period.

and lower during spring $(22 \pm 1 \text{ to } 28 \pm 14 \text{ ppbv})$. O₃ levels exhibit a secondary enhancement during November $(41 \pm 9 \text{ ppbv})$. Similar to O₃ variability, CO levels are also highest during winter $(155 \pm 43 \text{ to } 228 \text{ ppbv})$, suggesting that the BoB is most polluted during winter season which is mainly attributed to the strong continental outflow [*Naja et al.*, 2004]. CO levels also discern a secondary enhancement during November $(197 \pm 44 \text{ ppbv})$ similar to O₃. In contrast to O₃, CO levels are moderately higher during spring $(145 \pm 38 \text{ to } 162 \pm 3 \text{ ppbv})$. Notably, despite numerous efforts by several groups (Table 2), measurements of O₃ during May to August are still lacking. Measurements of O₃ precursors are even more lacking and therefore highly desirable to better understand the chemical and dynamical processes over the BoB.

4.2. Variations in CH₄ and NMHCs

[28] Variations in CH₄, CO, and C₂–C₄ NMHCs measured during the cruise are shown in Figure 9. The mean values for different air masses are also presented in Table 1. CH₄ values varied between 1.6 and 1.9 ppbv for most of the samples. CH₄ values were highest around 10 November. The variation of C₂H₆ was very similar to the variation of CO (R^2 = 0.68) indicating colocated sources. The average C₃H₈ for all the air samples collected during the cruise was 0.142 ppbv with a sigma of 0.105 ppbv. Similar variation in C₃H₈ values (σ > 60%) were also observed during the Trace-P measurements [*Wang et al.*, 2003]. Highest C₃H₈ value (>0.3 ppbv) was observed on 5 November in the NE-BoB air mass.

[29] During the BOBPS campaign over the BoB [Sahu et al., 2006], C_2H_6 and C_3H_8 values for oceanic air masses were 0.598 ± 0.140 and 0.192 ± 0.060 ppbv, respectively. The C_2H_6 values during this cruise for the pristine, marine air (Table 1) are close to the Sahu et al. [2006] oceanic values while C_3H_8 values for this air mass are very low compared to Sahu et al. [2006] values. However, our C_3H_8 measurements in IO air mass compare very well with INDOEX BoB plume results of 0.050 ± 0.036 ppbv C_3H_8 [Muhle et al., 2002].

 C_3H_8 values less than 0.025 ppbv were detected south of 16°N over BoB during INDOEX. It is also pertinent to mention here that the air masses encountered by *Sahu et al.* [2006] were coming either from southern oceanic regions or from the Indian landmass. In our case, the air masses originated from southern marine regions during the first few days only. The air masses during major part of the present campaign were directed from north and northeast marine regions and adjoining continental regions, as explained in section 3.1. The average C_3H_8 values for the NE-BoB, N-BoB, and E-BoB air masses (Table 1), as well as the total average C_3H_8 (0.142 ppbv), are somewhat close to *Sahu et al.* [2006] values (which were also affected by transport from continental regions).

[30] The C_2H_2 values were below 0.2 ppbv in marine air masses encountered until 2 November (Table 1). After this, the values are observed to be clearly increasing, indicating transport from continental sources (Figure 9). This is corroborated by good correlation between C_2H_2 and O_3 (R = 0.86). Both $n-C_4H_{10}$ and $i-C_4H_{10}$ were below 0.1 ppbv for most of the samples. In a few cases, n-C₄H₁₀ values were around 0.3 ppbv. The values of double-bonded hydrocarbons C₂H₄ and C₃H₆ were below 0.4 and 0.1 ppbv, respectively; however, their patterns do not bear resemblance to C2H6 or C3H8. The levels of C₂H₄ were higher in continental air masses (NE-BoB and N-BoB) compared to marine air masses (IO). However, this differentiation is not so clear for C3H6 (Table 1), indicating that these could represent background oceanic values for this time of the year. The average C2H4 and C3H6 values obtained during the cruise for all air samples were 0.125 ± 0.065 and 0.062 ± 0.028 ppbv, respectively. These values are in the range $(0.299 \pm 0.170 \text{ and } 0.129 \pm 0.050 \text{ ppbv for } C_2H_4 \text{ and } C_3H_6)$ obtained during post monsoon of 2002 by Sahu et al. [2006], if sigma is also considered. Better detection of alkenes (C₂H₄ and C₃H₆) in marine air masses (IO and E-BoB) could be impacted by local emissions over the ocean [Sahu et al., 2010].



Figure 9. Variations of CH₄, CO, and C_2 – C_4 NMHCs along the cruise track during 28 October to 17 November 2010. The time axis is divided to represent different air masses encountered during the cruise. The missing points mostly indicate that these species were not detected in samples.

4.3. Latitudinal Gradients

[31] Latitudinal gradients in O_3 and CO were computed by binning the observed concentrations into 0.25° bins for 8°N– 18°N latitudes. Though steep gradients were observed for both O_3 and CO, their patterns are very different (Figure 10). During the onward journey toward higher latitudes, O_3 and CO showed positive latitudinal gradients but this did not occur during the return leg. While O_3 values were steadily decreasing since 13 November when the ship was moving toward lower latitudes (away from northern landmasses), the CO values were on the rise. The causes have already been discussed in section 4.1. Figure 10 shows that the gradients were sharper at some places and flat at others. This is because the ship did not move directly across latitudes. Rather, there was substantial longitudinal coverage

as well, e.g., during 28 October to 2 November and between 14 and 17 November, the longitudinal variation of 10° (80° E-90°E) was more compared to latitudinal variation of 5° (8° E–13°E). This resulted in flatter gradients in both O_3 and COat 8°N-11°N compared to 13°N-18°N (Figure 10). The spread was different in different latitudinal bins because the ship had spent greater time in some latitudinal bands compared to others. Further, there are bound to be other effects, e.g., effect of diurnal features embedded in this estimated slope. The overall variation of O₃ was 3.95 ppbv per degree change in latitude, with increasing concentrations toward northern continental landmasses. CO values showed a latitudinal gradient of 16.56 ppbv/°, increasing toward northern latitudes. The positive gradients in the concentrations of air pollutants toward the northern BoB is a common feature [Lal et al., 2013 and references therein], which is mainly

Table 3. Latitudinal Gradients in O_3 (ppbv/°) and CO (ppbv/°) Reported Over the Bay of Bengal

Period	O ₃ (ppbv/°)	CO (ppbv/°)	Author
February 2003	1.4	10	Lal et al. [2007]
February-March 2001	1.45	15	Lal et al. [2006]
March-April 2006	1.3	9.9	Nair et al. [2011]
	5.4		Srivastava et al. [2011]
September-October 2002	1.3	4.2	Sahu et al. [2006]
October-November 2010	3.95	16.56	This Study
December (2008)–January (2009)	2.1		David and Nair [2011]

attributed to the relatively higher influences of the continental outflow over the northern part of BoB as compared with the marine air in the southern part. It is pertinent to mention here that the southern BoB is marked by absence of large, continental regions and hence devoid of strong anthropogenic sources of O_3 and CO.

[32] The O₃ and CO gradients obtained in this study have been compared with previously reported values over the BoB during different seasons and years in Table 3. The observed latitudinal gradient in O₃ (3.95 ppbv/°) as well as CO (16.56 ppbv/°) is significantly higher as compared with previous surface observations (1.3 to 2.1 ppbv/° for O₃ and 4.2 to 15 ppbv/° for CO) over the BoB. The larger gradients obtained in this study may be attributed to the spatial heterogeneity in trace gas concentrations in the N-BoB and S-BoB, which are under the influence of different transport regimes in November, i.e., the N-BoB is affected by emissions over the Asian region while the S-BoB is still cleaner. Large-scale biomass burning during this period could also contribute to these gradients. Further, the relatively larger gradient in O₃ compared to CO is a result of their lifetime, i.e., shorter lifetime of O₃ results in larger gradients between source (continents) and sink (marine) regions.

5. Air Mass Characterization

5.1. Emission Characteristics

[33] Simultaneous measurements of CO and volatile organic carbons (VOCs) can be used to get an insight into their sources due to unique emission signatures of different sources [Wang et al., 2003; Guo et al., 2007], e.g., more C₂H₆ is emitted from biomass burning compared to fossil fuel (FF) combustion (http://www.ipcc.ch/ipccreports/tar/ wg1/140.htm). In contrast, the predominant source for C₄H₁₀ is ff combustion. On the other hand, C₃H₈ emissions from FF are roughly 1.5 times that of biomass burning. For East Asia, the major sources of C2H6 are combustion of biofuel (BF, 45%) followed by industry (19%), and biomass (BM, 16%) with minor sources in transport (10%) and residential coal combustion (10%) [Streets et al., 2003]. Unlike C₂H₆, the major sources of butanes are the transport sector (58%), followed by industry (31%) [Streets et al., 2003]. C₂H₂ has sources in BF (45%), transport (26%), industry (12%), residential coal combustion (9%), and BM (8%) [Streets et al., 2003]. However, during this campaign, as only C2-C4 NMHCs were measured, we are limited in our interpretation of the sources.

[34] Higher C_4H_{10} values in the N-BoB air mass (Table 1) had indicated the influence of fossil fuel combustion in this

air mass. In general, emissions of the butane isomers are strongly coupled and are largely attributed to the use of fossil fuels (natural gas, liquified petroleum gas (LPG), gasoline) and to some extent BM/BF burning. The rates of reaction of C₄H₁₀ isomers with OH are nearly equal, and considering OH as the major sink, the ratio between these two isomers is expected to change little with photochemical processing during transport. Thus, this ratio is a strong tracer of the actual emission ratio [Baker et al., 2011]. The slope of i-C₄H₁₀/n- C_4H_{10} of 0.62 ($R^2 = 0.85$) in the N-BoB air mass indicates the influence of urban/industrial sources. The observed ratio is also higher than reported literature values of 0.33 for BF burning [Andreae and Merlet, 2001] and of 0.37-0.55 for urban measurements [Derwent et al., 2000; Parrish et al., 1998]. A ratio of $i-C_4H_{10}/n-C_4H_{10}$ of 1.1 has been reported for areas strongly influenced by the petrochemical industry [Jobson et al., 2004]. Thus, the N-BoB air mass seems to be influenced by a mixture of BF and FF but dominated by the latter.

[35] The interrelationships among different NMHCs and CO in the E-BoB air mass indicate influence of BM/BF (Figure 11). Negative slope of 0.29 ($R^2 = 0.66$) between C₃H₈ to C₂H₆ in E-BoB indicates greater impact of BM/BF (C_2H_6) in these air masses rather than FF (C_3H_8) . Low C_2H_2 to CO slope of 0.003 ppbv/ppbv ($R^2 = 0.64$) in this air mass is closer to the Asian outflow value (0.0044 ppbv/ppbv) [Talbot et al., 1997] and bears signatures of biomass burning (0.0046 ppbv/ppbv) [Wang et al., 2003]. CH₄ to CO slope of 0.1 ppbv/ppbv ($R^2 = 0.48$) and C₂H₂ to C₂H₆ slope of 0.3 (R^2) =0.64) for E-BoB air mass also indicate dominance of combustion products namely, C2H6 and CO. Decreasing C₃H₈ to CO ratio, as in E-BoB plume, was observed by Kurata et al. [2003] for biomass burning regions. Further, the C₂H₆/CO slopes of 0.01 ($R^2 = 0.8$) for E-BoB compares well with a value of 0.01 for a semiurban region in India (Hissar) [Lal et al., 2012], which was attributed to BM/BF burning effects. Moreover, C₂H₆/CO slopes of 0.0108 for BM burning and 0.0143 for BF burning were obtained by Andreae and Merlet [2001]. Widespread BM and BF burning emissions are presumed to occur in suburban and rural areas [Baker et al., 2011]. Further, trajectory analysis (section 3.1) showed that no major urban region was traversed by the E-BoB air mass. Negative associations between i-C₄H₁₀ with CO with $(R^2 = 0.49)$ in the E-BoB with a slope of 0.001 corroborates this fact.

[36] Thus, multiple chemical evidences indicate that the E-BoB air mass was influenced by BM/BF emissions. However, given the spread in data and the limited number of species measured, it is not possible to categorize our measurements into BM and BF types. Measurement of tracers such as CH₃CN and CH₃Cl [Blake et al., 2003] would have helped to segregate the actual contributions of BM and BF in the continental plumes. Nevertheless, model studies using results from the 1999 INDOEX campaign show that between 60% and 90% of CO can be attributed to BM/BF burning and that the burning of biofuels in particular represents a large fraction of total biomass burning [Lelieveld et al., 2001]. Also, it is pertinent to mention here that substantial amount of natural gas production occurs over the Myanmar, Thailand, and Indonesia regions (https://www.cia.gov/library/publications/ the-world-factbook/rankorder/ 2249rank.html). Although both C₂H₆ and C₃H₈ have sources from the burning of BF, they



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Figure 10. Latitudinal variation of (top) O_3 and (bottom) CO during 28 October to 17 November 2010. Half-hourly concentration data are used for these plots.

could also have significant sources from the use of FF, particularly LPG and natural gas [*Wang and Zeng*, 2004; *Simpson et al.*, 2012]. Nevertheless, the R^2 values for different slopes in NE-BoB and E-BoB air masses indicate that the E-BoB was more strongly influenced by BM/BF.

[37] Alkenes (C₂H₄ and C₃H₆) are short-lived compounds (due to their high reactivity) and can have significant local sources in surface ocean waters related to biological activity [*Bonsang and Lambert*, 1985]. C₃H₆ and C₂H₄ correlate very well in the IO air mass with a slope of 0.66 ppbv/ppbv (R^2 =0.98) (Figure 11). Uncorrelated CH₄ and CO in IO (0.944 ppbv/ppbv) air masses indicate that CH₄ in these air masses is mainly of marine (biogenic) origin and that these gases do not have significant common sources over the BoB [*Sahu et al.*, 2006].

5.2. O₃-NO_x-CO Relationships

[38] Although the amount of O_3 produced for each molecule of NO_x consumed is controlled by complex nonlinear chemistry (involving VOCs), the O_3 to NO_x slopes can be

used as rough indicators for the production efficiency of O3. Differences in photochemical age are the result of reactivity/transport effects and can be better estimated from NO_x/NO_y ratios. Trainer et al. [1993] have found O₃ to be strongly correlated with NO_z (NO_y - NO_x) for air masses with all degrees of photochemical processing. However, in absence of NOv measurements during the present campaign, we have to rely on O3/NOx ratios to study the ozone production efficiency. It must be mentioned here that the O₃ production from NOx over low NOx regions like oceans will be limited by availability of NO_x. During the present campaign, the O₃ to NO_x slopes show different rates of O₃ production in different air masses including a net negative value in air mass from Indian Ocean (Figure 12). The slopes of O_3 to NO_x are -2.17, 12.89, 38.75, and 13.34 ppbv/ppbv for the IO, NE-BoB, N-BoB, and E-BoB air masses, respectively. However, the R^2 values are very low (<0.1), indicating local perturbations and inhomogeneous transport effects [Wang et al., 2004]. Positive slopes for the NE-BoB, N-BoB, and E-BoB air masses are comparable to similar features



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Figure 11. Variation of CH_4 and NMHCs with CO in various air masses during the cruise. Four different colors represent different air masses namely, IO (black), NE-BoB (blue), N-BoB (red), and E-BoB (green). The fit lines in the diagram are based on robust regression.

observed over many rural and maritime locations downwind of major urban and industrial sources of the world. The O_3 to NO_x slopes are observed to be similar for both NE-BoB and E-BoB air masses, indicating similar O_3 -NO_x chemistry in these air masses which share common source regions. The large observed slopes in continental air masses accompanied by very low NO_x levels over the BoB indicate that transport from continental regions plays the dominant role in maintaining the O_3 levels over the BoB rather than in situ local production.

[39] However, O_3 -NO_x slopes are supposed to be more meaningful near polluted plumes due to shorter lifetime of NO_x . On the other hand, O_3 to CO ratios have previously been used to estimate the amount of O3 exported to the North Atlantic troposphere from North America [Parrish et al., 1998]. CO variations are generally used as a tracer of urban pollution, and it is suggested that O₃ produced from anthropogenic precursors could show a positive relationship with CO. Wang et al. [2004] attributed a positive O₃/CO slope to production of O₃ in aged air masses that had reduced CO levels. As an air parcel ages, the O3 and CO levels in the parcel are modified during transport, primarily by dilution with background free tropospheric air and O3 production resulting from the NO_x-VOC photochemistry. O₃/CO ratio in a polluted air parcel decreases as it ages and is transported further from the CO and O₃ source [Real et al., 2008]. Further, in the remote tropical MABL, where NO_x levels are supposed to be low coupled with intense solar radiation and water vapor, photochemical processing will simultaneously remove O_3 and CO. The slopes of O_3 to CO are $0.09, 0.37, 0.20, \text{ and } 0.11 \ (R^2 = 0.5, 0.9, 0.7, \text{ and } 0.9, \text{ respec-}$ tively) for the IO, NE-BoB, N-BoB, and E-BoB air masses, respectively (Figure 12). The lower slopes in IO and E-BoB are indicative of aged tropical marine air which is expected to be more depleted in O₃ than CO because of the shorter lifetime of O₃.

[40] The O_3 to CO ratio in the N-BoB compares well to a value of 0.16 obtained for Kaashidhoo (5°N, 73.5°E) in the

Indian Ocean. This ratio was estimated at 0.14 during INDOEX 1999 [Stehr et al., 2002]. The lower O3 to CO ratio over the Asian region was attributed to the photochemically less efficient O₃ production over the Indian region compared to the midlatitudes [Naja and Lal, 2002]. The O₃/CO slope of 0.11 for the E-BoB air mass compares well with the O3/CO value of 0.1 obtained in emission plumes transported from Asia across the Pacific Ocean observed during the Intercontinental Transport and Chemical Transformation experiment in 2002 [Nowak et al., 2004]. The O₃ to CO slope in the NE-BoB air mass is comparable to the values at Cape Verde Atmospheric Observatory (0.3–0.45 during October 2006 to September 2009), a remote site in the Atlantic Ocean [Carpenter et al., 2010], as well as values of 0.3-0.4 observed at the Azores [Parrish et al., 1998]. A smaller slope (0.18) in Hong Kong outflow compared to around 0.40 in pollution outflow from United States is attributed to a reduced efficiency in photochemical production and/or to a larger emission ratio of CO to NOx in China [Wang et al., 2004].

5.3. Principle Component Analysis

[41] Extensive measurements of O_3 , NO_x , CO, CH_4 , NMHCs, and meteorological parameters over the BoB during the post monsoon period of 2010 allowed application of principal component analysis (PCA, a multivariate statistical technique) [*Jackson*, 1991] to elucidate underlying relationships among the various chemical and dynamical parameters. The main idea of this method (of data reduction) is to form a smaller set of representative variables (uncorrelated or orthogonal principle components (PC), each containing a linear combination of some of the variables) from a large number of variables. The number of explanatory variables is reduced while retaining most of the original information by grouping the variables with similar characteristics into factors [*Ho et al.*, 2002]. The first PC is oriented to explain most of the data. The second PC is orthogonal to the first

Table 4. Structure Matrix for Variables Analyzed by the Method of

 Principal Components^a

	Components			
Variables	1	2	3	
O ₃ (ppbv)	0.882	-0.092	0.079	
CO (ppbv)	0.893	0.066	-0.017	
C_2H_4 (ppbv)	0.588	0.366	0.355	
CH ₄ (ppbv)	0.743	-0.036	0.318	
Residence hours (ocean)	-0.823	-0.211	-0.130	
Residence hours (land)	0.871	0.313	0.084	
Residence hours (1-750 m)	-0.778	0.091	-0.128	
MABL depth (m)	0.610	0.696	0.015	
NO _x (ppbv)	-0.263	0.489	0.435	
Wind speed (m/s)	0.250	0.717	-0.090	
Wind direction (°)	0.099	-0.686	-0.064	
Temperature (°C)	0.405	0.196	0.704	
Humidity (%)	-0.520	0.155	-0.703	
Solar radiation ($W m^{-2}$)	-0.031	-0.044	0.730	

^aThe major component for each variable is marked in bold.

and explains the next largest variation in the data. To carry out PCA, we interpolated all the data into 4 h intervals. The values for each component were then standardized by subtracting mean and dividing by the standard deviation, to ensure that some variables do not become unduly important because of scale effects.

[42] A "Kaiser-Meyer-Olkin Measure of Sampling Adequacy" (KMO represents the strength of connection between variables) of 0.73 indicated appropriateness of factor analysis to these variables. In general, KMO values greater than 0.5 indicate that pattern of correlations are relatively compact leading to distinct and reliable factors. The correlation coefficients showed that none of the coefficient was larger than 0.9; thus, problems arising from singularity (perfect correlations) in data are not expected in this analysis. It is to be noted that C_2H_6 and C_2H_2 were removed from the analysis after initial runs, as the correlation between C₂H₂ with O₃ was 0.86 while that between C₂H₆ and CO was 0.88. Further, the Bartlett's test was highly significant (p < 0.001) indicating that the R-Matrix is not an identity matrix; therefore, the variables used in this analysis are not totally uncorrelated. From the initial eigenvalues, it was seen that factors 1, 2, 3, and 4 explained 40.2%, 13.5%, 12.1%, and 8.6% of variances, respectively. The scree plot (figure not shown) showed that approximately three factors could be retained.

[43] The component matrix showed three major components, and the first three components are retained after rotation (Oblimin with Kaiser normalization) as well. The structure matrix (Table 4) shows the correlation between each variable in the analysis and its component. The first component contained most of the trace gasses (O3, CO, CH₄, C₂H₄ as well as % residence hours over land). This indicates that transport from continental source regions played a major role in the variability of these trace gasses during the campaign. Further, the residence hours over ocean and in the 1-750 m altitude are negatively loaded on to the first component. Thus, PCA independently confirms that transport from continental source regions would be less effective when residence time of air parcels is more at lower altitudes or over oceans. The second factor contained NOx, wind direction (-ve) and wind speed. This indicates that there could be significant source of NO_x over the BoB (probably emitted from various ships, trawlers, etc.), which could be picked up by low-altitude air masses with significant wind speed. Further, wind direction being negatively loaded with NO_x in the second component indicates that some of the NO_x could be of local origin. Further, since wind parameters (measured locally) are not loaded along with O₃ and CO, this means that these gases were generally not governed by very local sources.

6. Chemical Box Model Simulations

[44] To get an insight into the balance between chemical production and loss processes over the marine environment of BoB, observed diurnal patterns in surface O3 concentrations during selected days are simulated with a chemical box model NCAR Master Mechanism (NCAR-MM) developed at National Center for Atmospheric Research, Boulder, USA (http://cprm.acd.ucar.edu/Models/MasterMech/index.shtml). The NCAR-MM [Madronich, 2006] consists of highly detailed gas phase chemistry (about 2000 species participating in about 5000 reactions), and this includes about 306 photolysis reactions. The model can simulate the time evolution of an air parcel initialized with measured concentrations of trace gases. However, it is not sensitive to further dilution, emissions, and transport. Photolysis rate coefficients, i.e., j-values, are estimated using the Tropospheric Ultraviolet Visible radiative transfer model [Madronich and Flocke, 1999]. More details of the model can be seen elsewhere [Madronich, 2006]. In the present study, the model was initialized with measured concentrations of O3, H2O, NO, NO2, CO, CH4, C2H6, C₂H₄, C₂H₂, C₃H₈, C₃H₆, i-C₄H₁₀, and n-C₄H₁₀ while N₂, O₂, and photons are hardwired into the model. MABL heights and dilution are also added as inputs to the model.

[45] The model was operated for four different scenarios: (1) when the ship was encountering mostly clean, marine air (IO air mass) near the southern most part of its transect (2 November), (2) when the ship was close to Port Blair under regime of NE-BoB air mass (4 November), (3) when the ship was heading toward the North BoB and was under influence from Southeast Asia (6 November), and (4) when the ship was returning from the North BoB and was under influence of the N-BoB air mass (12 November).

[46] Another consideration in selecting these days was the number of available data points and their representativeness of distinct diurnal features. The comparison between the observations and model simulations is shown in Figure 13. Here instead of showing the absolute levels, change in O_3 (ΔO_3) is shown. ΔO_3 for box model simulations is the difference between the hourly data with the mean daily concentration. ΔO_3 for observations represents the difference between measured O_3 and predicted O_3 using a linear fit for the day. Overall, the model-simulated diurnal patterns as well as the variability agree well with the observations.

[47] The O_3 values were on the lower side, i.e., 25–35 ppbv on 2 November, and entrainment did not seem to play a major role on this day. The diurnal feature was that of a clean, marine region characterized by daytime loss. The day was marked by conspicuous O_3 destruction during daytime which may be attributed to photochemistry. O_3 loss in MABL is attributed to photolysis due to excited oxygen atoms O(1D), followed by reaction with water vapor, odd hydrogen



Figure 12. (top) O_3 –NO_x relationships in the four different air masses namely, IO (black), NE-BoB (blue), N-BoB (red), and E-BoB (green). (bottom) O_3 –CO relationships in these air masses. The fit lines in the diagram are based on robust regression.

radicals (HO_x), and surface deposition [*Horowitz et al.*, 2003]. Further, it has been suggested that reactive halogen species released into the atmosphere by the photodecomposition of organohalogens and via autocatalytic recycling on sea-salt aerosols may also contribute to O_3 destruction in the MABL [*Dickerson et al.*, 1999].

[48] However, the model was not exactly able to simulate the large daytime loss on 4 November and the sudden increase in O_3 values after 1700 IST. The sudden increase may be attributed to transport effects as surface wind speed was over 13 m s^{-1} on 4 November. The MABL was highest on 4 November (>1400 m), resulting in higher VC. However, the model was still able to simulate amplitude of about 7.8 ppbv of O_3 . Incorporation of halogen chemistry might have accounted for the daytime loss processes better on this occasion. The role of halogens needs to be accessed quantitatively, using reliable measurements, for the BoB.

[49] The diurnal variation on 6 November was characterized by higher O₃ levels (45-60 ppbv) and dominated by transport effects. The 6 November pattern is most perturbed with several instances of O₃ buildup on a basic pattern marked by daytime destruction and nighttime advection (import). However, the model was able to simulate the daytime loss which might be dominated by chemistry. Since CO values did not rise as sharply as O₃ during these nights, advection alone seems incompetent to explain the night time recovery. The preferential enhancement of O₃ with respect to CO on this day indicates exchange between the O₃-rich free troposphere and the O₃-poor boundary layer. The exchange process is supposed to be more important during the night than during the day, allowing O₃ nighttime recovery [Bremaud et al., 1998]. Initially, the box model was not able to closely match the high O₃ values between 2000 and 2400

IST. However using different entrainment rates during day (1 mm s^{-1}) and night (25 mm s^{-1}) [*Kawa and Pearson*, 1989; *Bremaud et al.*, 1998], the model was able to produce the nighttime recovery.

[50] The diurnal variation of O₃ on 12 November was very similar to the diurnal profile measured during the Soviet-American Gases and Aerosols Experiment 87 Indian Ocean cruise [Johnson et al., 1990]. A typical feature, represented by high O₃ values after sunrise, was observed on this day. The enhancement occurred in two steps, once after 0300 IST and the other after 0600 IST. The first enhancement may be attributed to advection of O₃ and precursor rich air into the MABL. Donahue and Prinn [1990] have suggested a sudden MABL deepening at dawn allowing influx of O3 rich air. The second one may be attributed to photochemistry. This photochemical production can occur under optimum levels of precursor gases. It must be d that CO and NO_x levels on this day had also showed early morning enhancement. Model simulation confirms the daytime O₃ production, suggesting that the amount of precursors was sufficient to result in net O₃ production on this day (Figure 14). This high O₃ is then slowly acted on by photochemical loss processes during the day. However, model simulation somewhat underestimates the O₃ production. The difference in model and observation could be associated with transport of O₃-rich air along with the precursors which is not considered in the box model.

6.1. O₃ Production and Loss Rates

[51] In remote MABL, O₃ mixing ratios generally show "virtually no diurnal variations" [*Liu et al.*, 1983]. Further, it is suggested that the general balance of O₃ in the MABL is governed by the competition between two processes: (a) entrainment of O₃ rich air from higher altitudes and large-


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Figure 13. (left) Comparison of observed diurnal variations of O_3 with simulations from the box model. (right) Sensitivity of the Box Model to changes in various input parameters (for 2 November 2010 over the BoB).

scale horizontal advection from source regions, and (b) net photochemical destruction throughout the day along with continuous deposition to the ocean. The box model can also be used to partly account for the sensitivity of O₃ variations due to these competitive processes namely, chemistry (NO_x, CO, and NMHCs) and dynamical parameters (e.g., boundary layer height, entrainment, etc.). In our case, the box model was found to be very sensitive to various background levels of O3, indicating the role of entrainment processes (Figure 13). This is corroborated by the fact that the model was sensitive to dilution effects as well. The model was also highly sensitive to NO2 values, and it is seen from Figure 13 that background NO₂ regimes can determine whether O₃ is produced or lost during daytime. We did not find the model-simulated O₃ to be highly sensitive to CO, hydrocarbons, or RH for 2 November. However, Monks et al. [2000] had observed that a 10% drop in water levels would lead to a 6% drop in radical levels.

[52] The O₃ formation $F(O_3)$ and O₃ destruction $D(O_3)$ rates may be represented by the following equations [*Davis et al.*, 1996]:

$$F(O_3) = k_1[NO][HO_2] + \Sigma k_i[NO][R_iO_2]$$
(3)

$$D(O_3) = k_4 [O^1 D] [H_2 O] + k_5 [HO_2] [O_3] + k_6 [OH] [O_3]$$
(4)

[53] The balance between $F(O_3)$ and $D(O_3)$ gives the O_3 net production potential $P(O_3)$. The O_3 production and loss rates were calculated using concentrations of peroxy species, OH, HO₂, etc. from the box model for 2 and 12 November. 2

November (which showed conspicuous daytime O_3 loss) was selected because the influence of transport, e.g., nighttime advection was minimum on that day. In contrast, 12 November is marked by daytime O_3 production. Sum of CH₃O₂ and C₂H₅O₂ has been used here to represent levels of peroxy radicals considering them as the major contributing species to this group.

[54] The daytime variation in estimated O₃ production and loss rates is shown in Figure 14. On 2 November, the chemical loss of O₃ loss was found to dominate O₃ production throughout the day as also indicated by the observed net O₃ destruction over the BoB. Maximum production occurred from the reaction of CH₃O₂ with NO and was almost closely matched by the reaction of HO2 with NO. The major contributor to the O₃ chemical loss was the reaction of O¹D with H₂O during the daytime. Liu et al. [1983] have found a net O₃ photochemical loss rate of 2 ppbv day⁻¹, with roughly 70% of the loss coming from the reaction of excited oxygen, O(1D), with water vapor to form OH, and 30% coming from reaction of O₃ with HO₂. The maximum production occurred around 0900 IST while the maximum loss occurred around 1100 IST on 2 November (Figure 14). On 12 November, maximum O₃ production is observed at 0900 IST. As the day progresses, the photochemical loss processes start to pick up (Figure 14). However, on this day, the losses are never sufficient to generate a net negative P(O₃). Apart from these photochemical production and loss processes, there are significant contributions of advection and entrainment processes toward O₃ buildup and physical processes in O₃ loss. However, their estimation is not within the scope of the present study.



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Figure 14. Calculated daytime variation of formation $F(O_3)$, destruction $D(O_3)$, and net production $P(O_3)$ rates for O_3 on (left) 2 November and (right) 12 November 2010 over the BoB.

7. Summary and Conclusions

[55] This study reports ship-based observations of O3 and its precursors over the BoB during 28 October to 17 November 2010. This is the period of sudden increase in the levels of pollutants over the Indian subcontinent after the withdrawal of the monsoon winds. Thus, measurements made during this period are likely to reflect direct impact of air masses originating from different source regions in South Asia (India, Bangladesh, Myanmar, Thailand, Vietnam, etc.) over a cleaner BoB. So far, measurements of O₃ precursors namely, NO_x, were not available for these post monsoon months over this marine region. Continuous monitoring of trace gases namely, O₃, CO, and NO_x along with intensive, sampling-based measurements of CH₄ and C_2 - C_4 hydrocarbons were achieved during this campaign. A wide range of O₃ concentrations were encountered from as low as 11 ppbv in the open ocean to over 60 ppbv in the North BoB. Large spatial heterogeneity was observed in the levels of these species due to different air masses over different regions of the BoB. During the present campaign, four distinct types of air masses characterized by heavy pollution from nearby source regions (N-BoB; 42% time over Northwest Myanmar, East Bangladesh, and Northeast India), mixed type (E-BoB; 22% time over Myanmar, Thailand, and Vietnam and 75% time over East BoB), affected by long-range transport of pollutants (NE-BoB; 59% time over continental South Myanmar, Vietnam, and Hong Kong region of China), and pristine marine type (IO; 97% time over oceanic regions) were identified. Among these, the continental air masses were fresher compared to marine air masses.

[56] Both O₃ and CO showed sharp latitudinal gradients of 3.95 and 16.56 ppbv/°, respectively, increasing toward northern continental landmasses. These latitudinal gradients were higher than previous studies over the BoB, which were conducted in other periods. Higher latitudinal gradients confirm the large spatial heterogeneity in O₃ and CO levels due to unique transport patterns over the north and south BoB during post monsoon. Principle component analysis indicated that transport from continental source regions played a major role in determining the chemical composition of the air masses during the campaign and presence of

regional sources of NO_x . These regional sources of NO_x , apart from transport from nearby land masses, could also be due to emissions from large number of ships and trawlers operating over the BoB, especially the international shipping lanes along Yemen–Sri Lanka–(Malaysia–Sumatra) corridor.

[57] Highest O₃ and CO levels were observed in air masses coming from Southeast Asia. Signatures of BM/BF burning were detected in these air masses (NE-BoB and E-BoB) using correlations of C_2H_2 , C_3H_8 , and C_2H_6 with CO. Potential Source Contribution Function analysis indicated fire impacted South of Myanmar (Kayin) and Thailand (TAK region) as potential contributors to high levels of CO measured on 14 November. C_4H_{10} and C_2H_2 were very high in air masses arriving from the North BoB and nearby land regions (eastern IGP, Bangladesh, and Myanmar), indicating influences of urban/industrial sources over Bangladesh, India, and Northwest Myanmar. The pristine nature of the IO air mass over the South BoB was confirmed from various chemical proxies.

[58] Diurnal variations of surface O₃ revealed effects of advection, entrainment, and photochemistry. This was corroborated by box model simulations. The model-simulated diurnal variations were found to be highly sensitive to background NO₂ and background O₃ levels as well as dilution. The model was able to simulate the observed daytime O_3 reduction in pristine oceanic air masses and photochemical buildup in polluted air masses. The model results were in good agreement with observations when transport effects were more homogeneous. Indirectly, the model enabled us to access if the diurnal variations were sensitive to transport or chemistry. It is suggested that future campaigns over the BoB should include more chemical tracers such as O₃, higher order VOCs, NOy, peroxyacetylnitrate, CH3CN, CH3CI, SO₂, dimethyl sulfide, and radicals like HO_x for a better understanding of transport effects and marine chemistry.

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Seasonal characteristics of SO₂, NO₂, and CO emissions in and around the Indo-Gangetic Plain

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Abstract Anthropogenic emissions of sulfur dioxide (SO₂), nitrogen dioxide (NO₂), and carbon monoxide (CO) exert significant influence on local and regional atmospheric chemistry. Temporal and spatial variability of these gases are investigated using surface measurements by the Central Pollution Control Board (India) during 2005-2009 over six urban locations in and around the Indo-Gangetic Plain (IGP) and supported using the satellite measurements of these gases. The stations chosen are Jodhpur (west of IGP), Delhi (central IGP), Kolkata and Durgapur (eastern IGP), Guwahati (east of IGP), and Nagpur (south of IGP). Among the stations studied, SO₂ concentrations are found to be the highest over Kolkata megacity. Elevated levels of NO2 occur over the IGP stations of Durgapur, Kolkata, and Delhi. Columnar NO2 values are also found to be elevated over these regions during winter due to high surface concentrations while columnar SO₂ values show a monsoon maximum. Elevated columnar CO over Guwahati during premonsoon are attributed to biomass burning. Statistically significant correlations between columnar NO2 and surface NO₂ obtained for Delhi, Kolkata, and Durgapur along with very low SO₂ to NO₂ ratios (≤ 0.2) indicate fossil fuel combustion from mobile sources as major contributors to the ambient air over these regions.

Keywords $SO_2 \cdot NO_2 \cdot IGP \cdot Seasonal variability \cdot Emissions$

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Introduction

Urban growth in Asia has been occurring on an unprecedented scale and involves a volume of population much larger than in any other region of the world (Roth et al. 2011). Demographic projections show that by the year 2025, 16 of the world's 29 megacities will be located in Asia, many of which have very basic problems in terms of environmental quality (Asian Development Bank 2008). Apart from being home to a burgeoning population, these regions (tropical/subtropical) of the globe are also major players in atmospheric chemistry as a result of myriad emission patterns and scenarios combined with intense photochemistry (Crutzen 1998; IPCC 2007). In a country like India, stress on the environment is a natural expenditure that has to be incurred as a price for fastpaced development and its ramifications in the form of emissions pertaining to fossil fuel combustion. These emissions, containing sulfur dioxide (SO₂) and nitrogen dioxide (NO_2) , have the potential to impact the chemistry and radiative balance on a regional scale.

 SO_2 plays a pivotal role in the global sulfur cycle (Delmas and Servant 1998). Being an important consumer of photo-oxidants and its subsequent oxidation into particulate sulfate (SO_4^2) (Seinfeld and Pandis 2006), it remains an intrinsic part of atmospheric chemistry. Thus, knowledge of SO_2 concentrations is indispensable to accurate modeling of atmospheric chemistry and radiation budget, especially in regions where its concentrations are substantial. SO_2 may be transported several hundred kilometers (Mallik et al. 2013) by virtue of an average tropospheric lifetime of ~1.8 days resulting from combined effects of gas-phase oxidation and dry deposition (Faloona 2009). Changes in the abundance of

 SO_2 (and hence SO_4^{2-}) will impact the radiation field, and consequently the climate (IPCC 2007; Tsai et al. 2010). Anthropogenic activities, viz. coal and oil burning and natural processes like volcanic eruptions, release sulfur dioxide into the atmosphere. During 1995, thermal power generation accounted for 46 % of SO₂ emissions in India, followed by industry (36 %), road transport (8 %), and biomass burning (6 %) (Garg et al. 2001). As of 2010, the contribution from powergenerating sector has increased and the present sectoral shares to SO₂ emissions are 60 % from power sector, 32 % from industries, 6 % from residential, and about 2 % from the transport sector (Lu et al. 2011). Some other sources of SO₂ are industrial activities such as flaring at oil and gas facilities, diesel power generation, and commercial/residential fuel use.

Nitrogen oxides (NO_x) play a pivotal role in tropospheric ozone (O_3) formation. Since $NO_x (NO+NO_2)$ is a precursor of O_3 , an increase in NO_x (along with myriad volatile organic compounds) may affect O₃ and OH concentrations in the troposphere (Crutzen 1998). NO₂ is the major gaseous pollutant in the NO_x group arising from combustion of fossil fuels and biomass burning. While only a small part of NO₂ is emitted directly into the atmosphere by combustion processes, most of the NO₂ is formed by photooxidation of NO (the major nitrogenous product of combustion). The largest natural sources of NO are lightning and microbial activity in soils (Bond et al. 2002; Bouwman et al. 2002). NO_x emission over the Asian region is observed to be increasing very fast, compared to Europe and USA (Akimoto 2003). The NO_x emission over India is estimated around 4.59 Tg for the year 2000 with an annual growth rate of around 5.5 % (Streets et al. 2003). Vehicular traffic, and diesel engine-generating sets are major contributors to ambient NO₂ levels in a city. The NO_x emission breakup over the Indian region is 34 % from road transport sector, 30 % from power generation, and 30 % from industry (Garg et al. 2006). However, the sources vary conceivably from region to region in India.

Both SO₂ and NO₂ are primary criteria pollutants with detrimental environmental effects; short-term exposures to elevated levels can have significant health effects as well (WHO 2005). These gases also have adverse effects on vegetation, crops, and materials. It has been estimated that every 1 % increase of SO₂ emissions in Asia results in about 0.9 % rise in sulfate aerosols (Manktelow et al. 2007). Though global SO₂ emissions have stabilized since 1990, Indian emissions have shown a 70 % increase since 1996 and estimated at 8.8 Tg-SO₂ for the year 2010 (Lu et al. 2011). Both NO_x and SO₂ have precarious associations with acid deposition (Hidy 1994). Elevated concentrations of NO₂ can also affect visibility through creation of a "reddish brown" haze.

The significance of SO₂ and NO₂ as elucidated above necessitates their continuous observations from the perspectives of atmospheric chemistry as well as climate research and demand detailed analysis of their levels and variability, particularly for the Asian region. Documenting the long-term temporal changes in SO_2 and NO₂ over India associated with changes in local emissions, resulting from rapid urbanization and everescalating demand for energy, is crucial for understanding chemistry-climate relationships and subsequently to formulating mitigation policies with regard to air pollution. The present paper deals with the tempo-spatial pattern of these two important gases near the surface and in the total column over geographically distinct regions covering India. An effort is made to distinguish this variability in terms of in situ emissions and transport effects by the analysis of their levels, seasonality, and ratios. The stations chosen are Delhi (central IGP), Jodhpur (west of IGP), Kolkata and Durgapur (eastern IGP), Guwahati (east of IGP), and Nagpur (south of IGP).

Site description and experimental methodology

Delhi, the capital city of India with a humid subtropical climate, houses around 129,000 industrial units and three coal-fired power plants (combined capacity 1,100 MW). The region is characterized by intensely hot summers and cold winters. The predominant wind direction is from the north and northwest (except during the monsoon), which brings air from industrialized regions in Punjab and Haryana to Delhi. The vehicular population of Delhi (Table 1) is the highest in India. Jodhpur (600 km southwest of Delhi) is the second largest city of Rajasthan State of India. It has a hot, semiarid climate and lies very close (200 km) to the Thar Desert. Kolkata is a megacity located on the banks of river Hooghly, about 50 km from the Bay of Bengal, with a tropical wet and dry climate. The Kolkata metropolitan area, along with the suburbs, has a population exceeding 15 million, making it the

Table 1Table showing geo-
graphical locations of the sta-
tions studied in terms of their
latitude and longitude, popula-
tion, total number of registered
motor vehicles (in millions;
obtained from Road transport
yearbook 2011), and the OMI
grid used to represent the region

Stations	Latitude (°N)	Longitude (°E)	Population (millions)	Vehicles (millions)	(OMI grid) Lat-span (°N)	(OMI grid) Long-span (°E)
Delhi	28.63	77.22	16.71	5.5	28–29	77–78
Jodhpur	26.26	73.02	0.87		26–27	72.5-73.5
Durgapur	23.50	87.32	0.50		23–24	86–89
Kolkata	22.57	88.36	11.39	1.0	22–23	88-89
Guwahati	26.15	91.74	0.83		25.5-26.5	91.5-92.5
Nagpur	21.15	79.09	2.09	0.9	20.5-21.5	78.5–79.5

13th most populous urban area in the world. It has a number of industries and very heavy vehicular traffic. Often, in April–June, the city is struck by heavy rains or dusty squalls followed by thunderstorms. Durgapur, an industrial township located 160 km northwest of Kolkata, is home to the Durgapur Steel Plant, three large power plants, and several chemical and engineering industries. Guwahati, the largest city of Assam and home to a major petroleum refinery, is a rapidly growing city. It has a humid subtropical climate and experiences more than 1,700 mm annual rainfall. Nagpur, located at the dead center of the country, has two major thermal power stations (1,920 MW) and houses the largest industrial area in Asia.

The Central Pollution Control Board (CPCB) has been monitoring ambient air quality across stations spanning the entire Indian region with the help of the State Pollution Control Boards and other agencies under the National Air Quality Monitoring Programme (NAMP). Under NAMP, four air pollutants, viz. SO₂, oxides of nitrogen as NO2, suspended particulate matter, and respirable suspended particulate matter, have been identified for regular monitoring (http://cpcb.nic.in/air. php). The monitoring of pollutants is carried out for 24 h (four-hourly sampling for gaseous pollutants) to have around 100 observations in a year from each site. The data are available online (http://cpcbedb.nic.in/). The CPCB data have been used in several studies: Biswas et al. (2011), Middey and Chaudhuri (2012), Guttikunda and Calori (2013), etc. In the present analysis, we focus mainly at the relative characteristics of the data from six urban stations in and around the Indo-Gangetic Plain (IGP), which have been selected on the basis of location, regularity of measurements available, and population (above 0.5 millions) (Fig. 1, Table 1). The data, available on different days, is averaged for entire month and these monthly values spanning the 5-year period of 20052009 have been used for the present analysis. The CPCB norms for annual SO₂ (NO₂) levels over India are pegged at 50 (40) μ g m⁻³ for industrial and residential areas and 20 (30) μ g m⁻³ for sensitive areas (NAAQS report 2011). The 24-h National Ambient Air Quality (NAAQ) standard for both these gases is 80 μ g m⁻³. The NAAQ refers to the levels of air quality necessary, with an adequate margin of safety, to protect public health, vegetation, and other property.

SO₂ is measured using the "Improved West and Gaeke" method (US EPA 1982; Harrison and Perry 1986; IS 5182 Part 2 2001; NAAQS report 2011). In this method, SO₂ from ambient air is absorbed in an aqueous solution of potassium tetrachloromercurate. The SO₂ reacts with the mercuric salt to form a dichlorosulphitomercurate complex, which resists oxidation. Once formed, this complex is stable to strong oxidants such as ozone and oxides of nitrogen and therefore the absorber solution may be stored for some time prior to analysis. The complex is made to react with acid bleached pararosaniline and formaldehyde to form an intensely colored pararosaniline methylsulfonic acid. The absorbance of the solution is determined photometrically. This method is sensitive to low parts per billion by volume (ppbv) levels. The minimum detection limit is ~4 μ g m⁻³ (1 ppbv=2.6 μ g m⁻³). Relative standard deviation for this analytical procedure at the 95 % level is 4.6 % using standard samples.

 NO_2 is measured by "Jacob and Hochheiser modified" method (Jacob and Hochheiser 1958; NAAQS report 2011). Ambient NO_2 is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion produced during sampling is determined colorimetrically by reaction of the nitrite ion with phosphoric acid, sulfanilamide, and *N*-(1-naphthyl)-ethylenediamine-dihydrochloride and measuring the absorbance of the intensely colored



Fig. 1 Study locations for the present analysis. The 2.5 arc minutes resolution, gridded population density map for 2005 has been obtained from SEDAC (Center for International Earth Science Information Network CIESIN et al. 2005)

azo dye at 540 nm. The nominal range of the method is 9 to 750 μ g NO₂ m⁻³ (5 to 400 ppbv; 1 ppbv=1.9 μ g m⁻³). Further details are given in Harrison and Perry (1986).

The SO₂ and NO₂ columnar data used in this study are obtained from the "Ozone Monitoring Instrument" (OMI) using the Giovanni interface (http://daac.gsfc.nasa.gov/giovanni/). The OMI products (version

3, level 2) spanning the 5-year period of 2005–2009 were taken for various grids covering the study locations (Table 1). OMI retrievals of SO₂ columns from the solar radiation backscattered by the Earth's atmosphere are available on a $0.125^{\circ}\times0.125^{\circ}$ grid with global daily coverage. The OMI pass has a local equator crossing time of 1330 hours (LT) in the ascending node. The

improved sensitivity permits daily global measurement of passive volcanic degassing of SO_2 and of heavy anthropogenic SO_2 pollution to provide new information on the relative importance of these sources for climate studies (Krotkov et al. 2006; Mallik et al. 2013). OMI-derived tropospheric NO₂ columns can track NO₂ pollution near the surface, which is an important precursor of urban smog (Boersma et al. 2004).

Carbon monoxide (CO) columns have also been compared to SO₂ and NO₂ columns for a better elucidation of emissions and transport processes. CO columns over the study grids are obtained from "Measurements Of Pollution In The Troposphere" (MOPITT) for the period 2005-2010. MOPITT measurements yield atmospheric profiles of CO and CO total column values using near-infrared radiation at 2.3 µm and thermal-infrared radiation at 4.7 µm. MOPITT measurements enable the analysis of the distribution, transport, sources, and sinks of CO, a trace gas produced by methane oxidation, fossil fuel consumption, and biomass burning. For the present analysis, we have used 1° x1° monthly gridded CO data (L3, version 4) available at ftp://l4ftl01.larc.nasa. gov/MOPITT/ MOP03M.004.

Table 1 details geographical locations of the stations studied in terms of their latitude and longitude, population, total number of registered motor vehicles (in thousands, obtained from Road transport yearbook 2011), and the OMI grid used to represent the region.

Results and discussion

Levels and variability from ground based measurements

The monthly variation of surface SO_2 and NO_2 over the study locations is shown in Fig. 2. Two conspicuous features are observed, viz. (a) winter maxima in both SO_2 and NO_2 seem to a common feature for all the stations barring Jodhpur; (b) NO_2 levels over the IGP stations are distinctly higher compared to Guwahati (a valley region), Jodhpur (a desert region), and Nagpur (an urban region in central India). These features will be explored in detail later in the paper. Figure 2 shows a clear increase in surface NO_2 over Delhi, Durgapur, and Kolkata during 2005–2009. Further, SO_2 levels over Delhi show a decrease during 2005–2009, which may be attributed to various government measures in recent years such as reduction of sulfur in diesel, use of cleaner fuel such as compressed natural gas (CNG), implementation of better engines in new vehicles for lower emissions (Bharat Stage-III emission norms), fuel regulations, directives to use cleaner coal, and installation of flue gas desulfurization equipments in power plants (CPCB 2003; Badami 2005). The average SO₂ concentration over Delhi was 2.95±0.99 ppbv during 2005–2009 as against 4.2±1.7 ppbv during 2000-2006 (Kandlikar 2007). This corresponds to a 30 % drop in SO₂ levels. Datta et al. (2011) have reported winter SO₂ concentrations of the order of 2.55 ppbv over Delhi. A compilation of SO₂ values over different regions of India is given in Mallik et al. (2012). It is interesting to note that Kandlikar (2007) had also attributed a 33 % drop in SO₂ levels over Delhi during 2001-2006 to a reduction of sulfur in gasoline and reduced sulfur emissions from coal-fired power plants. It must also be noted from Lu et al. (2011) that the contribution to SO_2 emissions from residential sector in India has increased during 1996-2010 while that from transport sector has decreased. The International Energy Agency (IEA) has reported that the residential sector contributes about 20-30 % of the non-power generation coal use (International Energy Agency 2010). Hettige et al. (1997) mentioned the environmental Kuznets curve which points out that pollution from industry, transport, and households increases until development generates enough wealth to promote significant pollution control.

The general statistics of SO2 and NO2 over different stations during the period 2005-2009 are shown in Table 2. The mean concentration of SO₂ is highest over Kolkata (4.1 ppbv) and is followed by Nagpur (3.6 ppbv). Both of these places are dotted with several industries including petrochemicals, chemicals, iron, steel, metallurgy, textiles, leather, etc. The variability (1 sigma) is largest over Kolkata (2.8 ppbv). Being a megacity, Kolkata is expected to be affected by multiple emission sources. Source apportionment study in another metropolis in India had revealed major contributions of SO₂ from industries (56 %) followed by use of diesel generator sets (23 %) during power cuts, and transport (16 %) (TERI 2010). The minimum value for SO₂ is also very high over Nagpur (2.4 ppbv) followed by Durgapur and Jodhpur (2.0 ppbv each). Among the stations studied, the SO₂ maximum culminates over Kolkata (13.6 ppbv). Modeling studies also



Fig. 2 Variability in surface SO₂ and NO₂ over different urban stations during 2005–2009 based on CPCB (India) measurements

corroborate the high background levels of SO_2 over Kolkata (Adhikary et al. 2007).

The mean concentrations of NO_2 are highest over Kolkata and Durgapur (~31 ppbv each) followed by Delhi (27 ppbv). Kolkata has been confronting with a multitude of environmental problems related to traffic and transportation, drainage and sewerage, garbage collection and disposal system, etc. Durgapur, the steel city of India, and an industrial hub, is also reeling under exacerbating air pollution (Nandi and Gorain 2010). Higher levels of NO₂ over Delhi, Kolkata, and Durgapur call for immediate strategies to ameliorate soaring levels of pollution. The pattern of NO₂ mean and sigma is similar to the pattern in NO₂ maxima, indicating dominant effect of stereotype sources of NO₂ over these regions rather than multiple sources (this is in contrast to SO₂). It is to be noted from Garg et al. (2001) that use of gasoline/diesel in transport sector and coal combustion in thermal power sector account for over 60 % of NO_x emissions in India. The

Stations	SO ₂ (ppbv)				NO ₂ (ppbv)			
	Maximum	Minimum	Mean	Sigma	Maximum	Minimum	Mean	Sigma
Delhi	5.71	1.54	2.95	0.99	54.24	16.72	27.42	6.98
Jodhpur	3.40	2.02	2.50	0.36	14.59	9.93	11.80	0.96
Durgapur	5.65	2.07	3.12	0.78	54.74	16.49	31.47	8.74
Kolkata	13.66	1.61	4.12	2.78	52.16	13.84	30.93	9.31
Guwahati	4.41	1.51	2.70	0.82	15.71	5.85	8.66	1.94
Nagpur	9.65	2.44	3.61	0.92	26.80	8.25	16.06	3.82

Table 2 Table showing statistics of surface level SO₂ and NO₂ over the study regions during 2005–2009. Data from CPCB (India)

Deringer

NO₂ minima are higher for Delhi and Durgapur (~16.7 and 16.5 ppbv) followed by Kolkata (~13.8 ppbv). The maxima for Delhi, Durgapur, and Kolkata is >50 ppbv over each city. As mentioned in the "Introduction" section, the transport sector accounts for more than one third of total NO_x emissions over urban regions. Thus, a disproportionate rise in the number of vehicles accompanied by heterogeneous traffic conditions can also result in higher observed concentrations for NO₂ in congested cities. In places like Delhi, although various measures such as implementation of fuel efficient engines etc. have been taken to mitigate ambient NO2 levels, the number of vehicles has increased exponentially at the same time (Table 1, Ghude et al. 2011). It is apparent from Table 1 that the total number of vehicles plying over Delhi is far more overwhelming than other cities, partly explaining the high NO₂ levels over Delhi (Table 2). The mean SO₂ and NO₂ concentrations over Guwahati are found to be 2.7 and 8.7 ppbv, respectively.

Comparison of surface measurements and satellite retrievals

Surface measurements are limited in their spatial coverage while satellite data can cover large spatial domains with long periods of consistent observations. The average monthly variation of surface concentrations of SO₂ and NO₂ during 2005-2009 has been compared with the corresponding OMI columns averaged over the same temporal span (Fig. 3, Table 1). The left panel is used to show SO₂ values (surface and columnar) while the right panel is used to show NO₂ values (surface and columnar). The logic behind this comparison stems from the fact that if surface contributions to the column are significant, then similar features would be obtained for both surface and column. Additionally, the comparison of satellite and ground measurements is physically meaningful because it tells the approximate sensitivity of a satellite sensor to the variation in the concentration of a gas in the surface layer (Meng et al. 2010). However, if surface emissions are overpowered by the effects of meteorology, chemistry, or dynamics, similar patterns are not likely to be seen. Nevertheless, a direct comparison between both is inevitably influenced by many factors, viz. vertical profiles of species, changes in boundary layer height and interferences from cloud, aerosol, etc.

It is observed from Fig. 3 that stations lying in IGP (Delhi, Durgapur, and Kolkata) show a pronounced winter maxima with respect to surface SO₂ and NO₂ values. The surface SO₂ and NO₂ do not exhibit any clear pattern over Jodhpur, a semiarid city in central Rajasthan with no pronounced winter. Most of the stations, however, show bimodal features with respect to columnar SO₂ and NO₂ loadings. A pronounced maxima in columnar SO₂ occurs, surprisingly, during monsoon (June in East-Central India except Guwahati and July in North-West India) and another elevation occurs during winter. However, the winter elevations over Durgapur and Kolkata are higher than the monsoon SO2 columns. Overall, the SO2 columns are mostly below 3×10^{15} molecules cm⁻². It is pertinent to mention here that the highest observed monthly SO₂ columnar values during 2005-2009 were in the range of 0.6-0.9 Dobson Units (DU) during November 2008 for Delhi, Durgapur, and several IGP stations (not shown in figure) due to the Dalaffilla volcanic eruption in Ethiopia (Mallik et al. 2013).

 NO_2 columns vary from a low of $2{\times}10^{15}$ molecules cm^{-2} over Guwahati to a high of 7×10^{15} molecules cm^{-2} over Delhi. Stations where seasonal amplification is sharper in surface NO₂ values, viz. Delhi, Kolkata, and Durgapur, columnar NO₂ values also show distinct winter peaks. Ghude et al. (2011) have also observed similar features. Over Delhi, Durgapur, and Nagpur, columnar NO2 exhibits a premonsoon elevation (March and/or April) apart from the regular winter elevation. Guwahati also exhibits premonsoon elevation but no winter elevation. NO2 values over Kolkata also show a winter maxima for surface as well as total column. Additionally, NO2 columns over all stations, except Jodhpur, show monsoon minima. The winter maxima in both surface and columnar NO₂ over Kolkata (also Delhi and Durgapur) suggest contributions from surface emissions dominating columnar values and the role of boundary layer which becomes very shallow during winter (Meng et al. 2010).

Seasonality in surface measurements and satellite retrievals

Since maximum columnar loadings of SO_2 are seen over the IGP during monsoon in contrast to elevated winter concentrations at the surface, effect of transport contributing to these loadings in the free troposphere is a possibility. The surface level winds during July over the



Fig. 3 Averaged monthly variations in SO_2 and NO_2 over different regions of India for the period 2005–2009. The station values (CPCB measurements) are plotted with *line and points* while the columnar values for the OMI grids are plotted as *bars*

IGP stations are mainly south-westerly which means they are traversing the highly industrialized western region of India and adding to the already significant levels of SO₂ in the IGP. This will not be true in case of NO₂, whose levels are constantly fed by vehicular emissions that are not supposed to vary drastically during a year. The strong seasonality in precipitation patterns in these regions induces a strong seasonality in the wet removal of SO_2 also (Rai et al. 2010). Another possibility is the minimal loss of SO_2 occurring from dry deposition during monsoon. Dry deposition is believed to be the second major loss process for SO_2 after oxidation (Faloona

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2009). Abhay and Mondal (2008) have pointed out that in the initial phase of the monsoon rainfall over the IGP, the concentration of suspended particulates are very high to neutralize the acidity of the atmosphere, but in the later phase of rain events, the neutralization is not possible due to removal of particulates, which leads to increased acidity of precipitation. Seasonal changes in wind speed impact the dry seasonal deposition of particles. Also, seasonality of wind-blown dust in scavenging SO₂ during dry season corroborates this argument (Adhikary et al. 2007).

The amplitude of seasonal variations in surface SO₂ over Jodhpur is negligible (Fig. 4) compared to Delhi, Kolkata, Durgapur, and Guwahati. This suggests that the sources and sinks of these species are relatively wellbalanced and stable throughout the year at this site. Similar features have been discussed by Meng et al. (2010) for several locations in China. With respect to surface SO₂, a clear amplification in winter w.r.t. other seasons is observed over Kolkata. Increase in trace gas concentrations during winter is a classic feature explained in terms of lower dispersion potential attributed to atmospheric stability (Tasdemir et al. 2005). Additionally, lifetimes of SO2 molecules are longer (shorter) during the winter (summer), when there are fewer (more) hydroxyl radicals (OH) in gas-phase and peroxy radicals (H₂O₂) in aqueous-phase available for oxidative conversion to sulfate (Warneck 1988). Further, in contrast to other seasons, the winter to summer ratio in SO_2 is highest over Kolkata (Fig. 4). This feature points to boundary layer effects causing dilution of SO₂ concentrations during summer. Further, Kolkata is affected by pre-monsoon thunderstorms during summer, which might cause local SO₂ emissions to be dispersed, causing lower summer concentrations. Additionally, thunderstorms are associated with moist winds, which can potentially scavenge off SO₂.

For surface NO₂, the seasonal variability is very distinct over all stations except Jodhpur (Fig. 4), resulting in better delineation of the winter maxima (Aneja et al. 2001; Goyal and Sidhartha 2002). The elevation in surface NO₂ during winter compared to other seasons is conspicuous over Kolkata and Durgapur. The winter to monsoon ratio in surface NO₂ is highest for all the stations clearly delineating monsoon minima in surface NO₂. Summer concentrations of surface NO₂ at Durgapur and Guwahati are more compared to post-monsoon values (Fig. 4). A contrary feature is exhibited over Delhi, Kolkata, and Nagpur, where summer concentrations of surface NO₂ are lower than post-monsoon values. Guttikunda and Gurjar (2012) have pointed out that mixing layer heights over Delhi could be several times more in summer compared to winter while surface wind speeds during summer could be three times more than during winter (<1 m/s). These result in higher ventilation coefficient in summer leading to effective dispersion of pollutants emitted near the surface. The seasonal amplitudes of surface CO is similar over all the stations with a winter maximum (ratio of DJF to other seasons >1) and a monsoon minimum (highest DJF/JJA value). Overall, surface CO is always enhanced in premonsoon compared to post-monsoon.

Over Kolkata, where SO₂ concentrations exhibited a maximum winter to summer ratio, interestingly NO₂ values show a maximum winter to monsoon ratio (Fig. 4). This implies that SO₂ values over this station decrease more in summer while NO₂ values decrease more in monsoon. This is because dry deposition, which is a major loss process for SO₂, is operative during summer when most of the IGP is under the ambit of transport from western India and Arabian region. During monsoon, dry deposition minimizes due to washout of dust particles by marine air masses, and hence loss of SO₂ reduces (this also corroborates the high columnar SO₂ during monsoon over the study grids). However, absence of continental air masses also causes reduction in NO2 levels during monsoon compared to summer over Kolkata. Further, vehicular emissions (which contribute more to NO₂ levels than SO₂ levels) could be slightly lower during monsoon over Kolkata, where traffic conditions are not very favorable during monsoon.

To get an insight into the simultaneous variability of columnar SO₂ and NO₂ during different seasons, a ternary plot is used (Fig. 5). For this purpose, columnar measurements of SO₂ and NO₂ are seasonally averaged (December, January, and February for winter; March, April, and May for pre-monsoon; June, July, and August for monsoon) and normalized by the sum of all the three seasons for the respective study regions. Figure 5 clearly shows that contributions to columnar SO₂ is highest during monsoon (all points >0.6 in the JJA axis). Further, it is revealed that increase in SO₂ concentrations during winter is very prominent over stations in Eastern and Central India (Kolkata, Durgapur, and Nagpur; except Guwahati, a valley region) compared to North-West sector (Delhi and Jodhpur). It is also observed that while

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Fig. 4 Seasonal ratios of SO₂, NO₂, and CO over the study regions. *DJF* (winter: December, January, and February), *MAM* (pre-monsoon: March, April, and May), *JJA* (monsoon: June, July, and August), and *SON* (post-monsoon: September, October, and November)

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Fig. 5 Ternary plot of normalized, seasonally averaged (December, January, and February for winter; March, April, and May for pre-monsoon; June, July, and August for monsoon) columnar

retrievals of SO_2 and NO_2 over different urban regions of India based on satellite (OMI) data

monsoon contribution to columnar SO_2 (>0.6) is always more than the pre-monsoon contributions (<0.4) for all the stations, such clear delineation in these seasons is not observed for columnar NO2. With respect to seasonal contributions to columnar NO2, all stations except Jodhpur lie aligned in the winter axis. As mentioned before, Jodhpur has a typical desert climate without a pronounced winter. Further, in case of columnar NO₂, Guwahati lies ahead in the pre-monsoon (MAM) axis. This feature is also reciprocated in columnar CO values over Guwahati (discussed later, Fig. 6) and is related to the geographical location of Guwahati, a major city in the Brahmaputra Valley. Since columnar SO2 and NO2 concentrations can be significantly influenced by airborne transport of the pollutants, the location of monitoring stations w.r.t. sources and the effect of prevailing wind patterns play deterministic role in governing these concentrations.

Variability in surface and columnar CO

Simultaneous study of SO₂, NO₂, and CO can reveal useful information on emission sources dominating over a region. The predominant sources of these gases are different, e.g., CO can be used as a tracer of combustion while SO₂ can be used to trace power plant emissions. CO columnar values (MOPITT daytime retrievals) over the study regions are shown in Fig. 6. While most of the stations over the IGP show a winter maxima in surface CO (also evident in Fig. 4), interestingly the

columnar values peak during pre-monsoon (March-May). However, over Guwahati, both surface level and columnar CO are elevated around March. The CO values over Guwahati are also notably higher compared to other stations. Guwahati is a major metropolis in the northeast and an important hub for transportation. The city is additionally affected by emissions from refineries on the eastern sector. Further, the region is impacted by largescale biomass burning during the pre-monsoon, which is also visible in MODIS fire imageries. High BC (daily median values of 9–41 μ g m⁻³) over Guwahati has been observed (Chakrabarty et al. 2012). Columnar NO2 values are also found to be elevated over Guwahati during March-April (Fig. 3). Its climate is mildly subtropical with warm, dry summers from April to late May, a strong monsoon from June to September, and cool, dry winters from late October to March. The maximum temperatures and maximum wind speeds occur during pre-monsoon over Guwahati. The high levels of surface and columnar CO over Guwahati along with substantial levels of SO₂ indicate additional impact of local, point sources (Fig. 6). It must, however, be noted that the seasonal pattern of CO and SO₂ over Guwahati are dissimilar. The high levels could also be impacted by valley region dynamics by virtue of its location on the foothills of the Shillong Plateau. An environmental impact assessment report over Guwahati found that the study region was extremely stable (F class stability) for 63 % time of the year, indicating poor dispersion of pollutants. Further, an increase in SO2 concentrations from 2005 to 2009 is



Fig. 6 Monthly variations in MOPITT derived columnar and surface CO over different urban regions of India during 2005–2009

observed for Guwahati in both surface measurements and column retrievals (figure not shown). This is also accompanied by a positive annual trend in observed aerosol optical depth (AOD) and rainfall in northeast stations (Ramchandran et al. 2012).

Association among surface concentrations and columnar values

The Pearson's correlation coefficient is used to determine if there is a possible linear association between SO_2 , NO_2 , and CO values used in this study. A paired *t* test is used to calculate the difference between each set of pairs and the list of differences is analyzed based on the assumption that the differences in the entire population follow a Gaussian distribution. If the pairing is effective, correlation will be positive and the *p* value will be small implying that the two groups are significantly correlated. Surface measurements of SO_2 and NO_2 exhibit a sample statistic (correlation coefficients) above 0.5 for most of the stations studied that are statistically significant at

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over 95 % (Guwahati and Nagpur) and over 99 % (Delhi, Durgapur, and Kolkata) (Fig. 7).

An interesting observation is that while both Durgapur and Nagpur have good correlations between columnar NO₂ and columnar CO, the columnar NO₂ over Nagpur is not well correlated with surface NO₂, unlike Durgapur. This indicates that surface level NO₂ sources are much prevalent over Durgapur but comparatively exiguous over Nagpur. This indicates that while Nagpur is affected mainly by industrial emissions, Durgapur is affected both by industrial and vehicular sources. The case becomes stronger later when we study the SO_2/NO_2 values over these places. It is interesting to note that statistically significant correlations between surface NO2 and columnar NO2 are obtained for Delhi and Kolkata. Meng at al. (2010) have also obtained significant linear correlation (p < 0.05) between satellite and ground NO2 for several stations over China. The NO₂ values for Kolkata and Delhi passed the paired t test with Shapiro-Wilks normality statistics at 95 % confidence interval. As explained above, largescale surface emissions from these megacities would dominate columnar NO2 values over the respective regions, thus producing good agreement between surface and columns.

For most of the large cities, NO₂ and CO columns show good correlation. The correlation of MOPITTderived surface CO with surface level NO₂ concentrations are 0.72, 0.69, 0.61, and 0.49 for Kolkata, Durgapur, Guwahati, and Delhi, respectively. The correlations of MOPITT-derived surface CO with surface level SO₂ concentrations are 0.47 for Durgapur and ~0.40 for Delhi, Guwahati, and Kolkata. It must be mentioned that CO is governed more by emissions (anthropogenic; incomplete combustion of carbonaceous materials) and dynamics, while SO₂ is affected by chemistry, physical loss processes, dynamics, and emissions (both natural and anthropogenic). Overall, the correlations of satellite versus ground measurements vary substantially from region to region.

Ratios

Emission factor for SO₂ due to coal burning in power sector varies between 8 and 16 g kg^{-1} for the Indian region (Streets et al. 2003). Considering average emissions of 0.8 % SO2 and 1.1 % NO2 from coal burning in power plants (http://archive.osc.edu/research/archive/ pcrm/emissions/summary.shtml), the emission ratio (by weight) of SO₂/NO₂ in vicinity of power plants would be around 0.75. In India, coal and oil product combustion have almost equal shares in total NO_x emissions. Compared to coal burning, SO₂ emission factors are higher for oil (0.04 for diesel oil and 0.08 for fuel oil) (Garg et al. 2001). Emission factor for NO₂ due to oil burning in transport sector varies between 15 and 58 g kg⁻¹ for the Indian region (Streets et al. 2003). In the present study, the mean ratios of SO_2 to NO_x (most of the NO_x over urban regions studied here is likely to be



Fig. 7 Correlations of SO₂, NO₂, and CO for surface and columnar values during the period 2005–2009

contributed by NO2, when considering annual or monthly means) for surface measurements vary between 0.1 and 0.6 (Fig. 8). For Delhi, Kolkata, and Durgapur, the mean ratios are below or around 0.13. Such low ratios indicate emissions from mobile sources (combustion of diesel/petroleum) as major contributors to the ambient air. Most of these places are notable for high pollution levels with prolific vehicular traffic which release more NO₂ than SO₂. A SO₂/NO₂ value of 0.12 during evening (traffic hours) over Ahmedabad during May 2010 was attributed to vehicular influences (Mallik et al. 2012). A SO₂/NO_x value of 0.58 for New Delhi was obtained by Aneja et al. (2001) for the token period of 1997-1998. Lower values for New Delhi obtained in this study (2005-2009) indicate an increase in NO2 emissions compared to SO₂ emissions impacted by fast increasing vehicular traffic (Table 1, Sheel et al. 2010; Ghude et al. 2011). Surface SO₂ data over Delhi show a negative trend of -0.33 ppbv/year while surface NO₂ is found to increase at 1ppbv/year (it must be noted that these values are just for comparison as we are not discussing absolute trends in the present work). Columnar NO2 over Delhi has been found to increase at the rate of 11.3±3 % during 1996–2006 (Sheel et al. 2010). The growth rate of vehicles over Delhi during 2005–2009 was 0.56 million per year as compared to only 60,000 per year over Nagpur for the same period (Road transport yearbook 2011). Kandlikar (2007) has pointed out that the increasing trend in NO_x concentrations over Delhi is linked more to the rapid changes in the vehicle fleet, which quickly negated the benefits to



Fig. 8 Box plot showing median, 10th, 25th, 75th, and 90th percentiles of SO_2 (in parts per billion volume)/ NO_x (in parts per billion volume) for different urban regions of India

CNG conversion. The AOD over Delhi also reveals an increasing trend related to anthropogenic activities (Ramchandran et al. 2012). In most of the cases, the low SO₂ to NO₂ ratios possibly indicate impact of a higher denominator (high NO₂); a lurking effect of mobile sources (Aneja et al. 2001). The dominant impact of NO₂ over Delhi and Kolkata is also supported by the good correlations obtained between surface and columnar NO₂ over these places.

 SO_2 to NO_x ratios higher than 0.3 are obtained for Guwahati and Nagpur. These cities seem to have considerable impacts from SO_2 -rich point sources. Both these rapidly growing cities are characterized by predominant influence from industries; mainly high SO_2 emissions from power plants, refineries, chemical industries, etc. SO_2/NO_x ratios for point sources in US varied between 0.44 and 2.3 (Aneja et al. 2001).

Summary and conclusions

Surface measurements of SO₂ and NO₂ by the CPCB (India) during 2005-2009 for six urban agglomerations in and around the IGP have been analyzed to get an insight into their temporal and spatial distributions. SO₂ concentrations are found to be highest over Kolkata. Very high levels of NO2 over Durgapur, Kolkata, and Delhi regions, mostly representing impacts of fossil fuel combustion, emphasize the need for strategies to ameliorate soaring levels of pollution over these places. Surface SO₂ and NO₂ concentrations over IGP stations, viz. Delhi, Durgapur, Kolkata, and Guwahati, are highest during winter. However, columnar SO₂ over most of these places show a monsoon maximum, probably due to transport from source regions to higher heights and ineffective removal of surface SO₂ due to reduced dry deposition. Columnar NO₂ shows mixed features with both winter and pre-monsoon elevations. Columnar CO loadings are highest during pre-monsoon over most of the stations. High columnar values of SO₂ and CO are observed over Guwahati, indicating influence of point sources. Columnar maxima in NO2 during winter over Delhi, Kolkata, and Durgapur are also reciprocated in elevated surface concentrations, indicating major contributions of near surface local emissions to columnar loadings. Statistically significant correlations between columnar NO2 and surface NO2 obtained for these locations show impact of vehicular traffic pervading over these regions. This feature is also supported by

very low mean SO₂ to NO_x ratios (≤ 0.15), indicating emissions from mobile sources as major contributors to the ambient air. Ratios higher than 0.3 are obtained for Guwahati and Nagpur, which have an overwhelming influence from industries, power plants, etc. The correlations between surface and columnar values are not good for SO₂ as major emission sources (e.g., stacks of power plants) release this gas far above the surface to be acted upon by various transport and transformation processes. The current work is an attempt to characterize emissions using measurements of gas phase tracers over the densely populated IGP, which is a very important region of the world. High resolution data and modeling studies would enable detailed investigations of the emission characteristic in and around the IGP in light of natural and anthropogenic influences and the processes controlling their transformations and transport.

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