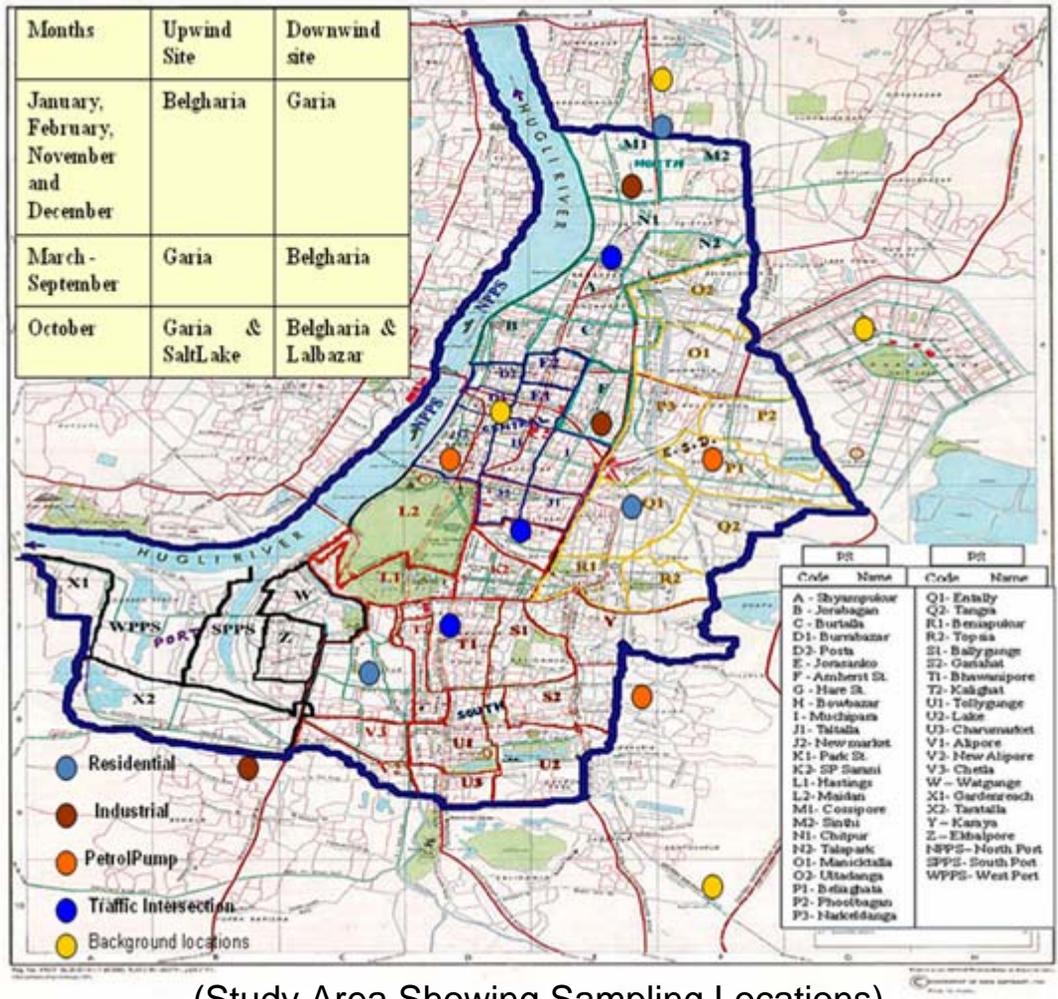


Study of Urban Air Quality in Kolkata for Source Identification and Estimation of Ozone, Carbonyls, NOx and VOC Emissions



Central Pollution Control Board
(Ministry of Environment & Forests)

website : cpcb.nic.in ; email : cpcb@nic.in

(August, 2010)

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FOREWORD

The fast urbanization, increasing traffic, economic growth trajectory, industrialization, and higher levels of energy consumption has resulted an increase in pollution load in the urban environment. It has become essential to keep a continuous watch on emissions and profiles of various air pollutants specially the Hazardous Air Pollutants (HAPs) such as VOCs, Ketones, Aldehydes and Ozone. The Study of HAPs in urban air is even more important in the South-East Asian region including India where high levels of solar irradiation in combination with anthropogenic and biogenic ozone precursors favour photochemical ozone production. The adverse effect of VOCs are well established and include their high Global Warming Potential (GWP), depletion of ozone layer, loss of bio-diversity etc.

Central Pollution Control Board (CPCB) carried out a detailed monitoring study through NEERI's Zonal Center, Kolkata to measure the levels of Ozone, VOCs including carbonyls in ambient air in the metropolitan city of Kolkata. The monitoring locations covered a wide range of urban activities from residential areas to industries and busy traffic intersections. The present report gives details of the study conducted, findings and recommendations for control of VOCs releases.

NEERI Director Dr. Tapan Chakraborty, Deputy Director Dr. (Mrs) Anjali Srivastava and her team deserves high appreciation for the contributed project studies.

The document will serve as a useful reference for all those concerned with the release sources, behavior and control of VOCs in urban air.

(S P GAUTAM)

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Executive Summary

Volatile Organic Compounds or VOCs play an important role in tropospheric chemistry by affecting the OH radical concentration, production of organic acids and photochemical oxidants. In order to develop efficient air pollution abatement strategies, it is important to know the sources and fate of VOCs, specially in the South-East Asian region where high level of solar irradiation favours photochemical ozone production. The production of elevated levels of lower tropospheric ozone is of particular concern since it adversely affects human health, vegetation and materials such as rubber, textiles and resin coatings.

Individual compounds of non-methane hydrocarbons (NMHC) have different effects on ozone formation due to their different reaction rates and pathways. It is therefore important to identify the profiles of different VOCs in the atmosphere and their emission source for development of control programme. Central Pollution Control Board (CPCB) has carried out a study through NEERI to measure the levels of Ozone, VOCs including carbonyls in ambient air in the metropolitan city of Kolkata. The report presents findings of the study and recommendations for actions to be taken including the strategy for mitigation of VOCs.

Chapter 1 presents a brief introduction of the study, objective and the scope of work. The objective and scope of study include, establishing monthly trend in the ambient levels of NO_x, carbonyls, ozone and VOCs in different area categories namely, industrial, commercial cum residential, refueling stations and traffic intersections, correlation of ozone concentration with NO_x and VOCs, and estimation of the relative contribution of different source categories of VOCs.

Chapter 2 presents details of sources and impact of VOCs present in atmosphere. Classification criteria for organic compounds as VOCs and their atmospheric chemistry have also been discussed.

Chapter 3 discusses the study area and the sampling locations where monitoring was performed. The sampling locations selected covered industrial area, commercial cum residential area, refueling station and traffic intersection.

Chapter 4 describes the methodology of sampling and analysis of different target pollutants namely, non carbonyl volatile organic compounds, carbonyls, ozone and NO_x. TO-17

method for sampling and analysis of VOC and TO-11A for sampling and analysis of carbonyls were used in the study.

Chapter 5 presents analysis of the monitoring data. High level of VOCs specially chloroform, acrolein, formaldehyde and acetone have been observed. NO_x concentration did not show much variation. The co-relation between VOC, NO_x and Ozone was found to be very complex. Ambient measurement of VOC/NO_x ratios indicated the air shed to be NO_x sensitive in terms of ozone formation.

Chapter 6 illustrates the contribution of various emission sources to the total level of VOCs in ambient air as estimated using the receptor model (CMB 8.0). Source apportionment of studies showed petrol and diesel exhaust, combustion of naphtha, mineral spirit and cigarette smoke, as the major sources of VOCs.

Chapter 7 gives details of the predicted ozone level using the probabilistic model. A reduced form of metamodel was used to simulate the effect of physical, chemical, and meteorological processing of highly reactive species in urban area. A polynomia expansion and probabilistic collocation method was used for the metamodel and its coefficients were fit for their applicability to wide range of atmosphere. The inputs used for the metamodel were combination of physical properties (average temperature, diurnal temperature range, date, and latitude), patterns and amounts of emissions, and the background concentration of pollutants. A good correlation was found between the observed and predicted concentration of ozone.

Chapter 8 deals with the methodology of exposure and risk assessment. Daily exposure of twenty three individual HAPs monitored in the present study has been estimated. Hazard Quotient of seventeen HAPs and Cancer Risks for nine HAPs have been calculated.

Chapter 9 summarizes the findings of the study. The finding are indicative of the need of developing source profiles of all the VOC emitting sources and monitoring of all oxides of nitrogen, inorganic nitrates, carbon monoxide, ROG, TOG and PM₁₀/PM_{2.5}. Study on the tropospheric reactivity of VOC species in controlled conditions is recommended. Mitigation strategy for control of VOCs has also been suggested.

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Chapter 1

Introduction

1.1 Preamble

Air pollution is increasing with growth in cities, increase in traffic, industrialization and higher levels of energy consumption. This has resulted into a very rapid increase in vehicular population and air pollution in the urban environment. The urban population has tripled from 62.4 million to 217.6 million between 1951 and 1991. Nearly two-thirds of the country's urban population is concentrated in 317 class I cities (population of over 100 000) and half of this lives in 23 metropolitan cities with population exceeding 1 million. Number of cities with population of over one million has increased from 5 in 1951 to 23 in 1991 (Pachauri and Sridharan 1998).

Parameters of urban ambient air quality have now acquired new dimensions due to increase in Hazardous Air Pollutants namely, Ozone, Volatile Organic Compounds (VOCs), ketones and aldehydes. The pressure on the policy makers has also become visible. Title III of the Clean Air Act Amendments (CAAA) of 1990 has identified one hundred and eighty nine pollutants as Hazardous Air Pollutants (HAPs) (**Table 1.1**). Subset of 97 amongst these is VOCs (**Table 1.2**) for which analytical procedure for measurement has already been developed by USEPA.

Ground-level ozone which is one of the criteria pollutant is not emitted directly, but it is formed by chemical reaction between oxides of nitrogen (NO_x) and volatile organic compounds in the presence of sunlight. Emissions from industries, electric utilities, motor vehicles and chemical solvents are some of the major sources of NO_x and VOCs. Breathing ozone can lead to chest pain, coughing, throat irritation, and congestion. It can worsen bronchitis, emphysema, asthma and also reduce lung function. Ground-level ozone can also damage vegetation and ecosystems. Estimation of Ground-level ozone is therefore very crucial in the context of urban air quality.

VOCs are the major class of pollutants causing concern. In-fact in United States VOCs is though not criteria pollutants but they are regulated under

criteria pollutants programme because they are ozone precursors. VOCs are part of the large hydrocarbon family which can get converted into vapour or gas without any chemical change. They are highly reactive hydrocarbons and participate in atmospheric photochemical reactions. VOCs that exist in air cover a wide range of aliphatic, aromatic hydrocarbons, their halogenated derivatives, alcohols, ketones and aldehydes. They are found both indoors and outdoors.

Many VOCs are of natural origin while many of them owe their existence to human activities. Based on the available toxicity, ambient monitoring, emission inventory data, existing exposure and risk assessment studies, USEPA identified forty potential HAPs as a first step in Urban Air Toxic Studies (**Table 1.3**). Some VOCs are toxic having both carcinogenic and non-carcinogenic hazard eg. Benzene, formaldehyde etc. while some react in air to form other harmful substances. For example ethylene, propane, toluene and butane and many other VOCs may take part in reactions which lead to formation of ozone containing smog. For ozone and smog studies, VOCs are often defined as compounds containing at least one carbon atom and having a vapour pressure of 0.01 kPa at 25°C excluding carbon monoxide and carbon dioxide.

Table 1.1: Hazardous Air Pollutants under the Air Toxics Programme of USEPA

Acetamide	Acetonitrile
Acetophenone	2-Acetylaminofluorene
Acrolein	Acrylamide
Acrylic acid	Acrylonitrile
Allyl chloride	4-Aminobiphenyl
Aniline	o-Anisidine
Asbestos	Benzene (including benzene from gasoline)
Benzidine	Benzotrichloride
Benzyl chloride	Biphenyl
Bis(2-ethylhexyl)phthalate (DEHP)	Bis(chloromethyl)ether
Bromoform	1,3-Butadiene
Calcium cyanamide	Captan
Carbaryl	Carbon disulfide
Carbon tetrachloride	Carbonyl sulfide
Catechol	Chloramben
Chlordane	Chlorine
Chloroacetic acid	2-Chloroacetophenone
Chlorobenzene	Chlorobenzilate
Chloroform	Chloromethyl methyl ether
Chloroprene	Cresols/Cresylic acid (isomers and mixture)
o-Cresol	m-Cresol
p-Cresol	Cumene
2,4-D, salts and esters	DDE
Diazomethane	Dibenzofurans
1,2-Dibromo-3-chloropropane	Dibutylphthalate
1,4-Dichlorobenzene(p)	3,3-Dichlorobenzidene
Dichloroethyl ether (Bis(2-chloroethyl) ether)	1,3-Dichloropropene
Dichlorvos	Diethanolamine
N,N-Diethyl aniline (N,N-Dimethylaniline)	Diethyl sulfate
Methyl bromide (Bromomethane)	Methyl chloride (Chloromethane)
Methyl chloroform (1,1,1-Trichloroethane)	Methyl ethyl ketone (2-Butanone)
Methyl hydrazine	Methyl iodide (Iodomethane)
Methyl isobutyl ketone (Hexone)	Methyl isocyanate
Methyl methacrylate	Methyl tert butyl ether

**Table 1.1: (Contd...)Hazardous Air Pollutants under the Air
Toxics Programme of USEPA**

4,4-Methylene bis(2-chloroaniline)	Methylene chloride (Dichloromethane)
Methylene diphenyl diisocyanate (MDI)	4,4'-Methylenedianiline
Naphthalene	Nitrobenzene
4-Nitrobiphenyl	4-Nitrophenol
2-Nitropropane	N-Nitroso-N-methylurea
N-Nitrosodimethylamine	N-Nitrosomorpholine
Parathion	Pentachloronitrobenzene (Quintobenzene)
3,3-Dimethoxybenzidine	Dimethyl aminoazobenzene
3,3'-Dimethyl benzidine	Dimethyl carbamoyl chloride
Dimethyl formamide	1,1-Dimethyl hydrazine
Dimethyl phthalate	Dimethyl sulfate
4,6-Dinitro-o-cresol, and salts	2,4-Dinitrophenol
2,4-Dinitrotoluene	1,4-Dioxane (1,4-Diethyleneoxide)
1,2-Diphenylhydrazine	Epichlorohydrin (1- Chloro - 2, 3-epoxypropane)
1,2-Epoxybutane	Ethyl acrylate
Ethyl benzene	Ethyl carbamate (Urethane)
Ethyl chloride (Chloroethane)	Ethylene dibromide (Dibromoethane)
Ethylene dichloride (1,2-Dichloroethane)	Ethylene glycol
Ethylene imine (Aziridine)	Ethylene oxide
Ethylene thiourea	Ethylidene dichloride (1,1-Dichloroethane)
Formaldehyde	Heptachlor
Hexachlorobenzene	Hexachlorobutadiene
Hexachlorocyclopentadiene	Hexachloroethane
Hexamethylene-1,6-diisocyanate	Hexamethylphosphoramide
Hexane	Hydrazine
Hydrochloric acid	Hydrogen fluoride (Hydrofluoric acid)
Hydroquinone	Isophorone
Lindane (all isomers)	Maleic anhydride
Pentachlorophenol	Phenol
p-Phenylenediamine	Phosgene
Phosphine	Phosphorus
Phthalic anhydride	Polychlorinated biphenyls (Aroclors)
1,3-Propane sultone	beta-Propiolactone
Propionaldehyde	Propoxur (Baygon)
Propylene dichloride (1,2-Dichloropropane)	Propylene oxide

**Table 1.1: (Contd...)Hazardous Air Pollutants under the Air
Toxics Programme of USEPA**

1,2-Propylenimine (2-Methyl aziridine)	Quinoline
Quinone	Styrene
Styrene oxide	2,3,7,8-Tetrachlorodibenzo-p-dioxin
1,1,2,2-Tetrachloroethane	Tetrachloroethylene (Perchloroethylene)
Titanium tetrachloride	Toluene
Toluene-2,4-diamine	2,4-Toluene diisocyanate
o-Toluidine	Toxaphene (chlorinated camphene)
1,2,4-Trichlorobenzene	1,1,2-Trichloroethane
Trichloroethylene	2,4,5-Trichlorophenol
2,4,6-Trichlorophenol	Triethylamine
Trifluralin	2,2,4-Trimethylpentane
Vinyl acetate	Vinyl bromide
Vinyl chloride	Vinylidene chloride (1,1-Dichloroethylene)
Xylenes (mixed isomers)	o-Xylene
m-Xylene	p-Xylene
Antimony compounds	Arsenic compounds (inorganic including arsine)
Beryllium compounds	Cadmium compounds
Chromium compounds	Cobalt compounds
Coke oven emissions	Cyanide compounds
Glycol ethers	Lead compounds
Manganese compounds	Mercury compounds
Fine mineral fibers	Nickel compounds
Polycyclic organic matter	Radionuclides (including radon)
Selenium compounds	

Table 1.2: Subset of HAPs which are VOCs

Compounds	
Methyl chloride (chloromethane); CH ₃ Cl	Methylhydrazine; CH ₆ N ₂
Carbonyl sulfide; COS	Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂
Vinyl chloride (chloroethane); C ₂ H ₃ Cl	2,2,4- Trimethyl pentane; C ₈ H ₁₈
Diazomethane; CH ₂ N ₂	1,4 –Dioxane (1,4 Diethylene oxide); C ₄ H ₈ O ₂
Formaldehyde; CH ₂ O	Bis (chloromethyl) ether; C ₂ H ₄ Cl ₂ O
1,3- Butadiene; C ₄ H ₆	Ethyl acrylate; C ₅ H ₈ O ₂
Methyl bromide (bromomethane); CH ₃ Br	Methyl methacrylate; C ₅ H ₈ O ₂
Phosgene; CCl ₂ O	1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (eis)
Vinyl bromide (bromoethene); C ₂ H ₃ Br	Toluene; C ₇ H ₈
Ethylene oxide; C ₂ H ₄ O	Trichloroethylene; C ₂ HCl ₃
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃
Acetaldehyde (ethanal); C ₂ H ₄ O	Tetrachloroethylene; C ₂ Cl ₄
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO
Propylene oxide; C ₃ H ₆ O	Ethylene dibromide (1,2-dibromethene); C ₂ H ₄ Br ₂
Methyl iodide (iodomethane); CH ₃ I	N-Nitroso-N-methylurea; C ₂ H ₅ ClO
Methyl isocyanate; C ₂ H ₃ NO	2-Nitropropane; C ₃ H ₇ NO ₂
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	Chlorobenzene; C ₆ H ₅ Cl
Carbon disulfide; CS ₂	Ethylbenzene; C ₈ H ₁₀
Methyl bromide (bromomethane); CH ₃ Br	Methyl methacrylate; C ₅ H ₈ O ₂
Phosgene; CCl ₂ O	1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (eis)
Vinyl bromide (bromoethene); C ₂ H ₃ Br	Toluene; C ₇ H ₈
Ethylene oxide; C ₂ H ₄ O	Trichloroethylene; C ₂ HCl ₃
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃
Acetaldehyde (ethanal); C ₂ H ₄ O	Tetrachloroethylene; C ₂ Cl ₄
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO
Propylene oxide; C ₃ H ₆ O	Ethylene dibromide (1,2-dibromethene); C ₂ H ₄ Br ₂
Methyl iodide (iodomethane); CH ₃ I	N-Nitroso-N-methylurea; C ₂ H ₅ ClO
Methyl isocyanate; C ₂ H ₃ NO	2-Nitropropane; C ₃ H ₇ NO ₂
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	Chlorobenzene; C ₆ H ₅ Cl

Table 1.2: (Contd...)Subset of HAPs which are VOCs

Carbon disulfide; CS ₂	Ethylbenzene; C ₈ H ₁₀
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	Acrylic acid; C ₃ H ₄ O ₂
Methyl chloroform (1,1,1 trichloroethane); C ₂ H ₃ Cl ₃	N, N-Dimethylformamide; C ₃ H ₇ NO
Methanol; CH ₄ O	1,3-Propane sultone; C ₃ H ₆ O ₃ S
Carbon tetrachloride; CCl ₄	Acetophenone, C ₈ H ₈ O
Vinyl acetate; C ₄ H ₆ O ₂	Benzyl chloride (a-chlorotoluene); C ₇ H ₇ Cl
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl
Benzene; C ₆ H ₆	Bis-(2-Chloroethyl) ether; C ₄ H ₈ Cl ₂ O
Acetonitrile (cyanomethane); C ₂ H ₃ N	Chloroacetic acid; C ₂ H ₃ ClO ₂
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	Aniline (aminobenzene); C ₆ H ₇ N
Triethylamine; C ₆ H ₁₅ N	1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂
Ethyl carbamate (urethane); C ₃ H ₇ NO ₂	Diethyl sulfate; C ₄ H ₁₀ O ₄ S
Acrylamide; C ₃ H ₅ NO	Cresylic acid (cresol isomer mixture)
N,N-Dimethylaniline; C ₈ H ₁₁ N	o-Cresol; C ₇ H ₈ O
Hexachloroethane; C ₂ Cl ₆	Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂
Hexachlorobutadine; C ₄ Cl ₆	Phenol; C ₆ H ₆ O
Isophorone; C ₉ H ₁₄ O	1,2,4-Trichlorobenzene; C ₆ H ₂ Cl ₃
N-Nitrosomorpholine; C ₄ H ₈ N ₂ O ₂	Nitrobenzene; C ₆ H ₅ NO ₂
Styrene oxide; C ₈ H ₈ O	

Table 1.3: List of Urban Air Toxics Identified by USEPA

Compounds	
1,1,2,2- Tetrachloroethane	Ethyl Acrylate
1,1,2- Trichloroethane	Ethylene Dibromide (1,2-Dibromoethane)
1,2-Dichloropropane (Propylene Dichloride)	Ethylene Dichloride (1,2-Dichloroethane)
1,3-Butadiene	Ethylene Oxide
1,3-Dichloropropene	Formaldehyde
1,4-Dichlorobenzene	Hydrazine
Acetaldehyde	Lead Compounds
Acrolein	Manganese Compounds
Acrylamide	Mercury Compounds
Acrylonitrile	Methyl Chloride (Chloromethane)
Arsenic Compounds	Methyl Chloride (Dichloromethane)
Benzene	Methyl Diphenyl Diisocyanate (MDI)
Beryllium Compounds	Nickel Compounds
bis (2-Ethylhexyl) phthalate	Polycyclic Organic Matter (POM)
Cadmium Compounds	Quinoline
Carbon Tetrachloride	Styrene
Chloroform	Tetrachloroethylene (Perchloroethylene)
Chromium Compounds	Trichloroethylene
Coke Oven Emissions	Vinyl Chloride
Dioxins/Furans	Vinylidene Chloride (1,1 –Dichloro ethylene)
2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD)	2,3,7,8-Tetrachlorodibenzofuran (TCDF)
Polychlorinated Biphenyl Compounds (PCBs)	Hexachlorobenzene

The present monitoring study was carried out to cover pollutants namely, Ozone, and VOCs including carbonyl in the ambient air in Kolkata. This was done by dividing Kolkata city area into three zones namely, North, South and Central. One monitoring location of each category area viz. industrial, commercial cum residential, refueling stations and traffic intersections were selected in each of three zones. The study area showing the sampling locations is given in **Figure 1.1**.

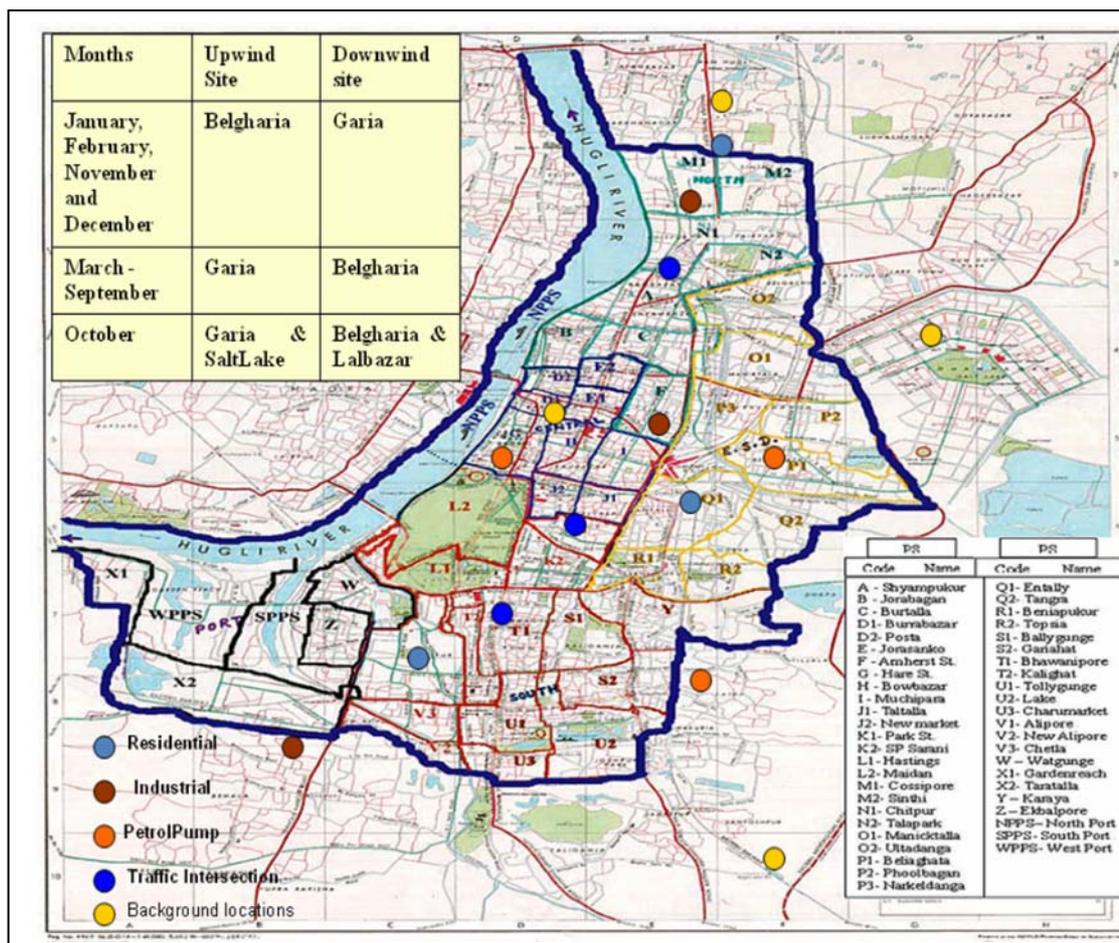


Figure 1.1: Study Area Showing Sampling Locations

1.2 Objectives

The project was taken up with an overall objective of studying the sources and atmospheric chemistry of VOCs and other carbonyls in urban air involving NO_x and ozone. The specific objectives of the study were:

- Obtaining of the ambient level of NO_x, carbonyls, ozone and selected VOCs.
- Estimation of ambient level of NO_x, VOC, carbonyls and Ozone in industrial areas, commercial cum residential and at refueling stations and traffic intersections.
- Obtaining of monthly trends in the ambient level of VOCs, carbonyls and Ozone in the identified areas.
- Prediction of surface concentration of NO_x, Ozone, carbonyls and VOCs.

- Source identification of VOCs and estimation of their relative contribution.
- Health Risk assessment, and
- Preparation of VOCs mitigation strategy.

1.3 Scope of Work

- Identification of VOCs including carbonyl compounds present in the ambient air of Kolkata.
- Estimation of ambient VOC and ground level Ozone concentration in the city.
- Estimation of ambient level of VOCs and ground level Ozone in industrial, commercial and residential areas, and at refueling stations and traffic intersections.
- Estimation of monthly trend in ambient level of VOCs and ground level Ozone for different areas.

Chapter 2

Characterization of VOC

2.1 VOC Definition

VOCs are organic compounds with boiling points between 50°C to 260°C and vapour pressure equal to or more than 0.01 kPa at 25°C. The term encompasses a very large and diverse group of carbon containing compounds including aliphatic, aromatic and halogenated hydrocarbons, aldehydes, esters, acids, alcohols, ketones and others.

USEPA has recognized that some of the VOCs have such a low reactivity that they do not have significant impact on the formation of ozone. It defines VOCs as “any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate) which participates in atmospheric photochemical reactions”.

WHO defines VOCs as “all organic compounds in the boiling range 80°C to 200°C excluding particles”. This definition does not exclude any compound on the basis of their low photochemical reactivity.

2.2 Sources of VOCs in Ambient Air

The sources of Volatile Organic Compounds (VOCs) are numerous. Broadly they can be divided into, natural and anthropogenic.

Natural sources of VOCs are forests, termites, wetlands and tundras. In Canada, natural emissions from forests are the largest source of VOC emissions. Forest species such as Oak, Poplar, Cottonwood and Eucalyptus emit isopropene (2 methyl-1, 3-butadiene). Acetaldehyde occurs as an intermediate product in the respiration of higher plants and ripening fruits such as apple. Fermentation process, forest fires, volcanoes, animal wastes and insects are sources of acetone, 2-Butanone, acetaldehyde etc. Low level of styrene occurs naturally in fruits, vegetables, nuts, beverages and meats.

In wetlands production of methane occurs in sulphate-depleted environment. Both wetland and tundras experience increased natural

methane production when the soil moisture content is high. Termites produce an astonishing 4% of the total worldwide fluxes of methane.

Anthropogenic sources of VOCs include industrial, fossil fuel combustion in transportation and electricity generation, landfills and waste treatment plants, and household products. Important industrial sources of VOC emission are manufacturing of paints, varnishes, solvents, chemical, fertilizers and petroleum refining and processing.

2.2.1 Characterisation of VOCs

Her Majesty's Inspectorate of Pollution (HMIP) (Marlowe et al., 1996) categorised Volatile Organic Compounds (VOCs) according to their harmfulness. National Atmospheric Emissions Inventory (NAEI) in the UK and the Toxic Release Inventory (TRI) in the USA also made an inventory of VOCs. The NAEI lists 677 compounds. A variety of data on toxicological and chemical reactivity properties have then been used to categorise substances on this list in terms of the potential impact they may have on atmospheric quality and human health if they are released in significant quantities. A final total of 933 VOCs, have been categorised as high, medium or low risk to the environment and human health. Out of these 933, 154 (17%) are classed as high or medium risk. A comparison (**Figure 2.1**) of the HMIP, NAEI and USTRI VOC lists found 77 VOCs in common. Also, 250 VOCs are found on two inventories namely HMIP and NAEI and the remaining 15 figuring in only one list.

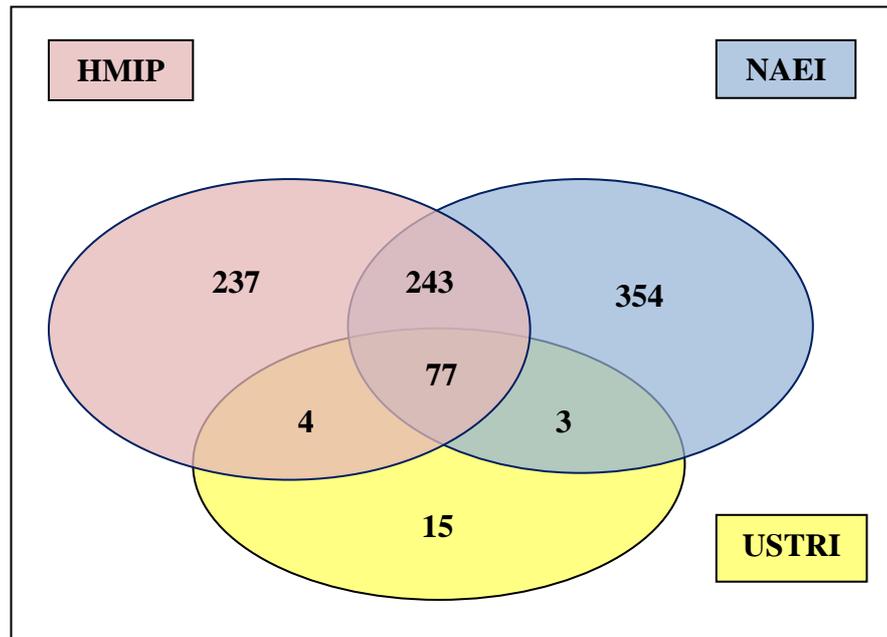


Figure 2.1: Venn diagram showing comparison of the three data sources

2.3 Impact of VOCs

The impact of VOCs can be divided into seven categories:

- Impact on human health
- Impact on Tropospheric ozone production
- Impact on Stratospheric ozone depletion
- Impact on climate change
- Impacts on natural ecosystems
- Damage to materials, and
- Odour

2.3.1 Impact on Human Health

VOCs can affect human health by virtue of their carcinogenic, mutagenic or reproductive effects. In addition their inhalation/ingestion may also be toxic. The main data source relating to their hazards to human health is the Chemicals Hazard Information and Packaging (CHIP) Approved Supply List (ASL). The health hazard categories in CHIP that are relevant to human health and the environment are very toxic, toxic and harmful. In addition the substances can be classified as Carcinogenic, Mutagenic or a Reproductive Toxicity (abbreviated to reprotoxin) and graded from 1 to 3. 1

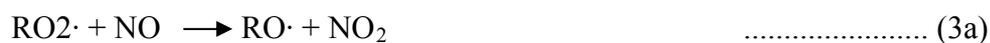
being the most harmful. While CHIP is a well-established source of toxicity data and it contains information on many VOCs, there are many more substances in the initial list for which there are no CHIP data. This may be because of either no data available or there is no evidence of toxicity.

International Agency for Research on Cancer (IARC) classification of carcinogenicity to humans has been used to support the CHIP data. There are three categories in the IARC classification, 1 (carcinogenic to humans), 2A (probably carcinogenic to humans) and 2B (possibly carcinogenic to humans). Category 1 and 2A substances are considered high risk and category 2B substances are considered medium risk.

2.3.2 Reactions of VOCs in the troposphere

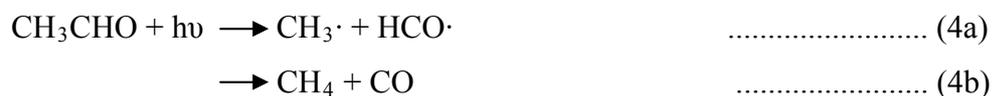
Reaction mechanisms of VOCs

Volatile Organic Compounds react in the air at a different rate and have different reaction mechanisms. These compounds react with OH radical, ozone, NO₃ radicals or Cl atoms, or they photolyze. For most of the studied VOCs, the OH involving reactions are mostly in the daytime (*Atkinson, 2000*). NO₃ photolyses rapidly in the troposphere and therefore only exists in sufficient concentrations to play a role in night-time chemistry. Chlorine atoms can be important in the marine boundary layer. For some carbonyls, Methyl Tertiary Butyl Ether (MTBE) and Tertiary Amyl Methyl Ether (TAME) wet depositions may also be an important sink (*Kawamura et al., 2001, Achten et al., 2001 and Kolb and Püttmann, 2006*). For the alkanes, the OH radical reaction is the main reaction in the troposphere, but reactions with NO₃ radicals and Cl atoms are also important (*Atkinson, 2000*). Alkanes do not undergo photolysis or react significantly with ozone. Alkane reactions proceed by hydrogen atom abstraction from the C-H bond forming alkyl radicals (reaction 1). These alkyl radicals (R·) react rapidly with O₂ to form alkyl peroxy radicals (RO₂·) (reaction 2). The main reaction for the RO₂· radicals in air is with NO, producing NO₂ and alkoxy radicals (RO·) (reaction 3a) (*Derwent, 1999*). For larger alkanes, the addition of NO to form an alkyl nitrate (RONO₂) may also be an important path (reaction 3b) (*Finlayson-Pitts and Pitts, 2000*).



At very high NO₂ concentration, reactions with NO₂ to form peroxyxynitrate (RO₂NO₂) may become important. Alkoxy (RO·) radicals have several possible atmospheric fates depending on their structure. These include, reaction with O₂ forming hydrogen peroxy radical (HO₂·), decomposition and isomerization. Alkenes are highly reactive towards OH·, O₃ and NO₃·. Their reaction rate with O₃ is much smaller than with the OH radicals. However, concentration of O₃ is much larger and therefore O₃ reactions are important removal processes, especially for the larger alkenes (e.g. biogenic hydrocarbons) (Hakola et al., 2003; Atkinson, 2000). Reaction rate for NO₃ is also high and the NO₃ reaction is assumed to be a major fate for at least biogenic hydrocarbons during night (Hakola et al. 2003). In case of alkenes, OH· and NO₃· add to the double bonds and alkyl radicals are formed. The reactions of these alkyl radicals are analogous to the reactions of alkyl radicals formed in the alkane reactions. In the O₃ reaction, ozone adds to the carbon double bond, forming an energetically-excited primary ozonide (Finlayson-Pitts and Pitts, 2000). This r decomposes forming an ester (minor) or an unsaturated hydroperoxide (major). In addition to this, the primary ozonide can be collisionally stabilized forming the so-called stabilized Criegee intermediate (hydroxyperacid) which further reacts with various different compounds, e.g. water vapour. The only significant loss process for alkynes is a reaction with OH radicals. (Finlayson- Pitts and Pitts, 2000). The reaction is an addition to the triple bond forming the alkyl radical. The reactions of these alkyl radicals are analogous to the reactions of the alkyl radicals formed in the alkane reactions. Under atmospheric conditions, aromatic hydrocarbons are oxidized by OH and NO₃· radicals with the OH radical reactions dominating the tropospheric removal process (Atkinson, 2000). In aromatic reactions, the abstraction of H-atoms or the addition of an OH radical to the double bond may occur. The reactions of benzyl and alkyl-substituted benzyl radicals formed from the H-atom

abstraction are analogous to those for the alkyl radicals discussed above. OH-aromatic adducts react with O₂ and NO₂. The gasoline additives MTBE and TAME react with the OH radical (Kolb and Püttmann, 2006). The major tropospheric loss process for halogenated hydrocarbons is by reaction with the OH radical (Atkinson, 2000). Halogenation generally decreases the reactivity towards the OH radicals, O₃ and NO₃ radicals compared to the corresponding alkanes and alkenes and therefore the reactions of most halogenated HCs are very slow in the troposphere. Carbonyls (aldehydes and ketones) undergo photolysis and reactions with OH and NO₃ radicals. The reactions of OH· and NO₃· with aldehydes occur by abstraction of the H-atom from the –CHO group, forming acyl radicals (RCO·) (Finlayson-Pitts and Pitts, 2000). The RCO radical adds O₂ to form the acyl peroxy radical. This radical reacts in turn with NO and NO₂ in an analogous way to alkyl peroxy radicals (Atkinson, 2000). From the reaction with NO₂, peroxy acyl nitrates are formed; for example, acetaldehyde is a classic precursor to peroxyacetyl nitrate (PAN). PAN thermally decomposes back to a peroxyacetyl radical and NO₂. The reactions of ketones are similar to those of alkanes with abstraction by OH· and NO₃· occurring from the alkyl chain (Finlayson-Pitts and Pitts, 2000). In addition to OH· reaction, photolysis is an important loss process for carbonyls in the troposphere (Atkinson, 2000 and paper V). In these photo-dissociation reactions both free radicals and stable products are formed; for example, in the photolysis of acetaldehyde two sets of products, methyl (CH₃·) and acyl (HCO·) radicals (reaction 4a) or stable methane (CH₄) and carbon monoxide (CO) (reaction 4b), are formed (Finlayson-Pitts and Pitts, 2000):



2.3.3 Lifetime of VOCs

Based on OH radical estimates Hakola et al. (2003) studied the average daytime lifetimes involving the OH reaction in Finland. The studies conducted by him showed VOCs life time from a few hours for monoterpenes to several hundred years for some halogenated HCs. The

lifetimes of VOCs for OH reactions were found to be 20 times shorter in summer than in winter in Finland. The lifetimes of alkenes for ozone reactions vary from a few hours to 14 days.

2.3.4 Reaction products of VOCs

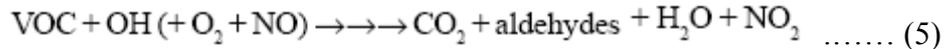
In the publication Master Chemical Mechanism, 2006 the laboratory data for reaction schemes of 135 VOCs are provided. The full degradation scheme of butane consists of 510 reactions and 186 species of which 20 are themselves primary emitted VOCs for which separate schemes are given.

Reaction products formed in chamber studies are mainly carbonyls, alcohols, organic nitrates and acids, found in both gas and aerosol phases (Hamilton et al., 2005; Forstner et al., 1997; Yu et al., 1997). Concentrations in chambers are often 1000 times higher than in the real atmosphere, but some of the products identified in modeling or chamber studies have also been detected in the ambient atmosphere (Hamilton et al., 2004; Edney et al., 2003).

The reactions of aromatic hydrocarbons are extremely complex. Numerous reaction pathways have been identified and a very large variety of different kinds of products has been found in chamber studies. Compounds include carbonyls, dicarbonyls, organic acids, aromatics, furans, furanones and pyranones (Hamilton et al., 2005; Yu et al., 1997; Forstner et al., 1997). Many of the products are capable of producing secondary organic aerosol (Hamilton et al., 2005; Izumi and Fukuyama, 1990; Takekawa et al., 2003; Odum et al., 1997; Grosjean, 1992). For isoprene, methyl vinyl ketone, methacrolein and formaldehyde have been found to account for 60 % of the total OH reaction products (Pinho et al., 2005). Reactions of alkynes with OH radicals give as major products the corresponding dicarbonyls, i.e., ethyne gives glyoxal and propyne gives methylglyoxal (Finlayson-Pitts and Pitts, 2000), while the main product of the OH radical reaction of MTBE has been found to be tert-butylformate (TBF) (Kolb and Püttmann, 2006).

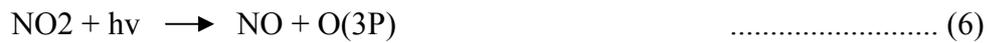
The hydroxyl radical is the key reactive species in the chemistry of ozone formation. The VOC-OH reaction initiates the oxidation sequence. For the higher VOC species, the chemical steps involve alkyl radical (RO) and

alkyl peroxy radicals (RO₂) formation, generation of OH, oxidation NO-NO₂ and formation of aldehydes, CO₂ and H₂O.



2.3.5 Tropospheric ozone production

In the troposphere, ozone is produced by photolysis of NO₂ (Sillman, 1999; Atkinson, 2000). Ozone then rapidly oxidises NO back to NO₂, as shown in reactions 6 to 8.



..... (7)



However, there are other oxidants (hydroperoxy and alkylperoxy radicals) also present in atmosphere to convert NO to NO₂. These free radicals are formed in the reactions of VOCs (reactions 1-3). The relations between ozone, NO_x and VOCs are complex. In some conditions ozone formation is controlled almost entirely by NO_x, while in other conditions ozone production increases with increasing VOC and does not increase with increasing NO_x.

In the earlier classifications of VOCs, Photochemical Ozone Creation Potential (POCP) was used as a measure of the capacity of a VOC to contribute to low level ozone production. The alternative to POCP is Integrated Downwind Ozone Production (IDOP) which, unlike POCP provides a level of production of ozone in the atmosphere for a given emission of 1 tonne per hour rather than an indication of the potential to form ozone as in the POCP method. POCP was designed to assess the relative importance of VOC emission sectors such as transport or solvent production. However, IDOP has been designed specifically for the regulation of VOC emissions to the atmosphere (**Derwent & Nelson 2002**). **IDOP value >4 is considered as high risk, a value <4 and >0.2 is medium risk and a value <0.2 indicates a low risk compound.**

2.3.6 Stratospheric ozone depletion

Stratospheric ozone depletion is a major environmental issue for last over 20 years because of the potential impact on climate and human health caused by increased exposure to UV radiations. Chlorofluorocarbons (CFCs) have been identified as the main concern in ozone depletion and were first legislated under the Montreal Protocol and additional amendments. Subsequently halons (haloalkanes), HCFCs and other VOCs have also been identified as of potential concern. In particular methane, non-methane hydrocarbons and chlorine-containing substances may also contribute to ozone depletion. The standard measure of the potential for a VOC to contribute to the destruction of stratospheric ozone is Ozone Depletion Potential (ODP). ODP is derived from a mathematical model and expressed as a proportion of the ODP of trichlorofluoromethane, which has an ODP of 1.0.

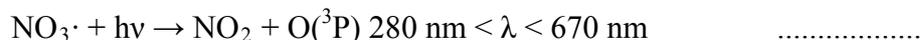
2.3.7 NO_x Transformation Chemistry

Most of the NO_x emitted into the atmosphere has an anthropogenic (combustion processes) origin, and it is released mainly as nitrogen oxide (NO). In the troposphere, NO reacts rapidly with ozone to generate NO₂, but in the presence of sunlight this reaction leads to other chemical reactions. NO can also react with peroxyalkyl (RO₂·) produced by the attack of hydroxyl radical to some VOC or with hydro peroxy radical.

In the presence of sunlight, nitrogen dioxide reacts mainly with OH· to produce nitric acid (Atkinson, 2000):



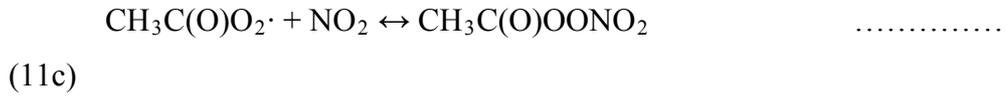
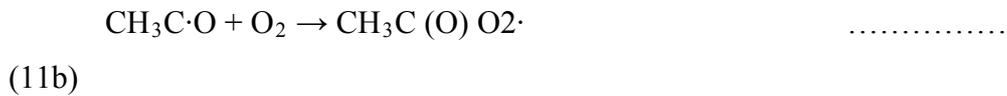
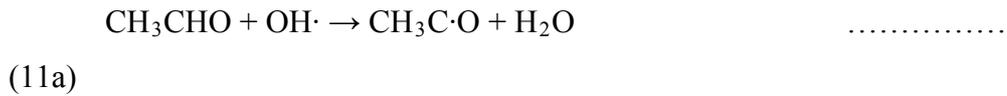
During daylight, NO₃· undergoes a quick photolysis by absorption of visible light, so daytime concentrations of nitric acid are negligible.



(10a)



In urban environment, with intense photochemical activity, NO_2 can react with a peroxyacyl radical, like $\text{CH}_3\text{C}(\text{O})\text{O}\cdot$ product of the photo decomposition of aldehydes and ketones, with formation of PAN and other nitrous organic compounds (Wayne, 2000):

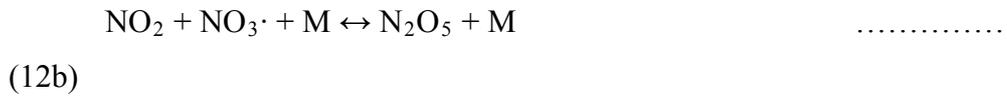


Thermal decomposition of PAN depends on temperature. PAN is probably the most important nitrogen source in the high layers of the troposphere, where temperatures are lower, dispendig NO_2 when air descends and heats.

The key differences between day and night chemistry can be summarized as:

- (1) absence of photolytic reactions during day time, and
- (2) accumulation of nitrate free radical, $\text{NO}_3\cdot$, which is rapidly photolyzed during the day, so its daytime concentration is negligible.

During the night, the processes that occur are:



NO₃ can be reconverted to NO₂ or thermally decompose:



Finally, N₂O₅ gets converted into nitric acid in the presence of water vapor:

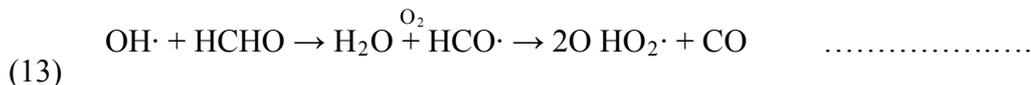


(12f)

As seen from above, nitrogen oxides are converted into nitric acid by a route not involving OH· radicals.

2.3.8 Reactions of Aldehyde

Aldehydes undergo photolysis and reaction with OH· and NO₃· radicals, the first two being the major loss processes (Seinfeld, 1989). The formaldehyde-OH· reaction yields the formyl (HCO·) radical, which subsequently reacts with O₂ to form HO₂· and CO:



For the higher aldehydes, the acyl (RCO·) radical initially formed rapidly adds oxygen to yield a peroxyacyl radical [RC(O)OO·]. The peroxyacyl radical can react with NO or NO₂, the latter reaction leading to the peroxyacyl nitrates. It is estimated that 80 to 90% of the formaldehyde in the urban atmosphere results from the photo oxidation of other organics and only about 10% to 20% from direct emissions.

Photochemical dissociation of aldehydes (RCHO) leads to the formation of radicals that through a rapid series of reactions lead ultimately to the formation of OH·:





Aldehydes are the most reactive products expected to be formed from non carbonyl VOC group as described in the **Figure 2.2**.

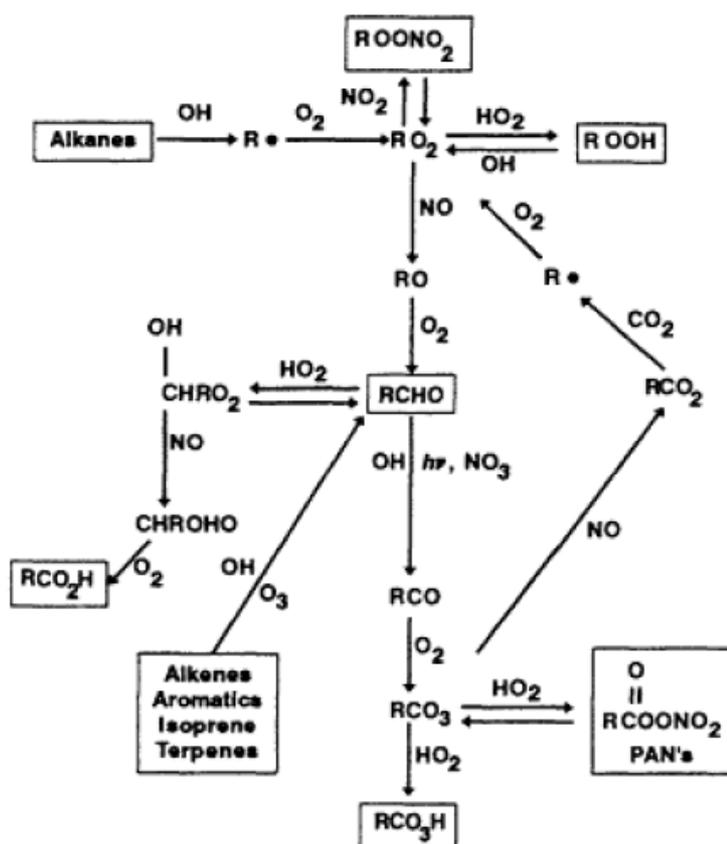
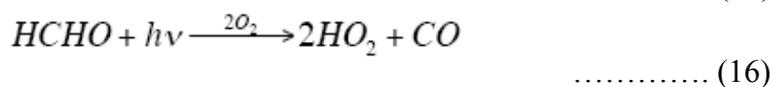
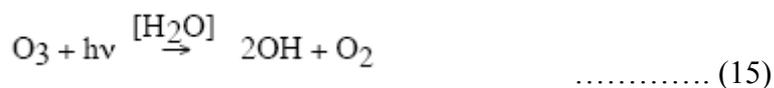


Figure 2.2: Reaction Pathways Involving VOC, O₃ and NO_x

It may be seen that there are two main sinks for RO₂ radicals: peroxides and nitric acid (HNO₃). When peroxides represent the dominant radical sink, chemistry is NO_x-sensitive and when HNO₃ represents the dominant sink, conditions are NO_x-saturated.

Odd hydrogen radicals consist of OH, HO₂ and species with the form RO₂. This family is directly connected to the chemistry of ozone production, because the initial reaction of the ozone production sequence (VOC+OH, eqn. 5) is governed by OH and subsequent steps depend on HO₂ and RO₂. The ozone production rates depend on the abundance of OH, which depends on sources and sinks of odd hydrogen radicals as a whole. Radical sources include photolysis of ozone, formaldehyde, and other secondary VOC.

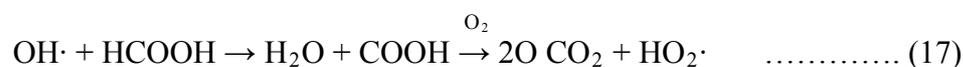


The oxidation of NMHC forms the carbonyl compounds, the aldehydes and ketones (CHO). The oxidation of aldehydes and ketones can be an additional source of ozone and oxidizing free radicals, and the photolysis of aldehydes and ketones can be a primary source of radicals. The simplest aldehyde, formaldehyde (HCHO), is particularly important because it can be formed by the oxidation of methane. HCHO can also be emitted into the atmosphere as a direct product of hydrocarbon combustion (Lawson et al., 1990a). Thus the photolysis of HCHO could be a key process in the formation of tropospheric ozone.

2.3.9 Reactions of Ketones

Ketones are exemplified by acetone and its higher homologues. Photolysis and OH· reaction are the major atmospheric loss processes, although, with the exception of acetone, photolysis is probably of minor importance. The major reaction products from the atmospheric reactions of ketones are aldehydes and PAN precursors, and bifunctional oxygen-containing compounds may be formed in small yield. The most important uncertainties in carbonyl chemistry involve photolysis rates and quantum yields, the fate of hydrocarbonyls, and the existence of nitrate carbonyls resulting from higher alkanes. Because carbonyl photolysis is such an important source of free radicals, uncertainties in photolysis rate translate into uncertainties in ozone formation rates.

Carboxylic acids such as formic and acetic acid react with the OH· radical through the formation of an addition complex. For example, for formic acid:



The reactions of peroxy radicals leading to HO₂· and formaldehyde, this contributes to photochemical reactions including ozone formation (Grosjean et al., 2001).

2.3.10 Correlation of VOC, NO_x and Ozone in Ambient air

Ground level ozone is formed in a complex series of gas-phase reactions involving the interactions of volatile organic compounds (VOCs) and NO_x in the presence of sunlight. The amount of ozone formation caused by the emissions of various compounds depends not only on the compound but also on the environment where it is emitted. Ozone impacts can be quantified by "incremental reactivities", which are defined as the change in ozone formed when a small amount of compound is added to the emissions in a particular air pollution episode or scenario with certain meteorological condition, divided by the amount of compound added. Incremental reactivities are properties both of the compound and episode or scenario in which the compound may be emitted. These can be calculated with airshed models, for the atmospheric conditions and chemical mechanisms of the gas-phase atmospheric reactions of the compounds involved with ozone formation.

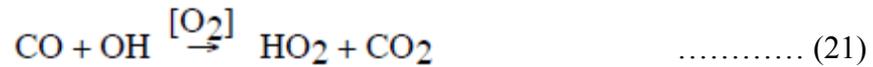
In the case of volatile organic compounds (VOCs), the use of "maximum incremental reactivity" (MIR) values to obtain a single ozone impact value for each compound for comparison or regulatory purposes has been proposed by. These are defined as the incremental reactivities of the compounds in scenarios where ozone formation has maximum sensitivities to VOC inputs. This reflects conditions where VOC controls are the most effective for reducing ozone.

Mixing ratio of VOC and NO_x in air can affect the formation of ozone by influencing the reaction pathways. The most important single environmental condition that affects the magnitudes of ozone impacts of VOCs is the relative levels of oxides of nitrogen (NO_x) present in the scenarios. The competitive reactions are as follows:

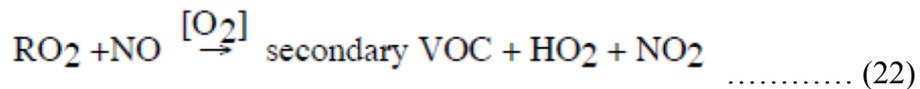




Ozone formation takes place through sequence of reactions. The sequence is almost always initiated by the reaction of various VOC or CO with the OH radical (reactions 20, 21).



Through reaction with HO₂ or RO₂ radicals NO is then converted to NO₂, which also generates OH through reactions 22 and 23.



In presence of sun light photolytic reaction causes NO₂ to generate atomic oxygen, which combines with O₂ to form O₃ (reactions 24, 25).



The rate of ozone formation is controlled primarily by the rate of the initial reaction of VOC with OH. VOCs have the highest ozone impacts under conditions where NO_x is abundant and zero impacts when NO_x is absent, because NO_x is required for ozone formation to occur. NO_x emissions actually have very large negative impacts on O₃ formation in scenarios where VOCs have the highest incremental reactivities. NO_x emissions have large and positive ozone impacts in scenarios with very low NO_x levels, where VOC impacts on ozone tend to be near zero or negative. The areas

can be described as "VOC-limited" or NO_x-limited". The ratio of VOC to NO_x characterizes the efficiency of ozone formation in VOC-NO_x-air mixtures. At high VOC/NO_x concentration ratio, OH will react mainly with VOC; at low concentration ratio, the NO₂ reaction can predominate. At ambient conditions, the second order rate constant for reaction 12 is about 1.7 x 10⁴ ppm⁻¹ min⁻¹. Considering an average urban mix of VOC, an average VOC + OH rate constant is about 3.1 x 10³ ppm C⁻¹ min⁻¹. Using these values, the ratio of the OH+NO₂ /VOC+OH rate constants is about 5.5. Thus, when the VOC/NO₂ concentration ratio is approximately 5.5:1.0, with the VOC concentration expressed on a carbon atom basis, the rates of the reactions of VOC and NO₂ with OH are equal. If the VOC/NO₂ concentration ratio is less than 5.5:1.0, the reaction of OH with NO₂ predominates over the reaction of VOC with OH. The OH+NO₂ reaction removes OH radicals from the active VOC oxidation cycle, retarding the further production of ozone. On the other hand, when the concentration ratio exceeds 5.5:1.0, OH reacts preferentially with VOC. Also, the reaction of O₃ with NO (reaction 26) contributes to the consumption of ozone at low ratios VOC/NO_x.



O₃-NO_x-VOC sensitivity for individual locations and events are often very uncertain. The split between NO_x-sensitive and VOC-sensitive chemistry is a major source of uncertainty in predictions for the relation between O₃ and precursor emissions. Sillman (2005) has pointed out that NO_x-VOC sensitivity is difficult to predict, and there are no simple "rules of thumb" for distinguishing NO_x sensitive from VOC-sensitive conditions. O₃-precursor sensitivity predictions are usually derived from 3-dimensional Eulerian chemistry/transport models. These models are subject to many uncertainties that affect their ability to identify NO_x-sensitive vs. VOC-sensitive conditions. Different assumptions in models may lead to very different results for predicted sensitivity to NO_x and VOC. Evaluation of chemistry/transport models is usually based on the ability of the model to

predict O₃ in comparison with ambient measurements. However, success in simulating the observed NO_x does not guarantee that models predict the O₃-NO_x-VOC sensitivity correctly. Frequently it is possible to create different model scenarios for an event that give similar O₃ but with very different predictions for NO_x-VOC sensitivity (Sillman et al., 1995, Reynolds et al., 1996, Pierce et al., 1998).

At nighttime and in the immediate vicinity of very large emissions of NO (e.g. power plants), ozone concentrations are depressed through the process of NO_x titration. This consists of the removal of O₃ through reaction with NO [reaction 26]. During the daytime, this reaction is normally balanced by the photolysis of NO₂ [reactions 24, 25]. However, in the vicinity of large NO emissions the result is net conversion of O₃ to NO₂. This is most common in the vicinity of large point sources. Ozone is depressed immediately downwind of these sources, and becomes elevated as the plume moves further downwind (Gillani et al., 1996). At nighttime, there is no photolysis of NO₂ reaction and reaction as per reaction 26 also leads to the removal of ozone.

Factors Affecting Reactivity

Kinetic and Mechanistic Reactivities:

Incremental reactivity, which is the amount of additional ozone formation caused by adding a small amount of the compound to the emissions, divided by the amount emitted (Carter and Atkinson, 1989; Carter, 1994) is considered for regulatory purposes.

Carter and Atkinson, 1989 proposed incremental reactivities as being a product of three factors for estimation of upper limit as follows:

$$\begin{matrix} \text{Incremental} \\ \text{Reactivity} \\ \text{(Ozone per} \\ \text{mass VOC} \\ \text{emitted)} \end{matrix} = \begin{matrix} \text{Kinetic} \\ \text{Reactivity} \\ \text{(VOC reacted} \\ \text{/VOC emitted)} \end{matrix} \cdot \begin{matrix} \text{Mechanistic} \\ \text{Reactivity} \\ \text{(moles O}_3 \\ \text{/mole VOC} \\ \text{reacted)} \end{matrix} \cdot \begin{matrix} \text{Mass Conv-} \\ \text{ersion Factor} \\ \text{(moles VOC} \\ \text{/mass VOC)} \end{matrix} \dots\dots\dots (27)$$

The kinetic reactivity is the fraction of the emitted VOC which undergoes chemical reaction in the atmosphere during the time period under

consideration. It is basically governed by the rate constants for the VOCs atmospheric reactions, and also on the overall levels of OH radicals, ozone, or light depending on how the VOC reacts. Kinetic reactivity is approximately proportional to atmospheric reaction rate for slowly reacting compounds, for rapidly reacting compounds the kinetic reactivity is approximately unity, and thus almost independent of the reaction rate. Therefore, if insufficient information is available to derive upper limit atmospherically relevant rate constants for a compound, then kinetic reactivities of unity can be used for upper limit estimation purposes. Most VOCs react significantly only with OH radicals. In this case, the fraction reacted in given scenario can be estimated by,

$$\begin{aligned} \text{Kinetic Reactivity} &\approx (1 - e^{-k_{\text{OH}} \cdot \text{EffIntOH}}) \\ &\approx k_{\text{OH}} \cdot \text{EffIntOH} \quad (\text{if } k_{\text{OH}} \cdot \text{IntOH} \ll 1) \end{aligned} \quad \dots\dots\dots (28)$$

Where, k_{OH} is the VOC's OH radical rate constant, and EffIntOH is a scenario-dependent "Effective Integrated OH" parameter which is related to, but is not exactly the same as, the integrated OH radical levels (Carter and Atkinson, 1989).

The mechanistic reactivity is the number of molecules of ozone formed for each molecule of VOC which reacts. It reflects both the nature of the VOCs reaction mechanism and also the efficiency of ozone formation from the reactions of VOCs in the particular scenario. Upper limits for mechanistic reactivities can be estimated based on the range of mechanistic reactivities of compounds with known mechanisms or ozone impacts.

Incremental reactivities in units of molecules of ozone formed per molecule of VOC emitted is the product of the kinetic and mechanistic reactivities.

Environmental Conditions

Both kinetic and mechanistic reactivities depend on the conditions of the environment where the VOC reacts. When a VOC reacts primarily with OH radicals the OH radical levels in the environment determine the fraction which reacts, and the NOx levels significantly affect the efficiency for O₃

formation once a VOC reacts, which determines its mechanistic reactivity (Carter and Atkinson, 1989).

OH Radical Rate Constants:

As VOCs react in the atmosphere with OH radicals, the rate constant for this reaction, or its upper limit, must be determined, or its upper limit must be estimated. Some VOCs due to absence of double bond or easily available hydrogen can be considered to be significantly unreactive.

If OH radical rate constant of the compound is not available the rate constant can be measured using the methods of Kwok and Atkinson (1995), then a rate constant which is two times the estimated value can be used for the purpose of making upper limit kinetic reactivity estimates. The factor of two increase is necessary to take into account the uncertainty of the estimation methods when making upper limit determinations.

Ozone Rate Constant:

Some VOCs, usually (but not always) those with C=C double bonds, can react with ozone at significant rates, and these reactions often have a net positive effect on ozone because of the subsequent reactions of the radicals formed.

Atkinson and Carter (1984) discuss possible approaches for estimating Ozone rate constants, but no comprehensive approach has been developed which gives reliable estimation of rate constants.

Therefore, if the compound contains groups which might possibly react with O₃ (e.g. C=C, C=N, or N-N bonds), and its O₃ rate constant has not been measured or its upper limit determined, then a kinetic reactivity of unity must be assumed when making upper limit reactivity estimates.

NO₃ Radical Rate Constant:

Some VOCs, usually (but not always) those with C=C double bonds, can react with NO₃ radicals at sufficiently high rates to affect their ozone impact. Atkinson (1991, 1994) also gives methods for estimating these rate constants. As with the OH radical rate constant, if the rate constant has to

be estimated, then the estimate should be increased by a factor of two for upper limit reactivity estimates.

Photolysis Rates:

Some VOCs can react in the atmosphere by direct photolysis, and if photodecomposition is sufficiently rapid and involves radical formation, then it can result in high ozone impacts for the VOC. Upper limit atmospheric photolysis rates can be estimated given the compound's UV-visible absorption spectrum for wavelengths ≥ 290 nm, and the actinic fluxes for direct overhead sunlight for clear-sky conditions, assuming unit quantum yields. The actinic fluxes given by Peterson (1976) should be sufficient for this purpose.

If the compound has non-negligible absorption cross sections in the $\lambda \geq 290$ nm region, then unit quantum yields should be assumed for making upper limit photolysis rate estimates, unless there is information justifying the use of lower quantum yields.

Estimation of MIR, Kinetic Reactivities from Rate Constants

For the Averaged Conditions MIR scenario, a value of

$$\text{EffIntOH}^{\text{MIR}} = 1.6 \times 10^{11} \text{ molec cm}^3 \text{ s} \dots\dots\dots (29)$$

is appropriate for use in upper limit kinetic reactivity estimates. This gives good fits to kinetic reactivities for VOCs with $k_{\text{OH}} < 5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, while slightly overestimating (by no more than ~5%) kinetic reactivities for faster reacting compounds.

For VOCs reacting significantly with O_3 or NO_3 radicals or undergoing photolysis, kinetic reactivities are given by,

$$\text{Kinetic Reactivity} \approx (1 - e^{-\text{Integrated Reaction Rate}}) \dots\dots\dots (30)$$

Where,

$$\frac{\text{Integrated Reaction}}{\text{Rate}} \approx k_{\text{OH}}^{\text{VOC}} \cdot \text{IntOH} + k_{\text{O}_3}^{\text{VOC}} \cdot \text{IntO}_3 + k_{\text{NO}_3}^{\text{VOC}} \cdot \text{IntNO}_3 + \int k_{\text{Phot}}^{\text{VOC}} dt \quad \dots\dots\dots 31)$$

Rate and IntOH, IntO₃, and IntNO₃ are the integrated levels of OH radicals, O₃, and NO₃ radicals, respectively, and $\int k_{\text{Phot}}^{\text{VOC}} dt$ is the integrated photolysis rate. For the Averaged Conditions MIR scenario, the integrated OH, O₃, and NO₃ are:

$$\text{IntOH}_{\text{MIR}} = 1.9 \times 10^{11} \text{ molec cm}^{-3} \text{ s}, \quad \dots\dots\dots (32)$$

$$\text{IntO}_3_{\text{MIR}} = 8.5 \times 10^{16} \text{ molec cm}^{-3} \text{ s} \quad \text{and} \quad \dots\dots\dots (33)$$

$$\text{IntNO}_3_{\text{MIR}} = 7.3 \times 10^{11} \text{ molec cm}^{-3} \text{ s} \quad \dots\dots\dots (34)$$

An estimate of the upper limit $\int k_{\text{Phot}}^{\text{VOC}} dt$ can be obtained using the measured cross-sections, the measured or upper limit quantum yields, and the clear-sky, direct overhead sun actinic flux data (such as those given by Peterson, 1976) to calculate the maximum photolysis rate, $k_{\text{Phot}_{\text{max}}}^{\text{VOC}}$. If there is no information available concerning the quantum yield for the photodecomposition of the compound (as usually is the case), then unit quantum yields at all wavelengths should be assumed. For the Averaged Conditions MIR scenario, the integrated photolysis rate can then be approximated from $k_{\text{Phot}_{\text{max}}}^{\text{VOC}}$ using:

$$\int k_{\text{Phot}}^{\text{VOC}} dt \approx 3.6 \times 10^4 \text{ s} \cdot 0.7 \cdot k_{\text{Phot}_{\text{max}}}^{\text{VOC}} \approx 2.5 \times 10^4 \text{ sec} \cdot k_{\text{Phot}_{\text{max}}}^{\text{VOC}} \quad \dots\dots\dots (35)$$

Where, 3.6×10^4 seconds is the length of time in the scenario and the 0.7 factor is the ratio of the average to the maximum photolysis rate, and was derived for the photolysis of NO₂ in the Averaged Conditions MIR scenario. Most photolysis reactions are more sensitive to shorter wavelength UV than is NO₂ photolysis, and would have a lower average-to

maximum ratio because their photolysis rates would vary more with solar zenith angle. Therefore, the 0.7 factor is considered appropriate for upper limit estimates. To be consistent with the units shown above, the units of should be $k_{\text{Phot}_{\text{max}}^{\text{VOC}}}$ -1.

Equations (21) and (22) can be combined to yield

$$\text{Kinetic Reactivity} \approx (1 - e^{-\text{Effective } k_{\text{OH}} \cdot \text{EffIntOH}}) \dots\dots\dots (36)$$

Where,

$$\text{Effective } k_{\text{OH}}^{\text{VOC}} = k_{\text{OH}}^{\text{VOC}} + \frac{\text{IntO}_3}{\text{IntOH}} k_{\text{O}_3}^{\text{VOC}} + \frac{\text{IntNO}_3}{\text{IntOH}} k_{\text{NO}_3}^{\text{VOC}} + \frac{3.0 \times 10^4}{\text{IntOH}} k_{\text{Phot}_{\text{max}}^{\text{VOC}}} \dots\dots\dots (37)$$

Using the IntOH, IntO₃, IntNO₃, and $k_{\text{Phot}_{\text{max}}^{\text{VOC}}}$ is s⁻¹ for the Averaged Conditions MIR scenario, we obtain,

$$\text{Effective } k_{\text{OH}}^{\text{VOC}} \approx k_{\text{OH}}^{\text{VOC}} + 5 \times 10^5 k_{\text{O}_3}^{\text{VOC}} + 4 k_{\text{NO}_3}^{\text{VOC}} + 1.3 \times 10^{-7} k_{\text{Phot}_{\text{max}}^{\text{VOC}}} \dots\dots\dots (38)$$

Where, the units of the bimolecular rate constants are cm³ molec⁻¹ s⁻¹, and the units of $k_{\text{Phot}_{\text{max}}^{\text{VOC}}}$ is s⁻¹.

The highest molar MIR mechanistic reactivities is in the range of approximately 30-35 which is observed for 1, 3, 5- and 1, 2, 3-trimethyl benzene, m-xylene, and biacetyl. The highest per carbon MIR mechanistic reactivities are for methyl nitrite, biacetyl, and methyl glyoxal, which are in the range of ~7-11. MIR mechanistic reactivities significantly greater than ~4 are observed for methane and a variety of olefins and aromatics.

The upper limit per molecule MIR mechanistic reactivities can be estimated by

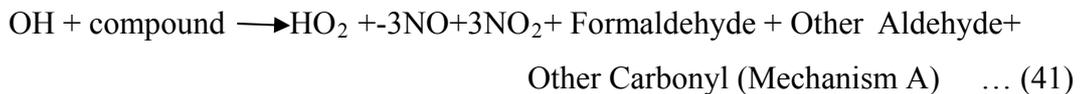
$$\text{Mechanistic Reactivity} \leq \text{MIN} (4 \cdot n_c, 35) \dots\dots\dots (39)$$

for compounds which are known to be non-photoreactive, and by

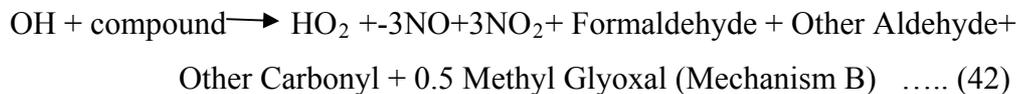
$$\text{Mechanistic Reactivity} \leq \text{MIN} (11 \cdot n_C, 35) \dots\dots\dots (40)$$

for photo-reactive compounds or compounds for which photo decomposition cannot be ruled out. The units are moles of ozone per mole carbon VOC which reacts, and n_C is the number of carbons in the molecule.

For some compounds, specifically saturated hydrocarbons or non-photoreactive compounds containing only alcohol, ether, or ester groups, our knowledge of atmospheric reaction mechanisms, and how various types of reactions affects reactivity, can permit somewhat lower upper limit estimates to be made. Compounds such as these will react significantly only with OH radicals, would probably convert no more than 3-4 molecules of NO to NO₂, and the most reactive products they are likely to form are higher aldehydes or, in the case of esters, possibly some α -dicarbonyls such as methyl glyoxal. Probably the most reactive reasonable mechanism for such compounds would be:



if the compound did not have a carbonyl group (i.e., not an ester), or



For Mechanisms A and B, equation 32 and 33 the Averaged Conditions MIR mechanistic reactivities can be fitted into the following empirical equations:

$$\text{MIR Mechanistic Reactivity A} = 19.5 - 8.9 \exp(-3.9 \times 10^{10} \cdot k_{\text{OH}}) \dots (43)$$

$$\text{MIR Mechanistic Reactivity } B = 28.5 - 14.5 \exp(-2.7 \times 10^{10} \cdot k_{\text{OH}}) \dots$$

Compounds	CAS.No	M.W	MIR (new)	MIR (old)	Change
methane	74-82-8	16.04	0.014	0.01	38%
ethane	74-84-0	30.07	0.26	0.31	-15%
propane	74-98-6	44.1	0.46	0.56	-18%
cyclopropane	75-19-4	42.08	0.082	0.1	-18%
n-butane	106-97-8	58.12	1.08	1.33	-19%
isobutane	75-28-5	58.12	1.17	1.35	-13%
cyclobutane	287-23-0	56.11	1.12	1.05	7%
n-pentane	109-66-0	72.15	1.23	1.54	-20%
branched C5 alkane(s)		72.15	1.36	1.68	-19%

(44)

Table 2.1 MIR values of some Alkanes

Ref: W.P.L (2009) California Air Resources Board Contract 07-339 “updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications”

Where, the units of the mechanistic reactivities are mole O₃ per mole VOC, and the kOH is the OH radical rate constants in units of cm³ molec⁻¹ s⁻¹.

Based on these considerations, it is said that for alkanes or saturated compounds containing no groups other than alcohols and ethers, and no atoms other than H, C, or O, then the upper limit mechanistic reactivity can be given by either Equation (39) or (43), whichever gives the lower value. MIR values of some Alkanes are given in table 2.1.

Likewise, if the compound contains a carbonyl group but no other groups besides alcohol or ether and no atoms other than N, C, or O, then the upper limit mechanistic reactivity can be given by either Equation (39) or (44), whichever is lower. For any other compound, only Equations (39) or (40) can be used, depending on whether the compound is or may be photo reactive.

2.3.11 Global Warming

The vast majority of VOCs have the potential to contribute to global warming by absorbing infrared radiation. Typically the more complex a VOC is, the greater it's capacity to absorb infrared radiation. Although the

lifetime of most VOCs in the atmosphere is relatively short there are exceptions, notably saturated short-chain hydrocarbons and halogenated compounds. Global Warming Potential (GWP) is defined as the extra amount of heat trapped in the atmosphere for a 1kg instantaneous release of a substance, expressed relative to the GWP of carbon dioxide, making CO₂ the benchmark against which the GWP of other substances is measured. The effect of a release is expressed over time, GWPs generally being expressed over a 20, 100 and 500 year period.

2.3.12 Impact of on ecosystems

VOCs have various ecological impacts. As the VOC group is a group of chemicals of high variety, the impacts also differ enormously within the group.

Bioaccumulation/Biomagnifications

Many VOCs are considered as “persistent organic pollutant”. Those are e.g. organic pesticides, which have a tendency to dissolve in water, vaporize and being very stable towards degradation. Certain VOCs like PCBs and some other organo chlorines are highly soluble in fat and tend to accumulate in animal lipid tissues (bioaccumulation). Those substances are then passed through food chains and can reach very high concentrations in predators at the top end (biomagnifications).

Loss of Biodiversity

Some toxic organo chlorines from the VOC group can severely lead to loss of biodiversity, because some damaged species of wildlife are very sensitive to these substances. The double crested Cormorant has been used as an indicator of organo chlorine levels in southern Canada’s biota. The measurements of VOCs are not only useful in order to estimate the dangerous effects of the substances included on wildlife, but also to trace chemicals that are present in extremely low concentrations in nature and are therefore difficult to measure directly. The concentrations of some pollutants in the eggs of fish eating birds may for instances are up 25 million times the concentrations in the waters, as a consequence of bioaccumulation and biomagnifications.

One of the known harmful impacts of VOCs on wildlife lies in the thinning of eggshells, causing deaths of young before hatching, thus leading to extinction on a regional or global basis. The most known substance responsible for this is the insecticide DDT or its secondary form, DDE. Some species of falcons have been saved from extinction of this kind by special programs, in the USA, Sweden etc.

Each year a great proportion (20%) of US honeybee colonies are wiped out by pesticides. Pesticides are also killing enormous numbers of insects, highly important in biological control of pests. Pesticides runoff are killing fishes worldwide, herbicides are killing lot of plants, regardless of whether they are referred to as weeds or not. These substances are persistence and hence their impact is not expected to fade immediately even after the pesticides or herbicides would be banned or substituted by other less harmful chemicals.

Hormone Miming

Some VOCs do also have impacts on wildlife by hormone miming. This is also a known problem in humans. The known consequences are lower fertility in males according to reduced number of sperm cells together with lower quality. Malformation of genitals has also been observed.

Plant Damage

Some VOCs cause damage to plants, either directly or more often indirectly through photochemical smog and some end products of photochemical reactions. Ozone is an important substance in this aspect. "A recent modeling study at University of Michigan suggest that by year 2025, between 30% and 75% of the world's cereal crops will be grown in areas that will be most severely affected. These include, the eastern United States, Japan, and an area spanning from Europe to eastern China. These regions also account for about 60% of world food crop production".

PAN (peroxyacyl nitrates) is another result from photochemical reactions. PAN is highly toxic to plants, "attacking younger leaves and causing "bronzing" and "glazing" of their surfaces". Exposure to very low concentrations of PAN for a short time will damage vegetation. "The sulphhydryl group of proteins in organisms is susceptible to damage by

PAN, which reacts with such groups as both an oxidizing agent and an acetylating agent”.

Climate Change

Some VOCs are very effective greenhouse gasses, they do have significant impacts on the biosphere through climate change. Methane (CH₄) is one of them. It traps approximately 25 times more heat than carbon dioxide even though it has shorter atmospheric residence time and is emitted into the atmosphere in lesser quantities. Its sources are mainly natural but there is a definite connection between the human activities and increase in methane concentration in the atmosphere. Comparing the historic data collected from ice cores to the modern ones taken from the current monthly measurements we can see the increased in methane concentration from about 700 ppbv in pre-industrial times to 1721 ppbv in 1994. However, there has been a decrease in methane growth rate for the past 20 years. In the middle of 1992, methane concentration even stopped growing for a short while but since 1993 it is back to the rate of about 8 ppbv /year.

	CH ₄
Pre-industrial concentration	700 ppbv
Concentration in 1994	1720 ppbv
Rate of Concentration Change	10 ppbv /yr 0.6% /yr
Atmospheric lifetime	12 yrs

Another group of VOCs involved in Green house effect are CFCs. These molecules, despite of their low concentrations in the atmosphere, are about 1,500-7,000 times as effective in heat trapping than that molecules of CO₂.

Resource Depletion

VOCs can directly or indirectly lead to resource depletion. Water pollution is an obvious example on direct impacts. VOCs are also involved in many reactions and processes which lead to climate change and ozone depletion. Depletion of stratospheric ozone is caused mostly by VOCs. Ozone is formed in the lower atmosphere in the presence of sunlight through a complex series of reactions between Volatile Organic Compounds (VOCs),

Oxides of nitrogen (NO_x), and ambient oxygen. The concentrations of ozone and its precursors are dynamic and nonlinear. Thus, ozone concentrations are not necessarily additive, but depend on the concentrations of all compounds involved in atmospheric chemistry. VOCs are emitted by anthropogenic sources such as evaporation of gasoline and solvents, and by biogenic sources such as vegetation. Individual VOCs differ widely in their capacity to generate ozone. NO_x is formed primarily by combustion processes and can contribute to either the creation or destruction of ozone, depending on the amount of VOCs present and the conditions.

2.3.13 Damage to materials

VOCs can cause damage to materials in two ways, either directly as a result of oxidising or corrosive properties, or by contributing to the production of ozone, which can attack natural and synthetic rubber, textiles and resin coatings. Such properties can accelerate building decay, particularly in the vicinity of the point discharge sources. The damaging effects of individual VOCs are recognised.

2.3.14 Odour problem due to VOCs

Many VOCs have a distinct odour, which may cause localised nuisance. If reported it is generally treated as a statutory nuisance under Health and Safety Regulations. The odour threshold value of a volatile compound is defined as the minimum concentration at which the compound can be detected by the sense of smell. Two types of odour thresholds, i.e. the absolute and the difference threshold are defined. The detection and the recognition thresholds are absolute thresholds. Absolute thresholds the minimum concentration which can be detected without any requirements to identify or recognize the stimulus, while the difference threshold is the minimum concentration at which a stimulus can be identified or recognized. The IPPC document H4 Part 2 (Horizontal odour guidance, assessment and control) discusses several methods to measure either the strength or the degree of annoyance caused by an odour. These include odour mapping, odour impact assessment, chemical analysis and olfactometry. Certain

VOCs are highly odourous and are likely to be considered an annoyance under most circumstances, even if they are not necessarily harmful. Odour thresholds of some VOCs are given in **Annexure I**.

2.4 Sources of VOCs in Urban Areas

In India evaporative emissions and vehicular emissions have been reported to be major sources of VOC emissions (Srivastava et al., 1998). Urban areas have become major sources of chemical emissions that can potentially affect climate and air quality on a local, regional and global scale. The major sources of VOCs are automobile emissions, gasoline marketing and storage tanks, petroleum and chemical industries, dry cleaning, fireplaces, natural gas combustion and aircraft. Individual VOCs are also produced from the evaporation of solvents and organic chemicals as well as from leaking valves, flanges, pumps and compressors at industrial facilities. The major source of VOCs in most urban areas is vehicle exhaust emissions.

In the indoor environment, volatile organic compounds are released by sources such as furniture, paint, adhesives, solvents, upholstery, draperies, carpeting, spray cans, clothing, construction materials, cleaning compounds, deodorizers, copy machine toners, felt-tip markers and pens and correction fluids. Concentrations of many VOCs emitted indoors are generally higher than outdoor concentrations because of the presence of indoor sources such as building materials, consumer and commercial product use and human activities such as cooking.

Globally, biogenic emissions of VOCs exceed those of anthropogenic origin (*Müller, 1992*). However, in urban areas the contribution of biogenic VOCs is much lower. Anthropogenic VOC sources include combustion processes, the use of fossil fuels, solvents, industrial production processes and biological processes (*Friedrich and Obermeier, 1999*). Whereas VOC emissions from combustion sources (e.g. traffic and wood combustion) mainly contain pure hydrocarbons, organic solvents and their vapours also consist of oxygenated HCs such as alcohols, carbonyls and esters. Traffic

and traffic-related sources are known to be a major source of non-methane hydrocarbons (NMHCs i.e., alkanes, alkenes, alkynes and aromatic HCs) in urban areas (Friedrich and Obermeier, 1999; Watson et al., 2001), but in residential or industrial areas other sources may also be important. In Nordic countries the use of wood as a fuel has increased lately (Haaparanta et al., 2003; Hedberg et al., 2002) and wood combustion is known to emit several different VOCs (i.e., NMHCs, halogenated hydrocarbons and oxygenated hydrocarbons) and other air pollutants (McDonald et al., 2000). For the lightest alkanes, natural gas emissions may also be important (Fujita, 2001). Although ethene is a major constituent of the VOC emissions from traffic and from wood combustion (Schauer et al., 2002 and McDonald et al., 2000), it is also a plant hormone and is emitted by plants, soils and oceans (Fall, 1999). In addition to this, terpenes (isoprene and monoterpenes) have mainly biogenic sources.

Some halogenated HCs have both anthropogenic and biogenic sources. The main global anthropogenic sources of chloroform are pulp and paper manufacturing, other industrial sources and water treatment (Aucott et al., 1999), while the main natural sources are the oceans, soil, termites and microalgae (Laternus et al., 2002). For chloromethane, industrial sources and biomass burning are the main anthropogenic sources, but large quantities are also emitted by the oceans and wetlands (Butler, 2000). Trichloroethene and tetrachloroethene are used as degreasing agents and tetrachloroethene is also used in dry-cleaning (Rivett et al. 2003). 1, 1, 1-trichloroethane is a solvent (Rivett et al. 2003) and chlorofluorocarbons (CFCs) have been used for example as aerosol propellants and refrigerants, but their use has been phased out as a result of the Montreal Protocol.

Tetra chloromethane has been a chemical intermediate for the production of CFCs. Carbonyls are also emitted from both anthropogenic and biogenic sources; in addition to this, they are formed in the atmosphere in the reactions of other organic compounds. Known primary anthropogenic sources are traffic and biomass burning (Schauer et al., 2002 and McDonald et al., 2000). However, the sources of carbonyls are not well characterized. In the global estimates by Singh et al. (2000), emissions from automobile exhausts and biomass burning comprised only 5% of the formaldehyde

produced from methane oxidation. The main sources of propanal and acetaldehydes were found to be oceanic, and for them too the oxidation of hydrocarbons was found to be more significant than the primary anthropogenic sources. Vegetation is an important primary source of acetone and probably also of certain other carbonyls (Singh et al., 2000; Janson and De Serves, 2001; Bowman, 2003).

2.5 Air Quality Standards for VOC

The ambient air quality standards include Benzene and Benzene A Pyrene (BAP). These are given in Table 2.2.

Table 2.2 National Ambient Air Quality Standards

Sl. No	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
1	Sulphur Dioxide (SO ₂), µg/m ³	Annual * 24 hours**	50 80	20 80	– Improved West and Gaeke – Ultraviolet fluorescence
2	Nitrogen Dioxide (NO ₂), µg/m ³	Annual * 24 hours**	40 80	30 80	– Modified Jacob & Hochheiser (Na-Arsenite)
3	Particulate Matter (size less than 10µm) or PM ₁₀ µg/m ³	Annual * 24 hours**	60 100	60 100	– Gravimetric – TOEM – Beta attenuation
4	Particulate Matter (size less than 2.5µm) or PM _{2.5}	Annual * 24 hours**	40 60	40 60	– Gravimetric – TOEM – Beta attenuation

Sl. No	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
	$\mu\text{g}/\text{m}^3$				
5	Ozone (O_2) $\mu\text{g}/\text{m}^3$	8 hours** 1hour**	100 180	100 180	– UV photometric – Chemiluminescence – Chemical Method
6	Lead (Pb) $\mu\text{g}/\text{m}^3$	Annual * 24 hours**	0.50 1.0	0.50 1.0	– AAS/ICP method after sampling on EPM 2000 or equivalent filter paper – ED-XRF using Teflon filter
7	Carbon Monoxide (Co) $\mu\text{g}/\text{m}^3$	8 hours** 1hour**	02 04	02 04	– Non Dispersive Infra Red (NDIR) spectroscopy
8	Ammonia (NH_3) $\mu\text{g}/\text{m}^3$	Annual * 24 hours**	100 400	100 400	– Chemiluminescence – Indophenol blue method
9	Benzene (C_6H_4) $\mu\text{g}/\text{m}^3$	Annual*	05	05	– Gas chromatography based continuous analyzer
10	Benzo (O) Pyrene (BaP)-particulate phase only, $\mu\text{g}/\text{m}^3$	Annual*	01	01	– Solvent extraction followed by HPLC/GC analysis
11	Arsenic (As), $\mu\text{g}/\text{m}^3$	Annual*	06	06	– AAS/ICP method after sampling on EPM 2000 or equivalent filter

Sl. No	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
12	Nickel (Ni), $\mu\text{g}/\text{m}^3$	Annual*	20	20	paper – AAS/ICP method after sampling on EPM 2000 or equivalent filter paper

* Annual arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.

** 24 hourly or 08 hourly or 01 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

Chapter 3

Study Area

3.1 Area Description

Kolkata is centered on latitude 22°34' North and longitude 88° 24' East. It is about 30 kms from the Bay of Bengal and the river tides at Kolkata range over 4m. Its population is about 15 million making it India's third largest metropolitan and world's 8th largest agglomeration. It is therefore very crucial to measure the ambient concentration of VOCs in Kolkata and get an idea about their impact on such a large susceptible population.

3.2 Selection of Sampling Locations

The city of Kolkata was divided into three zones namely North, South and Central and one monitoring location of each category area viz. industrial, commercial cum residential, refueling stations and traffic intersections were selected in each of these zones considering the potential for representing the maximum expected ozone concentration and maximum expected ozone precursor emission impact considering the prevailing wind directions. Wind data of ten years were compiled and analyzed to identify the upwind and the downwind locations. Wind roses for each month were plotted as an average of ten years. It was found that during the months of January, February, November and December the wind direction is predominantly between NW-N Sector and from SSE – S sector from March to July. During August & September the wind showed a little variation and is from S-E sector. During the month of October variation in the wind direction was observed to be large from N to S through E. The upwind location during January, February, November and December was therefore identified as Belgharia and Garia as the downwind location. During the months from March to September Garia becomes the upwind location and Belgharia becomes the downwind location. Due to large variation in month of October besides these two stations one location in Salt Lake in the East was monitored as upwind location. The downwind location was Lalbazar.

The locations selected are:

Zone \ Category	North	Central	South
Residential cum Commercial	Dunlop	Entally	Alipore
Industrial	Cossipore	Baithak Khana bazaar, Sealdah	Behala industrial Estate
Traffic Intersection	Shyambazar	Park Street Crossing	Rashbihari Crossing
Refueling Station	Beleghata Petrol Pump	Theathre Road Petrol Pump	Bose Pukur Kasba Petrol Pump

Selected Upwind – Downwind Locations

Months	Upwind Location	Downwind Location
January, February, November and December	Belgharia	Garia
March - September	Garia	Belgharia
October	Garia & SaltLake	Belgharia & Lalbazar

3.3 Description of Sampling Locations

Dunlop: Dunlop is located in north Kolkata, a residential area. Samplers were placed at the balcony of a house located at Dilip Ganguly Sarani, kolkata-700108. The sampler was placed 12 feet above ground level. The surrounding area is purely residential and is quite away from the main road. There is fair vegetation surrounding the location.



Entally: Entally is situated at Central Kolkata, a residential area. Air Samplers were placed at the balcony of Cultural Centre located at Anand Palit Road, Kolkata-700014. The sampler was placed at the height of 12 feet above ground level. The surrounding area is a mixture of residential and commercial place and is away from the main road. The traffic pressure on street in front of the location is moderate. The vegetation in surrounding area is much less.



Alipore: Alipore is located at South Kolkata, a residential area. The location is a governmental housing complex, near the National Library. Air samplers were placed at the height of 8 feet from the ground level. The surrounding area is purely residential and quite away from the main road. There is very good vegetation around the location.



industrial but some shops and

Cossipore: Cossipore, an industrial area is located at North Kolkata. The sampler was placed at the terrace of Cossipore Police Station, which is at a height of 12 feet from the ground. The surrounding area is mainly



residential places are also present. Vegetation is poor.

The location is close to the main road and the traffic congestion is very high.

Sealdah: Sealdah is located at Central Kolkata and is an industrial area. Sampler was placed at the windowsill of a local Club. The sampler was placed at a height of 4 feet from the ground. The surrounding area is mixture of small-scale industries and commercial places, mainly paper industry. The area is very congested with narrow busy lane. Vegetation is very poor and the location is about 200 m away from the main road. There is a very busy railway station in the vicinity of the sampling location.



Behala: The location is at Behala industrial estate, in south Kolkata. This industrial estate is a property of WB Small Industrial Corporation Ltd. The samplers were placed in front of the tool room of Mitra Estate, at a height of 6 feet. The adjacent area is surrounded by small-scale industries, like PVC pipe and polythenes, paint and engineering works. Vegetation in surrounding area is fair and the location is quite away from the main road.



Shyambazar: The location is at Shyambazar traffic crossing, north Kolkata. Sampler was placed at the traffic police kiosk (wooden structure) at a height of 6 feet from the ground. The surrounding area is mainly commercial area containing shops (like plastics, electronic goods, medicines, stationery etc.), restaurants, offices, schools, cinema halls, shopping malls etc. Traffic congestion is very high and it is one of the busiest crossings of Kolkata. Vegetation is very poor at the sampling location.



Park Street: The location is at Park Street traffic crossing, central Kolkata. Sampler was placed at the traffic police kiosk at a height of about 5 feet. The surrounding is commercial area consist of offices, big shopping plaza, bar and restaurants, cinema halls. Traffic congestion is very high and it is one of the main crossings of Kolkata. Vegetation is very high. The flyover is near by the sampling location. Indian museum, Asiatic society, Geological Survey of India, Shahid Minar is in the vicinity of the sampling location.



Rashbehari Avenue: The location is at Rashbehari Avenue traffic crossing, south Kolkata. The sampler was placed at the traffic police kiosk at a height about 5 feet. The surrounding area is mainly commercial with shops, offices, malls, colleges, schools, restaurants etc. There is Kalighat Metro



Station near by the sampling location. Vegetation is very poor and traffic congestion is high.

Belegkata: The samplers were placed at the Belegkata petrol pump, north Kolkata at a height of 5 feet from the ground level. The surrounding area is mainly residential with some commercial activities. Traffic congestion is less. Vegetation at the sampling location is thick.



Theatre Road: The sampling point is located at central Kolkata. Samplers were placed at refueling station at the height of 4 feet from the ground level. The surrounding is commercial area containing offices, shopping mall, restaurants, small shops etc. Vegetation is moderate and the traffic congestion is high at the site. Victoria Memorial, Birla Planetorium, Rabindra Sadan are in the vicinity of the sampling location.



Kasba: The sampling location is a refueling station (petrol pump), situated at south Kolkata. Samplers were placed at the height of 5 feet from the ground. The surrounding area is mainly residential with some shops, schools, and restaurants etc. traffic congestion is moderate. The vegetation is moderate at the location.



Table 3.1: GPS Positions of the Sampling Locations

Category	Location	Latitude	Longitude
Residential	Alipore	22°31'46.09"N	88°19'59.48"E
	Entally	22°33'24.44"N	88°22'15.45"E
	Dunlop	22°39'4.86"N	88°22'34.32"E
Industrial	Behala	22°27'53.16"N	88°18'25.50"E
	Baithakhana Bazaar	22°34'19.51"N	88°22'10.86"E
	Cossipore	22°37'8.64"N	88°22'46.55"E
Traffic Crossing	Rash Behari	22°31'0.45"N	88°20'44.25"E
	Park Circus	22°33'18.56"N	88°21'0.38"E
	Shyambazaar	22°36'6.72"N	88°22'24.69"E
Petrol Pump	Bosepukur	22°31'10.49"N	88°23'5.06"E
	Theatre Road	22°32'43.21"N	88°20'53.20"E
	Belegkata	22°33'56.66"N	88°23'36.89"E

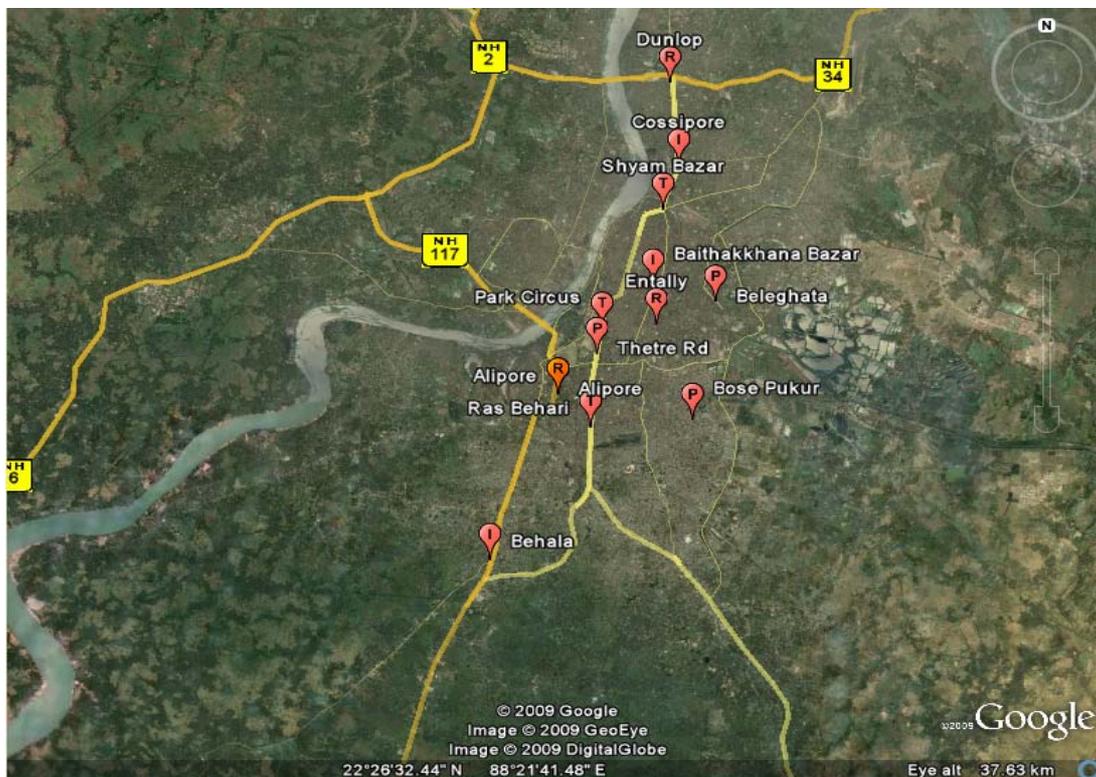
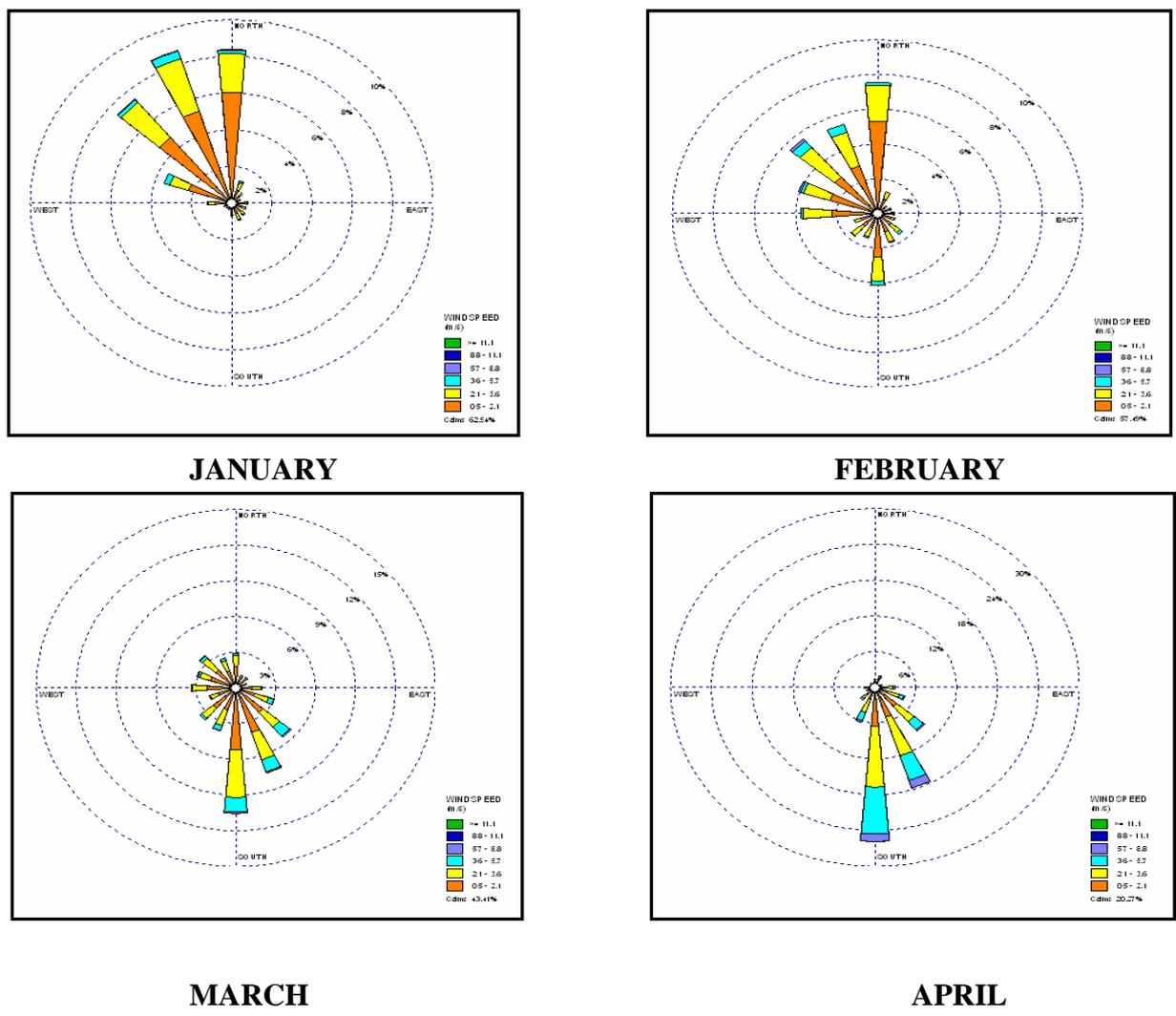
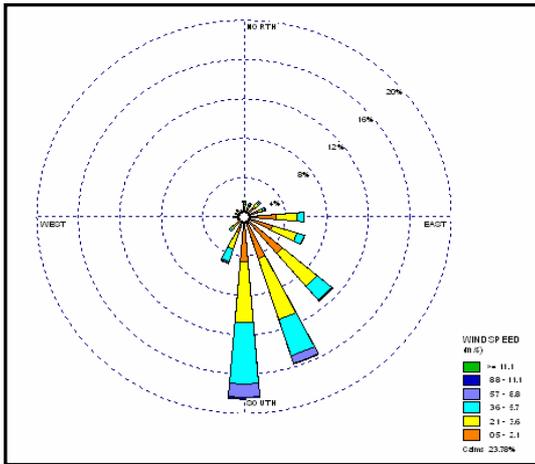


Figure 3.1: Study Area Showing Sampling Locations

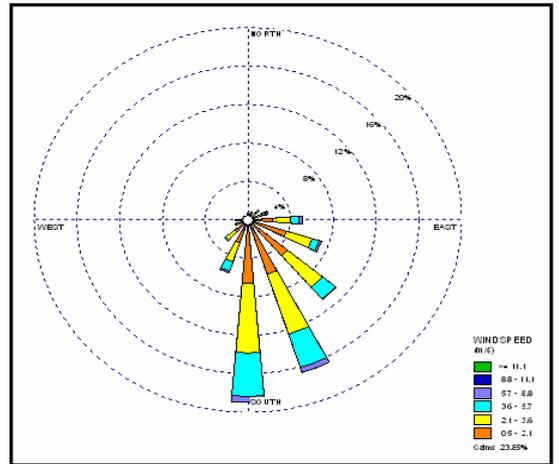
3.4 Meteorology

Kolkata is located at a point where river Hooghly merges into the sea. In fact the whole region is part of the great Gangetic delta. The temperature seldom crosses the 43 degree Celsius barrier and in winter rarely goes below 8°C. The city of Kolkata experiences a very humid and warm summer during the months of April to October with temperature reaching up to 42°C. During the winter months the temperature drops to about 9.6°C. The weather in Kolkata is influenced by the sea and has a very tropical type of climate with the summers being hot and humid. The maximum temperature rises during the summer months of May-June up to 24°C- 42°C and the minimum temperature falls during winter months of December-January up to 8°C - 26°C on an average. Climate is humid during the summer and exceeding by pleasant in winter. The average rainfall of Kolkata is 1605 mm. Monthly temperatures during 2008-09 (**Table 3.2**). Wind roses for the months of January to December as an average of 1998 to 2007 are given in **Figure 3.2**.

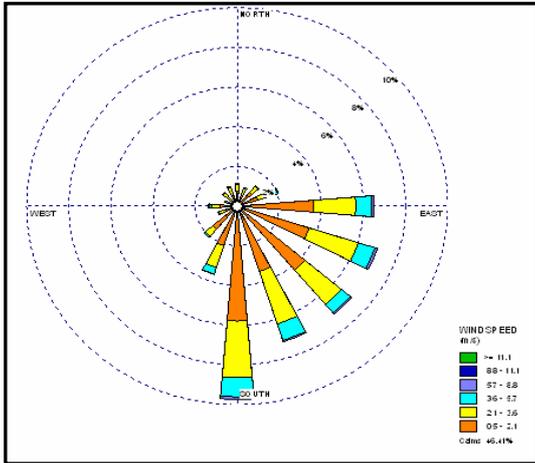




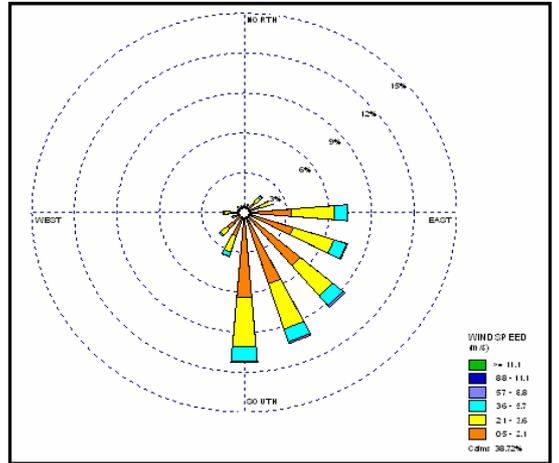
MAY



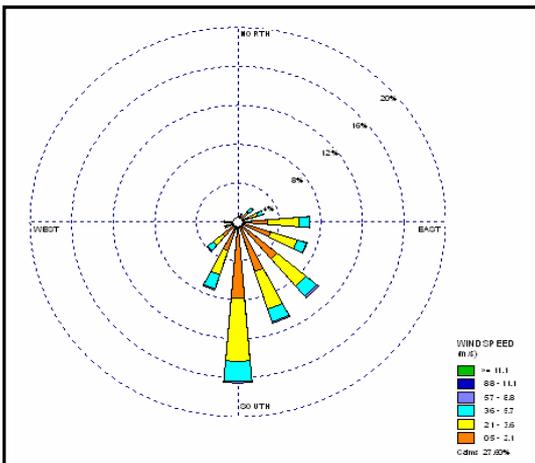
JUNE



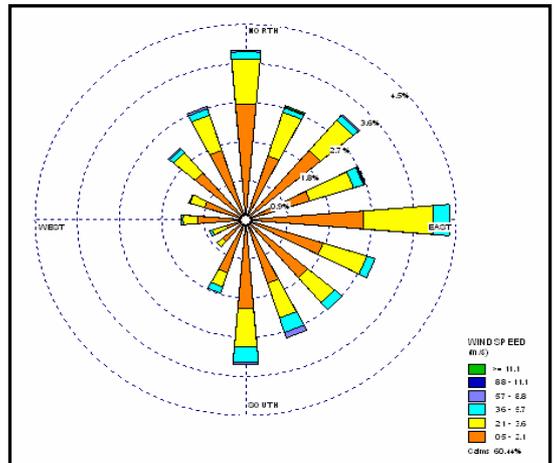
JULY



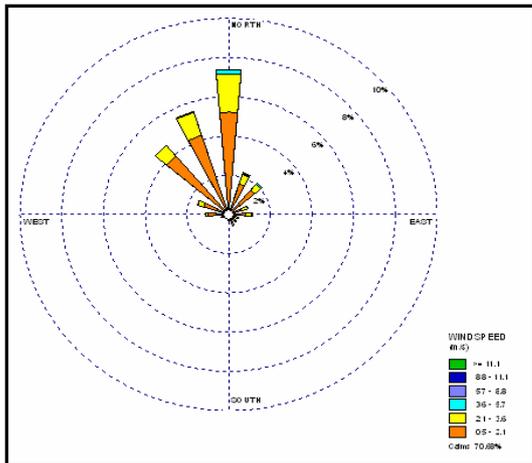
AUGUST



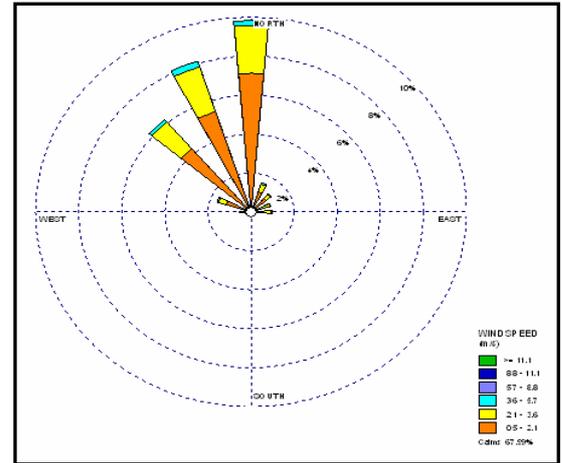
SEPTEMBER



OCTOBER



NOVEMBER



DECEMBER

Figure 3.2: Wind Rose for Each Month as an Average of 1998-2007

The observation of wind roses shows that during January, February, November and December the wind direction is predominantly between NW-N Sector. From March to July the winds are observed to be from SSE – S sector. During August & September the wind show a little variation and are from S-E sector. During the month of October variation in the wind direction is observed to be large it varies from N to S through E.

Table 3.2: Monthly Temperatures for Kolkata for Year 2008-09

Month	Minimum	Maximum	Average
November 08	15	31	24
December 08	12	30	20.4
January 09	12	30	20.7
February 09	12	35	23.3
March 09	16	36	27.1
April 09	20	40	31.4
May 09	20	45	29.5
June 09	23	37	31.2
July 09	25	37	28.8
August 09	25	35	28.8
September 09	25	35	29.1
October 09	19	34	27

Table 3.3: Most Predominant Wind Speeds and Directions During the Study Period are Given Below:

Month	Most predominant wind direction	Speed
November 08	NNW, NW	3.6-5.7
December 08	N, NNE	3.6-5.7
January 09	N, NNE	0.5-2.1
February 09	N, NNW, NNE	0.5-2.1
March 09	S, SSW, SSE	0.5-3.6
April 09	S, SSW, SSE	3.6-5.7
May 09	S, SSW, SSE	3.6-5.7
June 09	S, SSW, SSE	3.6-5.7
July 09	S, SSW, SSE	3.6-5.7
August 09	S, SSW, SSE	3.6-5.7
September 09	SE	3.6-5.7
October 09	N, NNW, NNE, E, S (Variable)	2.1-3.6

3.5 Frequency of monitoring

All sampling locations were monitored for NO_x, non carbonyl and carbonyl VOCs for a period of 24 hrs twice a month. Sampling duration was split as 12 noon - 06 pm, 06 pm to 06 am and 06am- 12 noon, to account for photochemical interactions. Ozone was monitored as half hourly average for 24 hours twice a month.

Chapter 4

Methods of Non Carbonyl & Carbonyl VOCs Measurement in Ambient Air

4.1 VOC Measurement Methods

USEPA has developed compendium of methods for measurement of VOCs in ambient air. Method TO-14A was developed for sampling and analysis of VOCs in ambient air. This method is based on collection of whole air samples in SUMMA passivated stainless steel canisters or separated by gas chromatography and measured by a mass spectrometer or a by a multi detector techniques. This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and sub atmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs have been successfully tested for storage stability in pressurized canisters. Not much conclusive data is available demonstrating stability of VOCs in sub atmospheric pressure canisters.

Collection of ambient air samples in canisters provides a number of advantages.

- i. Convenient integration of ambient samples over a specific time period says 8 or 24 hours.
- ii. Remote sampling and central analysis.
- iii. Case of storing and shipping samples.
- iv. Unattended sample collection.
- v. Analysis of samples from multiple sites with one analytical system.
- vi. Collection of sufficient sample volume to allow assessment of measurement precisions and /or analysis of samples by several analytical systems.
- vii. Storage stability for many VOCs over period of upto 30 days.

To realize the advantages care needs to be exercised in selection –cleaning and handling sample canisters and sampling apparatus to avoid loss or contamination.

4.1.1 Compendium Method TO-15

Many of the compounds that can be analyzed by TO-14 have been tested for stability in concentration when stored in specially prepared canisters under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed. Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short-term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with co-collected ozone or other gas phase species also account for some short-term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation also exist. No models are currently known to be available to estimate and characterize all these potential losses. Some of the VOCs have short atmospheric lifetimes and may not be present except near sources.

Compendium Method TO-15 applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

TO 15 methods applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were

higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days.

Compendium Method TO-15 extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multi-sorbent /dry purge technique or equivalent for water management thereby addressing a more extensive set of compounds than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitative target compounds. The GC/MS approach provides a more scientifically defensible detection scheme, which is generally more desirable than the use of single, or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., auto GCs and solid adsorbents) that are often used.

4.1.2 Method TO-17

Compendium Method TO-17 describes a sorbent tube/thermal desorption/gas chromatographic-based monitoring method for volatile organic compounds (VOCs) in ambient air at 0.5 to 25 parts per billion (ppbv) concentration levels. EPA has previously published Compendium Method TO-1 describing the use of

the porous polymer Tenax® GC for sampling nonpolar VOCs and Compendium Method TO-2 describing the use of carbon molecular sieve for highly volatile, nonpolar organics. Since these methods were developed, a new generation of thermal desorption systems as well as new types of solid adsorbents have become available commercially. These sorbents are used singly or in multisorbent packings. Tubes with more than one sorbent, packed in order of increasing sorbent strength are used to facilitate quantitative retention and desorption of VOCs over a wide volatility range. The higher molecular weight compounds are retained on the front, least retentive sorbent; the more volatile compounds are retained farther into the packing on a stronger adsorbent. The higher molecular weight compounds never encounter the stronger adsorbents, thereby improving the efficiency of the thermal desorption process.

EPA has developed data on the use of solid sorbents in multisorbent tubes for concentration of VOCs from the ambient air as part of its program for methods development of automated gas chromatographs. The experiments required to validate the use of these sorbent traps include capture and release efficiency studies for given sampling volumes.

The analytical approach using gas chromatography/mass spectroscopy (GC/MS) in this method is identical to that mentioned in Compendium Method TO-15 and is adapted for this method once the sample has been thermally desorbed from the adsorption tube onto the focusing trap of the analytical system.

4.1.3 Description of Method Adopted

The analytical strategy for the method adopted in the present study is similar to TO-17. A high resolution Gas Chromatograph coupled with Mass Spectrometer has been used.

Each peak in the chromatograph is identified using NIST Library. Mass spectra for individual peaks in the total ion chromatograph are examined with respect to fragmentation pattern of ions characteristic m/z for primary and secondary ions are given in **Table 4.1**. Mass abundance for most intense peaks of the VOCs is presented in **Table 4.2**. First three abundance were matched to identify the peak.

Table 4.1: Characteristics Masses (M/Z) Used for Quantifying the VOCs

Compound	CAS No.	Primary Ion	Secondary Ion
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	61	96
Methylene chloride; CH ₂ Cl ₂	75-09-2	49	84,86
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	75-34-3	63	65-27
Chloroform; CHCl ₃	67-66-3	83	85,47
Methyl chloroform (1,1,1 trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	97	99,61
Carbon tetrachloride; CCl ₄	56-23-5	117	119
Benzene; C ₆ H ₆	71-43-2	78	77, 50
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	62	64, 27
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	63	41, 62
1,3-Dichlorpropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	75	39, 77
Toluene; C ₇ H ₈	108-88-3	91	92
Trichloethylene; C ₂ HCl ₃	79-01-6	130	132, 95
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	97	83, 61
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	166	164, 131
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	107	109
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	112	77, 114
Ethylbenzene; C ₈ H ₁₀	100-41-4	91	106
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	91	106
Styrene; C ₈ H ₈	100-42-5	104	78, 103
p-Xylene; C ₈ H ₁₀	106-42-3	91	106
m-Xylene; C ₈ H ₁₀	108-38-3	91	106
Bromoform (tribromomethane); CHBr ₃	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	83	85
o-Xylene; C ₈ H ₁₀	95-47-6	91	106
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	105	120
1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl	96-12-8	57	155, 157
1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂	106-46-7	146	148, 111
Hexachlorobutadiene; C ₄ Cl ₆	87-68-3	225	227, 223
1,2,4-Trichlorobenzene; C ₆ H ₃ Cl ₃	120-82-1	180	182, 184

Table 4.2: Ion / Abundance for Selected VOCs Analyzed

Compound (Synonym)	Ion Abundance (amu % base peak)
Vinylidene chloride (1,1-Dichloroethane)	61 /100 96 /55 63 /31
Dichloromethane (Methylene chloride)	49 /100 84 /65 86 /45
1,1-Dichloroethane (Ethylidene chloride)	63 /100 27 /64 65 /35
Cis-1,2-Dichloroethylene	61 /100 96 /60 98 /44
Chloroform (Trichloromethane)	83 /100 85 /65 47 /35
1,2- Dichloroethane (Ethylene dichloride)	62 /100 27 /70 64 /34
Methylchloroform (1,1,1-Trichloroethane)	97 /100 99 /64 61 /64
Benzene (Cyclohexatriene)	78 /100 77 /25 50 /35
Carbon tetrachloride (Tetrachloromethane)	117 /100 119 /97
1,2-Dichloropropane (Propylene dichloride)	63 /100 41 /90 62 /70
Trichloroethylene (Trichloroethane)	130 /100 132 /92 95 /87
Cis-1,3-Dichloropropene	75 /100 39 /70 77 /30
Trans-1,3-Dichloropropene (cis-1,3 Dichloropropylene)	75 /100 39 /70 77 /30
1,1,2-Trichloroethane (Vinyl trichloride)	97 /100 83 /90 61 /82
Toluene (Methyl benzene)	91 /100 92 /57
1,2-Dibromoethane (Ethylene dibromide)	107 /100 109 /96 27 /115

Table 4.2 (Contd.): Ion / Abundance for Selected VOCs Analyzed

Tetrachloroethylene (Perchloroethylene)	166 /100 164 /74 131 /60
Chlorobenzene (Phenyl chloride)	112 /100 77 /62 114 /32
Ethylbenzene	91 /100 106 /28
m.p-Xylene	91 /100 106 /40
Styrene (Vinyl benzene)	104 /100 78 /60 103 /49
1,1,2,2-Tetrachloroethane (Tetrachloroethane)	83 /100 85 /64
o-Xylene (1,2-Dimethyl benzene)	91 /100 106/65 105/29

Varian GC-MS with injection mode was used. GC-MS operating conditions were:

GC Conditions

Column : 60 meter DB-624, 0.32 mm ID, 1.8 μ film thickness
 Head Pressure : 10 psi
 Flow Rate : 1.5 mL/ min
 Split Ratio : 100 : 1
 Transfer Line Temperature : 220°C
 Trap Temperature : 125°C
 Manifold Temperature : 40°C
 Column Programme

Temp(°C)	Rate (C/min)	Hold (Min)	Total(Min)
35	0	2	2
220	5	2	41

Ion Trap Conditions

Temperature	: 125°C
Emission Current	: 10 μ A
RF Storage Level	: 32 u
Scan Model	: 0.7 sec/ scan
Fil / Multi Delay	: 1 minute
Threshold	: 1 count
Background Mass	: 46 u for 6 min/ 34 u until run end
Mass Range	: 47 u- 260 u for 6 minutes, 35 u – 260 u until run end

Segment Breaks and Tune Factors

Segment	Ranges	Factor
1	10-80	90
2	81-160	130
3	161-169	20
4	170-650	100

The mass spectrum of BFB is acquired in the following manner. Three scans (the peak apex and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is done using a single scan no more than 20 scans prior to the elution of BFB. BFB peak is not subtracted.

m/z	Required Intensity (relative abundance)
50	8-40% of m/z 95
75	30-60% of m/z 95
95	Base peak, 100% relative abundance
96	5 – 9% of m/z 95
173	Less than 2% of m/z 174
174	50 – 120% of m/z 95
175	4 – 9% of m/z 174
176	93 - 101% of m/z 174
177	5 – 9% of m/z 176

4.1.4 Overview of Methodology

In the present method break through volume is defined as a volume of air sampled when the amount of analyte collected in backup up sorbent tube reaches a certain percentage (typically 5%) of the total amount by both sorbent tubes.

Safe sampling volume is defined as two third of the break through volume.

Determination of Break through Volume:

A synthetic mixture of 6 compounds of VOC Mix 15 was sampled for 20, 40 and 80 min at a rate of 100 ml /min. The total sampling volume was thus 2000, 4000, 8000 ml. The peak areas for the compounds detected showed linearity with respect to the sampling period (**Table 4.3**). This indicates a insignificant break through at the sampling volume up to 8000 ml.

Table 4.3: Linearity Test to Determine Break Through

Compared	Peak Area						% difference 81/21 vs 4
	21	41	81	41/21	81/21	81/41	
Methylenechloride	50351	110770	207950	2.1999	4.13	1.88	-3.25
1,2 dichlorobenzene	197279	374828	742162	1.899	3.76	1.98	6.00
Carbon tetrachloride	113235	251379	464263	2.21	4.10	1.85	-2.50
Chloroform	196067	411741	794071	2.10	4.05	1.93	-1.25
Benzene	416428	857842	1649055	2.06	3.96	1.92	1.00
Toluene	610108	1177508	2403825	1.93	3.94	2.04	1.50

Sampling System

A battery operated personal air sampler Staplex model PST – 3000-A was used to sample ambient air at the rate of 20 ml /min. Schematic diagram of the setup is shown in **Figure 4.1**. Uniform sampling rate was maintained using a rotameter.

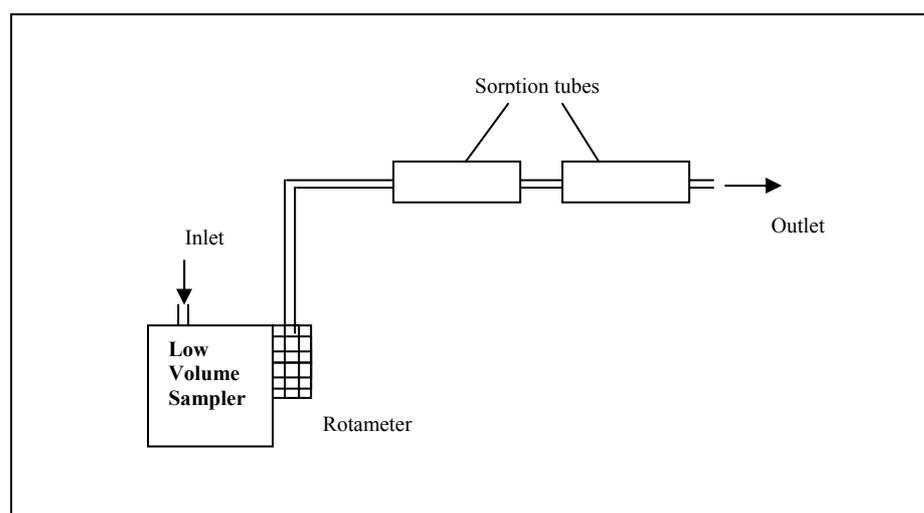


Figure 4.1: Sampling Setup

Thermal Desorption System

Schematic diagram of single stage thermal desorption unit used is shown in **Figure 4.2**. Desorption of sorbent tube is carried out by heating at 210°C for 25 minutes. Desorption can be accelerated by carrier gas flow of 20 ml/min. Desorbed sample was collected in 2 ml adapter with a septa.

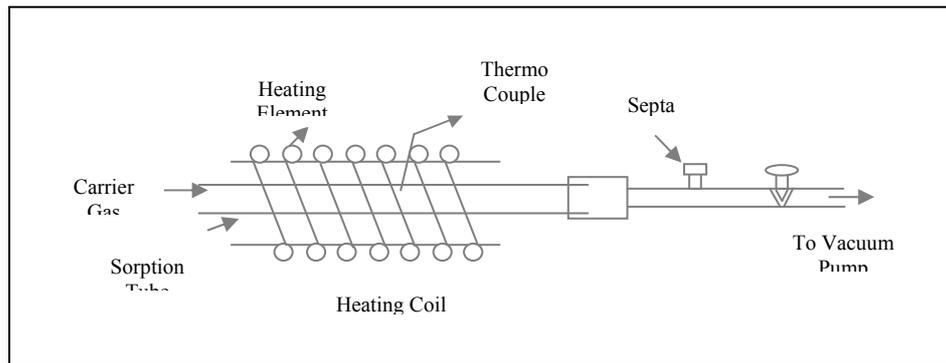


Figure 4.2: Schematic Diagram of Single Stage Thermal Adsorption Tube

Calibration

Calibration was done using liquid standards VOC mix 15 of Dr. Ehrenstorfer from Perkin Elmer.

In accordance with TO-15 Method gaseous concentration of the standard liquid was determined using the following equations:

$$V = nRT / P \quad \dots\dots\dots (1)$$

Where, $n = v d / M.W.$

V = Gaseous volume of infected compound at 25°C and 760 mm Hg pressure in liters

n = no of moles

R = Gas constant 0.08206 L – atm / mole °K

T = 298°K

P = 1 Standard pressure

v = Volume of infected liquid in ml

d = Density of neat standard in g/ml

M.W. = Molecular weight of the neat standard in g/g -mole

Three sets of five-point calibration curve were drawn.

Response Factor (RF): Response factors for each target compound relative to the external standard are calculated using the following equation:

$$RF = \frac{A_x C_s}{A_s C_x} \dots\dots\dots (2)$$

Where: RF = Response factor.

A_x = Area of the primary ion for the compound to be measured, counts. x

A_s = Area of the primary ion for the standard, counts. is

C_x = Concentration of internal standard

C_s = Concentration of the compound in the calibration standard

Mean Response Factor: The mean RF for each compound is obtained by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RF} = \sum_{i=1}^n \frac{x_i}{n} \dots\dots\dots (3)$$

Where: RF = Mean response factor.

x = RF of the compound at concentration i.

n = Number of concentration values, in this case 5.

Percent Relative Standard Deviation (%RSD): Using the RFs from the initial calibration, %RSD for all target compounds is calculated using the following equations:

$$\%RSD = \frac{SD_{RF}}{\overline{RF}} \times 100 \dots\dots\dots (4)$$

and

$$SD_{RF} = \sqrt{\frac{\sum_{i=1}^N (RF_i - \overline{RF})^2}{N - 1}} \dots\dots\dots (5)$$

Where: SD_{RF} = Standard deviation of initial response factors (per compound).

RF_i = response factor at a concentration level i.

RF = Mean of initial response factors (per compound)

According to technical acceptance criteria for calibration the calculated % RSD for each RF each compound in the calibration table must be less than 30% with at most two- exception up to a limit of 40%.

Percentage accuracy: Percent accuracy of the observation was determined as a relative difference of measured concentration and actual concentration spiked.

$$\text{Percentage accuracy} = \left[\frac{\text{Spiked concentration} - \text{measured concentration}}{\text{Spiked concentration}} \right] \times 100 \dots\dots (6)$$

Percentage accuracy of 15% to 20% has been observed.

Method Detection Limit

Method detection limit has been established by making seven replicate measurements of 0.002 µg. The standard deviation for these replicate concentrations is multiplied by student's t value for 99 percent confidence for seven values (3.14). **Table 4.4** gives method detection limits along with percentage relative standard deviation, correlation coefficient and reference spectrum for the compounds contained in VOC Mix 15.

Table 4.4: Method Detection Limits, Percentage Relative Standard Deviation, Correlation Coefficient and Reference Spectrum for VOC Mix 15

Compound Name	Reference Spectrum	RSD (%)	Correlation Coefficient	Method Detection Limit (µg)
Methylene chloride	45, 33, 75	4.01	0.997964	0.00125914
Ethene, 1,1-dichloro	96, 98, 33	4.386	0.997079	0.001377204
ethane 11 dichloro	33, 83, 63	4.51	0.998137	0.00141614
Propane, 2,2-dichloro	77, 96, 98	3.787	0.997029	0.001189118
Methane, bromochloro	45, 49, 33	3.588	0.998576	0.001126632
Chloroform	83, 85, 87	4.631	0.994875	0.001454134
Ethane, 1,1,1-trichloro	97, 99, 33	2.661	0.998697	0.000835554
Carbon Tetrachloride	119, 117, 75	4.948	0.997169	0.001553672
Benzene	78, 79, 77	3.018	0.998348	0.000947652
Trichloroethylene	132, 130, 134	3.419	0.997597	0.001073566
Propane, 1,2-dichloro	76, 77, 39	2.528	0.99907	0.000793792
Methane, dibromo	174, 95, 176	3.829	0.996883	0.001202306
Methane, bromodichloro	83, 85, 129	4.224	0.99806	0.001326336
1-Propene, 1,3-dichloro	75, 77, 39	3.619	0.998776	0.001136366
Toluene	91, 92, 90	3.129	0.99865	0.000982506
1-Propene, 1,3-dichloro-, (Z)	75, 77, 39	5.425	0.99761	0.00170345
Ethane, 1,1,2-trichloro	97, 96, 99	6.658	0.995209	0.002090612
Tetrachloroethylene	129, 166, 131	6.628	0.991351	0.002081192
Propane, 1,3-dichloro	76, 41, 77	5.29	0.996978	0.00166106
Methane, dibromochloro	129, 127, 131	7.971	0.994406	0.002502894
Ethane, 1,2-dibromo	109, 107, 108	5.564	0.99672	0.001747096
Benzene, chloro	112, 114, 113	5.289	0.996563	0.001660746
Ethylbenzene	91, 106, 92	3.879	0.998123	0.001218006
m xylene	106, 91, 105	4.917	0.996776	0.001543938
p-Xylene	106, 91, 105	4.741	0.996999	0.001488674
o- xylene	106, 91, 104	5.983	0.99595	0.001878662
Styrene	104, 106, 103	8.254	0.994769	0.002591756
Methane, tribromo	173, 175, 171	12	0.990694	0.003768
iso propyl benzene	105, 119, 103	6.103	0.995332	0.001916342
Benzene, bromo	158, 156, 157	3.629	0.999066	0.001139506
Ethane, 1,1,2,2-tetrachloro	83, 85, 131	4.397	0.998058	0.001380658

Table 4.4 (Contd.): Method Detection Limits, Percentage Relative Standard Deviation, Correlation Coefficient and Reference Spectrum for VOC Mix 15

Propane, 1,2,3-trichloro-	75, 77, 110	6.234	0.995364	0.001957476
Benzene, propyl	91, 120, 119	3.918	0.998399	0.001230252
2-chloro- Toluene,	91, 126, 128	3.253	0.999057	0.001021442
Benzene, 1,3,5-trimethyl	120, 105, 119	4.762	0.998765	0.001495268
4-chloro- Toluene,	91, 126, 128	3.365	0.99911	0.00105661
t butyl benzene	119, 57, 91	5.647	0.997361	0.001773158
Benzene, 1,2,4-trimethyl	120, 105, 119	3.074	0.999123	0.000965236
Benzene, sec butyl	105, 134, 104	3.695	0.998858	0.00116023
Benzene 1,3 dichloro	119, 134, 120	4.277	0.998237	0.001342978
p iso propyltoluene	119, 134, 120	5.093	0.997513	0.001599202
Benzene, 1,4-dichloro	146, 148, 147	5.191	0.998146	0.001629974
Benzene, butyl	134, 91, 133	14.28	0.99906	0.00448392
Benzene, 1,2-dichloro	146, 148, 147	2.423	0.998443	0.000760822
Propane, 1,2-dibromo-3-chloro	157, 155, 75	6.393	0.997631	0.002007402
Benzene, 1,2,4-trichloro	182, 180, 184	7.346	0.997567	0.002306644
1,3-Butadiene, 1,1,2,3,4,4-hexachloro	225, 227, 260	8.947	0.995306	0.002809358
Naphthalene	128, 129, 127	7.401	0.992432	0.002323914
Benzene, 1,2,3-trichloro	182, 180, 184	7.725	0.996253	0.00242565

Calculation Procedure

Concentrations of VOCs identified belonging to VOC Mix 15 were estimated from the calibration curve.

Concentrations in $\mu\text{g}/\text{m}^3$ were obtained from the concentrations estimated from calibration curve as follows:

$$C \mu\text{g}/\text{m}^3 = (C_e \times V) / (V_{inj} \times V_a) \dots\dots\dots (7)$$

Where, C_e = concentration obtained from calibration curve in μg

V = volume of adaptor in μl

V_{inj} = volume of sample injected in μl

V_a = Volume of air sampled in m^3

4.2 Measurement of Carbonyls

Environmental Protection Agency (U.S. EPA) method TO-11A was used for collecting and analyzing carbonyl compounds (U.S. EPA 1999a). This procedure has been written specifically for the sampling and analysis of formaldehyde. Other carbonyl compounds found in ambient air are also observed in the analysis result. Resolution of these compounds depend upon column and mobile phase conditions during HPLC analysis. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivative of formaldehyde interfere. Such interferences are often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). In addition, other aldehydes and ketones can be detected with modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acetone and propionaldehyde and 12 other higher molecular weight aldehydes and ketones (within an analysis time of about one hour), as identified below, by utilizing one or two Zorbax ODS columns in series under a linear gradient program:

1.	Formaldehyde	9.	o-Tolualdehyde
2.	Isovaleraldehyde	10.	Butyraldehyde
3.	Propionaldehyde	11.	2,5-Dimethylbenzaldehyde
4.	p-Tolualdehyde	12.	Methyl ethyl ketone
5.	Acetaldehyde	13.	Acetone
6.	Valeraldehyde	14.	m-Tolualdehyde
7.	Crotonaldehyde	15.	Benzaldehyde
8.	Hexanaldehyde		

The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4, and benzaldehyde region of the chromatogram. Ozone at high concentrations is found to interfere negatively by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from ozone was observed even at concentrations of formaldehyde and ozone typical of clean ambient air (i.e., 2 and 40 ppb,

respectively). Potassium iodide (KI) scrubbers were used to remove ozone interference.

Specifications of LpDNPH Cartridge used are as follows:

Adsorbent: Chromatographic grade silica coated with 2, 4-dinitrophenylhydrazine (DNPH)

Particle Size: 150-250 μ m (60/100 mesh)

DNPH Loading: 0.29% (1mg/cartridge)

Bed Weight: 350mg (approximate)

Length: S10: 7.4cm; S10x: 3.8cm; S10L: 4.0cm

Background: 0.02 μ g formaldehyde (per cartridge 0.02 μ g acetaldehyde 0.09 μ g acetone and other aldehydes 0.02 μ g)

Breakthrough volume was determined by attaching two LpDNPH cartridges in series at five sampling locations. If the back-up cartridge concentration exceeded 10% of the formaldehyde concentration on the front cartridge, then it was assumed that breakup occurred. In the present study maximum concentration in backup cartridge was observed to be 5% to 7%.

The back flush elution approach may add particulate particles also collected on the cartridge to the acetonitrile solution which can cause sample valve failure and increase column back pressure.

To minimize this, front flush of the cartridge contents with the acetonitrile reagent rather than back flush was adopted. 5 mL of formaldehyde free acetonitrile from the syringe was front flushed through the cartridge to a 5-mL volumetric flask. The use of 5mL of acetonitrile is sufficient for quantitative cartridge sample elution.

Analysis:

Carbonyl compounds were extracted and injected onto a C18, reversed-phase high performance liquid chromatography (RP-HPLC) column and were separated using gradient elution. The separated compounds were then quantified by UV detection at 360 nm.

Conditions set for analysis were as follows:

Column: C18 column, 4.1 mm x 250 mm, 5 µm particle size

Eluent 1: Acetonitrile

Eluent 2: THF 10%

Gradient:	Time (min)	A (%)	B (%)
	0	30	70
	20	50	50
	22	50	50
	37	75	25
	42	100	0
	47	100	0
	47.1	30	70
	52	30	70

Flow Rate: 0.3 mL/min

Inj. Volume: 10 µL

The standard used for quantification of carbonyls was procured from Supelco.

The details regarding the standard presented below in tabular form (Table 4.5)

Table 4.5: Details of Aldehyde Standards

Analyte	Cas No.	Derivative Gravimetric Conc. , µg/ml	Analytical Conc., µg/ml	Std. Dev.
Acetaldehyde-2,4-DNPH	1019-57-4	76.39	14.97	+/-0.05
Acetone-2,4-DNPH	1567-89-1	61.60	15.04	+0.04
Acrolein-2,4-DNPH	888-54-0	63.09	14.94	+0.04
Benzaldehyde-2,4-DNPH	1157-84-2	40.51	14.54	+0.04
Butyraldehyde-2,4-DNPH	1527-98-6	52.20	14.86	+0.04
Crotonaldehyde-2,4-DNPH	1527-96-4	53.50	14.88	+0.04
Formaldehyde-2,4-DNPH	1081-15-8	105.00	14.96	+0.05
Hexaldehyde-2,4-DNPH	1527-97-5	42.02	15.02	+0.09
Isovaleraldehyde-2,4-DNPH	2256-01-1	46.37	14.77	+0.04
m-Tolualdehyde-2,4-DNPH	2880-05-9	37.51	14.94	+0.06
o- Tolualdehyde-2,4-DNPH	1773-44-0	37.50	14.95	+0.04
p- Tolualdehyde-2,4-DNPH	2571-00-8	37.20	14.98	+0.02
Propionaldehyde-2,4-DNPH	725-00-8	61.49	14.98	+0.04
Valeraldehyde-2,4-DNPH	2057-84-3	46.37	14.90	+0.05
2,5-Dimethylbenzaldehyde-2,4-D	152477-96-8	35.03	14.95	+0.03

Calculations:

Calibration factor for each calibration, mean calibration factor, standard deviation, and percent relative standard deviation were calculated as follows:

$$CF = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Concentration of the Compound Injected (in ug/L)}} \quad \dots\dots (8)$$

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^n CF_i}{n} \quad \dots\dots(9)$$

$$SD = \sqrt{\frac{\sum_{i=1}^n (CF_i - \overline{CF})^2}{n-1}} \quad \dots\dots\dots (10)$$

$$RSD = \frac{SD}{\overline{CF}} \times 100 \quad \dots\dots\dots (11)$$

Where: CF = Mean calibration factor using the 5 calibration concentrations.

CF = Calibration factor for calibration standard i (i = 1-5). i

RSD = Relative standard deviation of the calibration factors.

n = Number of calibration standards.

The concentration of target analyte "a," in air was calculated using the following equation:

$$\text{Conc., std in ng/L} = \frac{(\text{Area})(\text{Vol})(\text{MW})(1000 \text{ ng/ug})}{(\text{RF})(\text{MWd})(V)(1000 \text{ mL/L})} \times \text{DF} \quad \dots\dots (12)$$

Where: Area = Area of the sample peak for analyte "a"

CF = Mean calibration factor for analyte "a" from the calibration in $\mu\text{g/L}$.

Vol = Total volume of the sample cartridge eluate (mL)

MW = Molecular weight of analyte "a" in g/mole

MW_d = Molecular weight of the DNPH derivative of analyte "a" in g/mole

V = Total volume of air sampled in liters (L).

DF = Dilution Factor for the sample cartridge eluate, if any. If there is no dilution, DF = 1

LpDNPH cartridge is a solid phase extraction tube containing high purity silica that has been surface coated with DNPH reagent. Carbonyls react with DNPH to form the stable hydrazone. The sensitivity of analysis of carbonyl compounds using LpDNPH Cartridges is presented below.

Table 4.6: Sensitivity (ppb, v/v) Of Analysis for Carbonyl Compounds in Ambient Air Using LpDNPH Cartridges by Gradient HPLC

Compounds	Volume of air Sampled in Litres					
	10	20	30	40	50	100
Formaldehyde	1.55	0.75	0.5	0.4	0.26	0.14
Acetaldehyde	1.46	0.66	0.5	0.36	0.26	0.14
Acrolein	1.32	0.65	0.45	0.35	0.26	0.13
Acetone	1.29	0.62	0.45	0.35	0.26	0.13
Propionaldehyde	1.28	0.64	0.45	0.35	0.26	0.13
Crotonaldehyde	1.2	0.61	0.41	0.31	0.24	0.12
Butyraldehyde	1.21	0.61	0.4	0.3	0.24	0.12
Benzaldehyde	1.1	0.55	0.4	0.3	0.23	0.11
Isovaleraldehyde	1.12	0.57	0.4	0.3	0.23	0.11
Valeraldehyde	1.12	0.57	0.4	0.3	0.23	0.11
o-Tolualdehyde	1.02	0.53	0.36	0.25	0.2	0.1
m-Tolualdehyde	1.02	0.53	0.36	0.25	0.2	0.1
p-Tolualdehyde	1.02	0.53	0.36	0.25	0.2	0.1
Hexanal	1.09	0.55	0.36	0.25	0.22	0.1
2,5-Dimethylbenzaldehyde	0.97	0.5	0.32	0.24	0.2	0.1

4.3 Measurement of O₃ in ambient air

O₃ monitoring for the selected sampling location was done using ambient ozone monitor (Horiba make). This instrument follows the cross flow modulation type, ultra-violet absorption method in conjunction with the comparative calculation method. This permits continuous measurement with great stability and high sensitivity (F.S. 0.1 ppm). Monitoring was carried out every month at each site.

The ultra-violet-absorption method works on the principle that ozone absorbs ultra-violet rays in the area of 254 nm. Measurements are taken from continuous, alternate injections of the sample gas and the reference gas into the measurement cell, controlled by a long-life solenoid valve. The cross flow modulation method is characteristically zero drift-free. All fluctuations in the mercury-vapor light source and in the detector are automatically compensated for by a comparative calculation circuit. Below given the summary of the instrument:

Instrument: Ambient O₃ Monitor (Model No. APOA370)

Make: Horiba

Principle: Ultra-violet-absorption method (NDUV)

Application: O₃ in ambient air

Range: Standard ranges: 0-0.1/0.2/0.5/1.0 ppm

Lower detectable limit: 0.5 ppb (3 sigma)

Response time (T₉₀): Within 75 sec at lowest range

Sample gas flow rate: Approx. 0.7 L/min

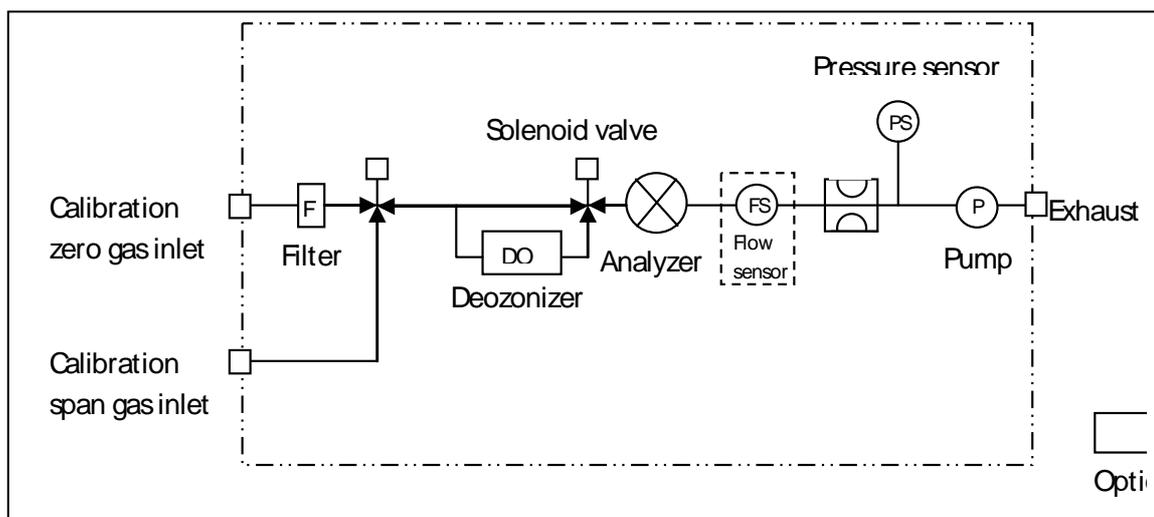


Figure 4.3: Schematic Diagram of Ambient Ozone Monitor

4.4 Measurement of NO_x

NO_x has been measured as NO₂ by Modified Jacob & Hochheiser (Na-Arsenite). In the method the NO₂ from ambient air is absorbed in a solution of sodium hydroxide and sodium arsenite. Sulphur dioxide is the major interfering compound. The interference of sulphur dioxide is eliminated by converting it to sulphuric acid by addition of hydrogen peroxide. The absorbed nitrogen dioxide is then reacted with sulphanilamide in the presence of phosphoric acid at a pH of less than 2 and then coupling it with N-(1Nepthyl) ethylenediamine dihydrochloride. The absorbance of the highly coloured azo dye is measured on spectrophotometer at a wavelength of 540 nm. The detection range of the NO₂ concentration is 9 – 750 µg/m³.

The volume of the air samples is calculated as:

$$V = \{(F_1+F_f)/2\} \times t_s \quad \dots\dots\dots(13)$$

where,

V= Volume of air sample, L

F₁=Air flow rate before sampling, L/min

F_f= Air flow rate after sampling, L/min

t_s= Sampling time, min

The NO₂⁻ concentration (µg /ml) in the analyzed sample is determined graphically from the calibration curve. The NO₂ concentration (µg of NO₂ per cubic meter of air) in the air sample is calculated as:

$$\mu\text{gNO}_2^- / \text{m}^3 = \frac{\mu\text{g}/\text{NO}_2^- \times V_s}{V_a \times 0.82 \times V_t} \times 1000 \quad \dots\dots\dots(14)$$

where,

V_a= Volume of air sample, L

0.82= Sampling efficiency

V_s= Final volume of sampling solution

V_t= Aliquot taken for analysis

1000= Conversion of L to m³

4.5 Quality Assurance and Quality Control

Quality Assurance Program (VOC)

Reagent and Materials Control: The purity of the carrier gas used GC was ensured to be 99.999%.

Sampling Protocol: Sampling protocol sheets were maintained for each sample. Details of the sample with regard to sampling location, air volume draw and any special activity during sampling was recorded.

Blanks and System Performance: Twenty percent of all injections made to the GC were blanks, where the blank was thermally desorbed gas from blank tubes.

System Performance was ensured by performing BFB tuning prior to sample injection. The BFB tuning criteria is given in Table on page 4.22.

Breakthrough volume: No breakthrough was observed for any of the compounds for an air volume of 8 litre (Table 4.3)

Recovery of analytes: Recovery of analytes were ensured by spiking a known concentration of VOC mix 20 and determining concentrations of the VOCs. Percent accuracy of the observation was determined as a relative difference of measured concentration and actual concentration spiked.

$$\text{Percentage accuracy} = \left| \frac{\text{Spiked concentration} - \text{measured concentration}}{\text{Spiked concentration}} \right| \times 100 \quad \dots (6)$$

Percentage accuracy of 15% to 20% has been observed.

Calibration and method detection limit (MDL): Calibration and method detection limit (MDL) are discussed in detail in previous sections. RSD varied from 2.423% for 1, 2, dichlorobenzene to 14.28% for butyl benzene. The linear correlation coefficients r^2 ranged from 0.990 to 0.999.

Mass Spectra identification Criteria: The spectral library match $\geq 85\%$ for a tentative identification was considered. The relative intensities of the major ions tallying within $\pm 20\%$ of first three abundances were considered.

Quality Assurance Program (Carbonyls)

Reagent and Materials Control: The purity of the carrier gas used HPCL was ensured to be 99.999%. Chromatographic grade Acetonitrile and THF of E Merck was used. Suppleco make LpDNPH cartages with quality certificates were used.

Sampling Protocol: Sampling protocol sheets were maintained for each sample. Details of the sample with regard to sampling location, air volume draw and any special activity during sampling was recorded.

Calibration and method detection limit (MDL): Sensitivity of analysis along with standard deviation and calibration details are discussed in detail in section 4.2.

Chapter 5

Results and Discussion

5.1 Results

5.1.1 Status of Carbonyl and Non- Carbonyl VOCs in Ambient Air

The Non carbonyl VOCs identified in the present study are listed in Table 5.1. Altogether, 165 Non carbonyl VOCs have been identified considering all the locations. Among the identified Non carbonyl VOCs as much as 35 falls under the category of Hazardous Air Pollutants (HAPs) identified by USEPA in Clean Air Act Amendment (CAAA) Title III. Considering different location categories; 86, 132, 85 and 130 Non carbonyl VOCs are identified in industrial, residential, petrol pump and traffic intersections respectively. Among these compounds, 28,35, 30, 31 Non carbonyls were categorized as HAPs in those respective locations.

Table 5.2 shows the carbonyls which have been identified and quantified. Four out of fourteen carbonyls are HAPs. It has been found that almost 16% of the VOCs identified are HAPs. Category wise distribution of HAPs are shown in **Table 5.3** and **Figure.5.1**

Table 5.1: VOCs Identified at Different Sampling Locations

CAS No.	Compounds	Traffic Intersection	Petrol Pump	Commercial & Residential	Industrial
95-49-8	2-chloro- Toluene	√\$	√\$	√\$	√\$
135-98-8	Benzene, sec butyl	√\$	√\$	√\$	√\$
542-75-6	1-Propene, 1,3-dichloro-,	√\$#	√\$#	√\$#	√\$#
106-43-4	4-chloro- Toluene	√\$	√\$	√\$	√\$
99-87-6	4-Isopropyltoluene	√\$	√\$	√\$	√\$
135-98-8	Benzene, (1-methylpropyl)	√\$	√\$	√\$	√\$
108-70-3	Benzene, 1,3,5-trichloro-	√\$	√\$	√\$	√\$
108-38-3	Benzene, 1,3-dimethyl-	√\$	√\$	√\$	√\$
95-49-8	Benzene, 1-chloro-2-methy	√\$	√\$	√\$	√\$
535-77-3	Benzene, 1-methyl-3-(1-methylethyl)	√\$	√\$	√\$	√\$
576-83-0	Benzene, 2-bromo-1,3,5-trimethyl	√\$	√\$	√\$	√\$
79-34-5	Ethane, 1,1,2,2-tetrachloro-	√\$#	√\$#	√\$#	√\$#
76-13-1	Ethane, 1,1,2-trichloro-	√\$#	√\$#	√\$#	√\$#
80-97-7	Ethane, 1,2-dibromo-	√\$	√\$	√\$	√\$

Table 5.1 (contd.): VOCs Identified at Different Sampling Locations

CAS No.	Compounds	Traffic Intersection	Petrol Pump	Commercial & Residential	Industrial
75-35-4	Ethene, 1,1-dichloro-	√\$	√\$	√\$	√\$
74-97-5	Methane, bromochloro-	√\$	√\$	√\$	√\$
75-27-4	Methane, bromodichloro-	√\$	√\$	√\$	√\$
74-95-3	Methane, dibromo-	√\$	√\$	√\$	√\$
96-18-4	Propane, 1,2,3-trichloro-	√\$	√\$	√\$	√\$
96-12-8	Propane, 1,2-dibromo-3-chloro-	√\$#	√\$#	√\$#	√\$#
78-87-5	Propane, 1,2-dichloro-	√\$#	√\$#	√\$#	√\$#
142-28-9	Propane, 1,3-dichloro-	√\$	√\$	√\$	√\$
594-20-7	Propane, 2,2-dichloro-	√\$	√\$	√\$	√\$
98-82-8	(1-Methylethyl) benzene	√	√	√	√
156-60-5	(E)-1,2 -Dichloroethane			√	
14686-13-6	(E)-2-Heptene			√	√
13269-52-8	(E)-3-Hexene			√	
674-76-0	(E)-4-Methyl-2-Pentene	√	√	√	
7688-21-3	(Z)-2-Hexene		√#	√#	
2097-47-0	(Z)-3-Hexane		√	√	√
691-38-3	(Z)-4-Methyl-2-Pentene			√	√
106-93-4	1,2 dibromomethane			√	
95-50-1	1,2 dichlorobenzene			√	
108-67-8	1,2,3 trimethyl benzene			√	
488-23-3	1,2,3,4-tetramethylbenzene	√\$	√\$	√\$	√\$
526-73-8	1,2,3-trimethylbenzene	√	√	√	√
95-63-6	1,2,4-Trimethyl benzene	√\$	√\$	√\$	√\$
108-67-8	1,3,5 -Trimethyl benzene	√\$#	√\$#	√\$#	√\$#
513-81-5	1,3-Butadiene, 2,3-dimethyl-			√	
87-68-3	1,3-Butadiene,1,1,2,3,4,4-hexachloro-	√\$#	√\$#	√\$#	√\$#
106-46-7	1,4 dichlorobenzene	√\$#	√\$#	√\$#	
2425-77-6	1-Decanol, 2-hexyl-	√			
18675-24-6	1-Decanol, 2-methyl-	√		√	
611-12-6	1-Ethyl-2-methyl benzene	√	√	√	√
620-14-4	1-Ethyl-3-Methylbenzene			√	
622-96-8	1-Ethyl-4-Methyl benzene	√	√	√	
592-41-6	1-Hexene	√		√	√
693-89-0	1-Methylcyclopentene			√	
2/8/3913	1-Octanol, 2-butyl-	√		√	
111-66-0	1-Octene				√
824-90-8	1-Phenyl-1-butene			√	
565-59-3	2, 3- Dimethyl pentane	√		√	

Table 5.1 (contd.): VOCs Identified at Different Sampling Locations

CAS No.	Compounds	Traffic Intersection	Petrol Pump	Commercial & Residential	Industrial
540-84-1	2,2,4-trimethylpentane	√#	√#	√#	√#
584-94-1	2,3- Dimethyl hexane	√	√	√	√
513-85-9	2,3-Butanediol		√		
2213-23-2	2,4- Dimethyl heptane	√	√	√	
589-43-5	2,4 –Dimethyl hexane	√	√	√	√
108-08-7	2,4-Dimethylpentane	√	√	√	√
2234-20-0	2,4-Dimethylstyrene	√		√	
5194-51-4	2,4-Hexadiene			√	
75-83-2	2-2 Dimethyl butane	√	√	√	√
513-35-9	2-Methyl -2-butene	√#		√#	√#
591-76-4	2-Methyl hexane	√	√	√	√
107-83-5	2-Methyl pentane	√	√	√	√
763-29-1	2-Methyl-1-Pentene	√	√	√	√
78-78-4	2-Methylbutane	√	√	√	
534-22-5	2-methyl-furan			√	
590-36-3	2-Pentanol, 2-methyl-	√#	√#	√#	
67-63-0	2-Propanol		√		
619-99-8	3-Ethyl hexane	√			
96-14-0	3-Methyl pentane	√	√	√	√
563-46-2	3-Methyl-1-butene	√	√	√	√
1453-58-3	3-Methylpyrazole		√		
934-80-5	4-Ethyl-1, 2-Dimethylbenzene	√		√	√
2216-34-4	4-Methyl octane	√		√	√
75-05-8	Acetonitrile	√#	√#	√#	√#
74-86-2	Acetylene		√	√	
638159-35-0	Benzenamine, 2,4-dibromo-			√	
71-43-2	Benzene	√\$#	√\$#	√\$#	√\$#
13880-55-2	Benzene 1,3 dichloro	√\$		√\$	
98-83-9	Benzene, (1-methylethyl)-			√	
7214-61-1	Benzene, (1-nitroethyl)-	√			
768-49-0	Benzene, (2-methyl-1-propenyl)-	√		√	
87-61-6	Benzene, 1,2,3-trichloro-	√\$		√\$	
141-93-5	Benzene, 1,3-diethyl-	√		√	
105-05-5	Benzene, 1,4-diethyl-	√		√	
1005-64-7	Benzene, 1-butenyl-, (E)-	√			
936-72-1	Benzene, 1-methyl-2-(2-propenyl)-			√	
637-50-3	Benzene, 1-propenyl-			√	
1758-85-6	Benzene, 2,4-diethyl-1-methyl-	√			
1560-06-1	Benzene, 2-butenyl-	√			
104-51-8	Benzene, butyl-	√\$		√\$	
103-65-1	Benzene, propyl-n	√\$	√\$	√\$	√\$
50-31-7	Benzoic acid, 2,3,6-trichloro-	√		√	
1918-00-9	Benzoic acid, 3,6-dichloro-2-methoxy-	√			
75-27-4	Bromodichloromethane	√	√		
75-15-0	Carbon disulfide	√#	√#	√#	√#
56-23-5	Carbon tetrachloride	√\$#	√\$#	√\$#	√\$#

Table 5.1 (contd.): VOCs Identified at Different Sampling Locations

CAS No.	Compounds	Traffic Intersection	Petrol Pump	Commercial & Residential	Industrial
108-90-7	Chlorobenzene			√\$#	√\$#
67-66-3	Chloroform	√\$#	√\$#	√\$#	√\$#
74-87-3	Chloromethane	√#	√#	√#	√#
2532-58-3	Cis-1, 3-Dimethyl cyclopentane			√	√
1502-05-2	Cyclodecanol	√			
110-82-7	Cyclohexane	√			√
1678-98-4	Cyclohexane, (2-methylpropyl)-	√			
624-29-3	Cyclohexane, 1,4-dimethyl-, cis-	√			
1795-16-0	Cyclohexane, decyl-	√			
13395-76-1	Cyclohexanone, 2,3-dimethyl-	√			
124-48-1	Dibromochloro methane	√	√	√	
84-66-2	Diethyl Phthalate			√	
112-40-3	Dodecane	√		√	
67-66-3	Ethane 1,1-dichloro-			√\$#	
71-55-6	Ethane, 1,1,1- Trichloro-		√\$#	√\$#	√\$#
7289-40-9	Ether, heptyl hexyl	√		√	
100-41-4	Ethylbenzene	√\$#	√\$#	√\$#	√\$#
1640-89-7	Ethylcyclopentane	√	√	√	√
151-56-4	Ethyleimine			√	
629-78-7	Heptadecane	√			√
20278-89-1	Heptane, 3,4,5-trimethyl-	√			
15869-80-4	Heptane, 3-ethyl-	√			
14676-29-0	Heptane, 3-ethyl-2-methyl-	√		√	
544-76-3	Hexadecane	√		√	
10143-60-9	Hexane, 1,1'-oxybis-	√			
585-71-7	Iso propyl benzene	√\$	√\$	√\$	
115-11-7	iso-Butene	√	√	√	
78-78-4	iso-Pentane	√	√	√	
100-97-0	Methenamine	√		√	
93-58-3	Methyl Benzoate	√			
78-93-3	Methyl ethyl ketone (2-butanone)	√#	√#	√#	√#
75-97-8	Methyl tert-butyl ketone			√	
108-87-2	Methylcyclohexane	√#	√#	√#	√#
96-37-7	Methylcyclopentane	√	√	√	√
616-09-1	Methylene chloride	√\$#	√\$#	√\$#	√\$#
108-38-3	m-Xylene	√\$#	√\$#	√\$#	√\$#
91-20-3	Naphthalene	√\$#	√\$#	√\$#	√\$#
124-18-5	n-Decane	√	√	√	√
629-94-7	n-Heneicosane	√			
593-49-7	n-Heptacosane	√		√	√
142-82-5	N-heptane	√	√	√	√
110-54-3	n-Hexane	√#	√#	√#	
593-45-3	n-Octadecane	√		√	√
629-92-5	Nonadecane	√			√
638-67-5	n-Tricosane	√			
1120-21-4	n-Undecane	√	√	√	√

Table 5.1 (contd.): VOCs Identified at Different Sampling Locations

CAS No.	Compounds	Traffic Intersection	Petrol Pump	Commercial & Residential	Industrial
7146-60-3	Octane, 2,3-dimethyl-	√			
2216-33-3	Octane, 3-methyl-	√			
15869-86-0	Octane, 4-ethyl-			√	
95-47-6	o-Xylene	√\$#	√\$#	√\$#	√\$#
629-62-9	Pentadecane	√			√
109-66-0	Pentane	√	√	√	√
108-95-2	Phenol	√#		√#	
527-84-4	2-iso-Propyltoulene			√\$	√\$
74-98-6	Propane	√		√	√
115-07-1	Propene	√	√		
106-42-3	p-Xylene	√\$#	√\$#	√\$#	√\$#
100-42-5	Styrene	√\$#	√\$#	√\$#	√\$#
611-20-1	t-butyl benzene	√\$		√\$	√\$
629-59-4	Tetradecane	√			
2425-54-9	Tetradecane, 1-chloro-	√			
108-88-3	Toluene	√\$#	√\$#	√\$#	√\$#
79-01-6	Trichloroethylene	√\$#		√\$#	
127-18-4	Tetrachloroethylene	√\$#	√\$#	√\$#	√\$#
75-69-4	Trichlorofluoromethane	√	√	√	√
629-50-5	Tridecane			√	√

√:- Identified, \$:- Quantified, #-: Hazardous

Table 5.2: Carbonyl Compounds Identified at Different Sampling Locations

CAS NO.	Compound Name	Traffic Intersection	Petrol Pump	Commercial & Residential	Industrial
50-00-0	Formaldehyde	√\$#	√\$#	√\$#	√\$#
75-07-0	Acetaldehyde	√\$#	√\$#	√\$#	√\$#
107-02-8	Acetone	√\$	√\$	√\$	√\$
67-64-1	Acrolein	√\$#	√\$#	√\$#	√\$#
123-38-6	Propionaldehyde	√\$#	√\$#	√\$#	√\$#
123-72-8	Butanal	√\$	√\$	√\$	√\$
110-62-3	Crotonaldehyde	√\$	√\$	√\$	√\$
110-62-3	Benzaldehyde	√\$	√\$	√\$	√\$
529-20-4	Isovalaraldehyde	√\$	√\$	√\$	√\$
1334-78-7	Valaraldehyde	√\$	√\$	√\$	√\$
100-52-7	o-tolualdehyde	√\$	√\$	√\$	√\$
123-73-9	m,p-tolualdehyde	√\$	√\$	√\$	√\$
66-25-1	Hexanal	√\$	√\$	√\$	√\$
5779-94-2	2,5-dimethyl benzaldehyde	√\$	√\$	√\$	√\$

√:- Identified, \$:- Quantified, #-: Hazardous

Table 5.3: Category wise Distribution of HAPs

Category	No. of VOCs identified	No. of HAPs identified	% of HAPs identified
Industrial	86	28	32.56
Petrol Pump	85	30	35.29
Residential	132	35	26.52
Traffic Intersection	130	31	23.85

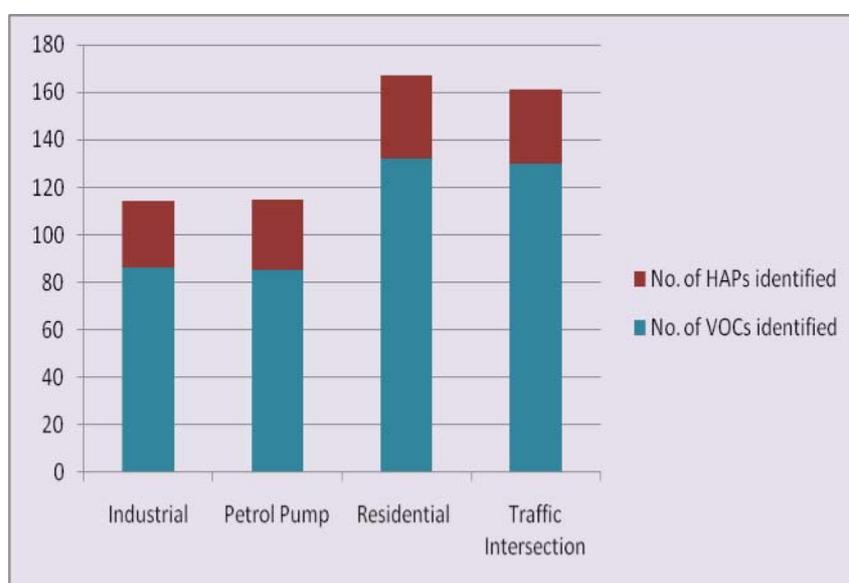


Figure 5.1: Comparative Distribution of HAPs and VOCs Identified from Each Sampling Category

In this report VOCs are categorized as Carbonyl and Non carbonyl VOCs. The sum of Carbonyl and Non carbonyl VOCs is denoted as TOTAL VOC. In order to make the outcome of the study more comprehensive the seasonal variation of Total VOCs, Total Carbonyl, Ozone and NO₂ for each sampling site is analyzed and then combined category wise. Results for each sampling category are discussed below.

Industrial Areas

Amongst the industrial areas highest concentrations of total Non carbonyl VOC is observed at Behala ($456.1 \mu\text{g}/\text{m}^3$) during winter season. The minimum concentration of $47.3 \mu\text{g}/\text{m}^3$ was observed at Cossipore during summer. Total Non carbonyl VOC concentration at Behala was higher as compared to Baithakkhana Bazar and Cossipore. At Baithakhanabazar total Non carbonyl VOCs ranged from $48.0 \mu\text{g}/\text{m}^3$ to $210.9 \mu\text{g}/\text{m}^3$ while at Cossipore it ranged from $47.3 \mu\text{g}/\text{m}^3$ to $282.5 \mu\text{g}/\text{m}^3$ and at Behala minimum concentration observed was $83.4 \mu\text{g}/\text{m}^3$ and maximum $456.1 \mu\text{g}/\text{m}^3$ (**Table 5.4 & Figure 5.2**).

Amongst the industrial areas highest concentrations of Carbonyls was observed at Baithakkhana Bazar ($1131.7\mu\text{g}/\text{m}^3$) during summer. The minimum concentration of $135 \mu\text{g}/\text{m}^3$ was observed at Behala during Summer. Carbonyls concentration at Baithakkhana Bazar was higher as compared to Behala and Cossipore At Baithakhana Bazar Carbonyls ranged from $461.6 \mu\text{g}/\text{m}^3$ to $1131.7\mu\text{g}/\text{m}^3$ while at Cossipore it ranged from $217.8 \mu\text{g}/\text{m}^3$ to $1111.5 \mu\text{g}/\text{m}^3$ and at Behala minimum concentration observed was $72.0 \mu\text{g}/\text{m}^3$ and maximum $1091.1 \mu\text{g}/\text{m}^3$ (**Table 5.5 & Figure 5.3**).

Table 5.4: Seasonal Variation of Total Non Carbonyls VOCs Observed at Industrial Locations

Seasons	Sampling Locations	1	2	3
		12:00 - 6:00pm	6:00pm-6:00am	6:am-12 noon
Summer	Baithakhana Bazar	53.4	67.12	61.7
	Cossipore	55.7	72.3	47.3
	Behala	98.0	79.0	98.1
	Upwind	56	62	58
	Downwind	87	113	72
Monsoon	Baithakhana Bazar	48.0	50.2	53.4
	Cossipore	64.6	77.3	66.5
	Behala	102.7	111.5	104.2
	Upwind	49	64	51
	Downwind	71	96	91
post monsoon	Baithakhana Bazar	177.1	146.3	170.5
	Cossipore	158.8	209.3	194.3
	Behala	302.3	83.4	198.1
	Upwind	89	114	100.7
	Downwind	123	145	111
Winter	Baithakhana Bazar	195.2	210.9	210.4
	Cossipore	236.1	282.5	234.4
	Behala	381.2	456.1	380.3
	Upwind	79	132	121
	Downwind	117	178	124

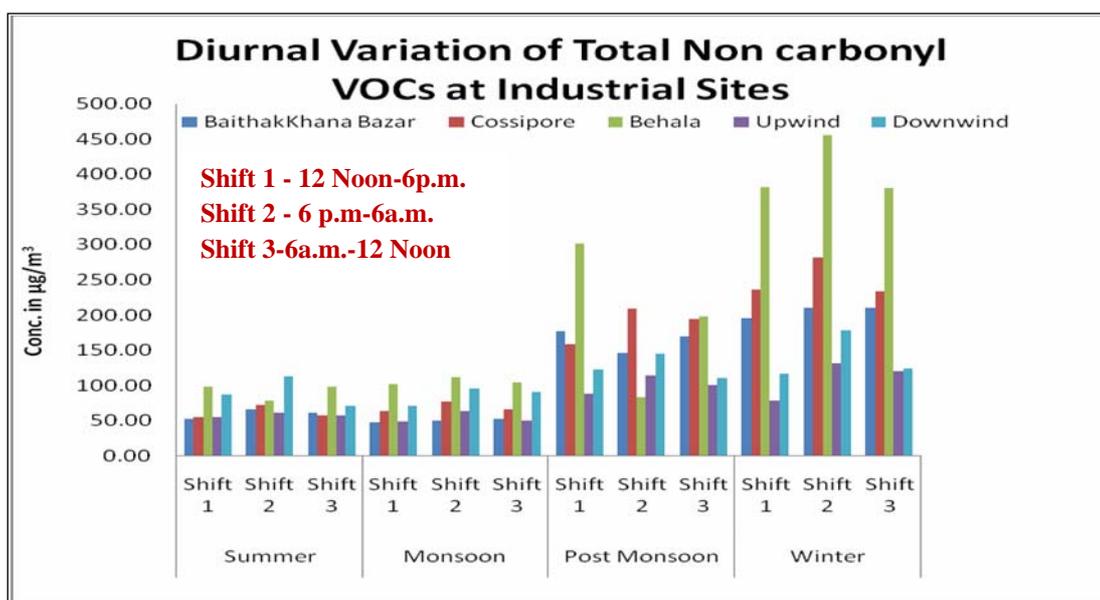


Figure 5.2: Seasonal and Diurnal Variation of Total Non Carbonyls VOCs Observed at Industrial Locations

Table 5.5: Seasonal & Diurnal Variation of Carbonyls Observed at Industrial Locations

	Industrial	Baithakkhana Bazar	Cossipore	Behala	Upwind	Downwind
Summer	Shift 1	1131.7	723.4	426.9	315.9	564.8
	Shift 2	511.7	908.2	1091.1	357.4	1072.0
	Shift 3	1056.0	649.9	135.0	578.7	1537.0
Monsoon	Shift 1	529.0	676.3	928.1	379.5	900.6
	Shift 2	557.9	993.0	732.2	389.1	652.8
	Shift 3	627.6	545.5	475.7	121.5	385.5
Pmonsoon	Shift 1	727.4	599.1	555.3	623.0	382.1
	Shift 2	637.7	323.0	268.8	667.9	840.7
	Shift 3	712.5	373.1	398.3	374.7	777.9
Winter	Shift 1	1082.5	880.5	731.2	495.5	893.1
	Shift 2	461.6	217.8	345.2	483.9	1480.4
	Shift 3	645.2	1111.5	891.2	223.3	517.1

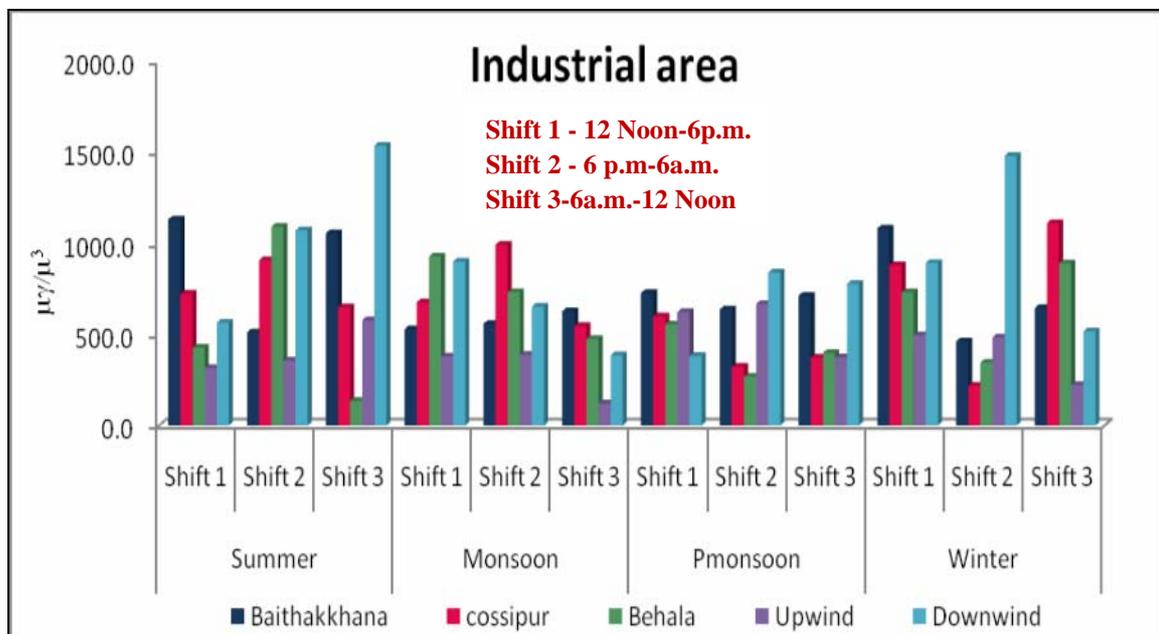


Figure 5.3: Seasonal Variation of Carbonyls Observed at Industrial Locations

Petrol Pumps

Table 5.6 & Figure 5.4 gives the Seasonal concentration of Total Non Carbonyl VOCs observed at Bose Pukur, Beleghata & Theatre Road petrol pumps. Maximum and minimum Total Non Carbonyl VOCs concentration were observed at Beleghata petrol pump during winter and summer respectively. At Bose Pukur petrol pump Total Non Carbonyl VOCs concentrations ranged from 131.1 $\mu\text{g}/\text{m}^3$ during monsoon to 561.9 $\mu\text{g}/\text{m}^3$ during Post monsoon. At Beleghata Petrol pump minimum concentration of 128.3 $\mu\text{g}/\text{m}^3$ during summer and maximum concentration of 1173.6 $\mu\text{g}/\text{m}^3$ during winter was observed. At Theatre Road petrol pump minimum concentration of 154.6 $\mu\text{g}/\text{m}^3$ during monsoon and maximum concentration of 741.7 $\mu\text{g}/\text{m}^3$ during winter have been observed.

Among these three petrol pumps highest concentration of total Carbonyls has been observed at Beleghata during Monsoon (1184.8 $\mu\text{g}/\text{m}^3$) and the minimum concentration at BosePukur Petrol Pump (130.7 $\mu\text{g}/\text{m}^3$) during Post-Monsoon. The Concentration of total Carbonyl was found higher at Beleghata as compared to other two petrol Pumps. The concentration of total Carbonyls at Bose Pukur ranged from 130.7 $\mu\text{g}/\text{m}^3$ to 1015.4 $\mu\text{g}/\text{m}^3$. At Theatre Road minimum and maximum concentration were 205.8 $\mu\text{g}/\text{m}^3$ and 688.8 $\mu\text{g}/\text{m}^3$ respectively (**Table 5.7 & Figure 5.5**).

Table 5.6: Seasonal Variation of Non Carbonyls VOCs Observed at Petrol Pumps

Seasons	Sampling Locations	1	2	3
		12:00 - 6:00pm	6:00pm-6:00am	6:am-12 noon
Summer	Beleghata	405.8	128.3	171.9
	Bose Pukur	141.0	459.4	136.3
	Theatre Road	221.0	319.8	276.1
	Upwind	56	62	58
	Downwind	87	113	72
Monsoon	Beleghata	212.0	187.6	307.6
	Bose Pukur	131.1	267.8	301.5
	Theatre Road	154.5	284.9	197.9
	Upwind	49	64	51
	Downwind	71	96	91
Post monsoon	Beleghata	260.6	346.1	686.4
	Bose Pukur	297.2	561.9	294.1
	Theatre Road	500.2	689.0	499.0
	Upwind	89	114	100.7
	Downwind	123	145	111
Winter	Beleghata	753.9	1173.6	650.0
	Bose Pukur	395.3	518.2	306.2
	Theatre Road	621.0	741.7	633.5
	Upwind	79	132	121
	Downwind	117	178	124

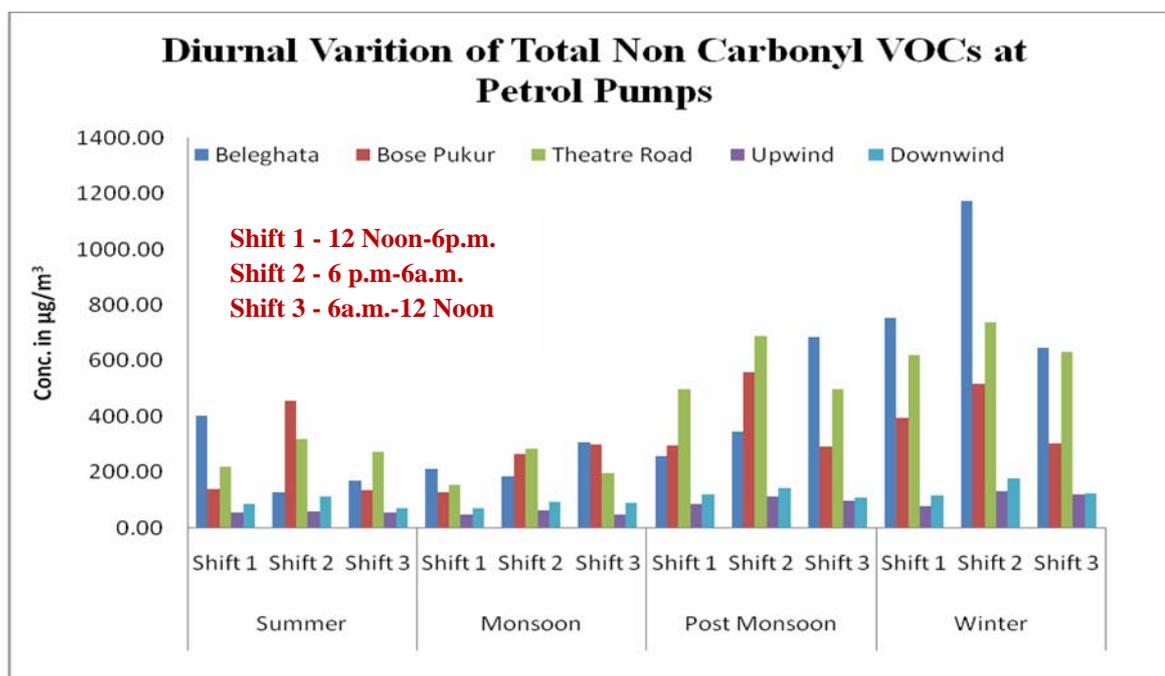
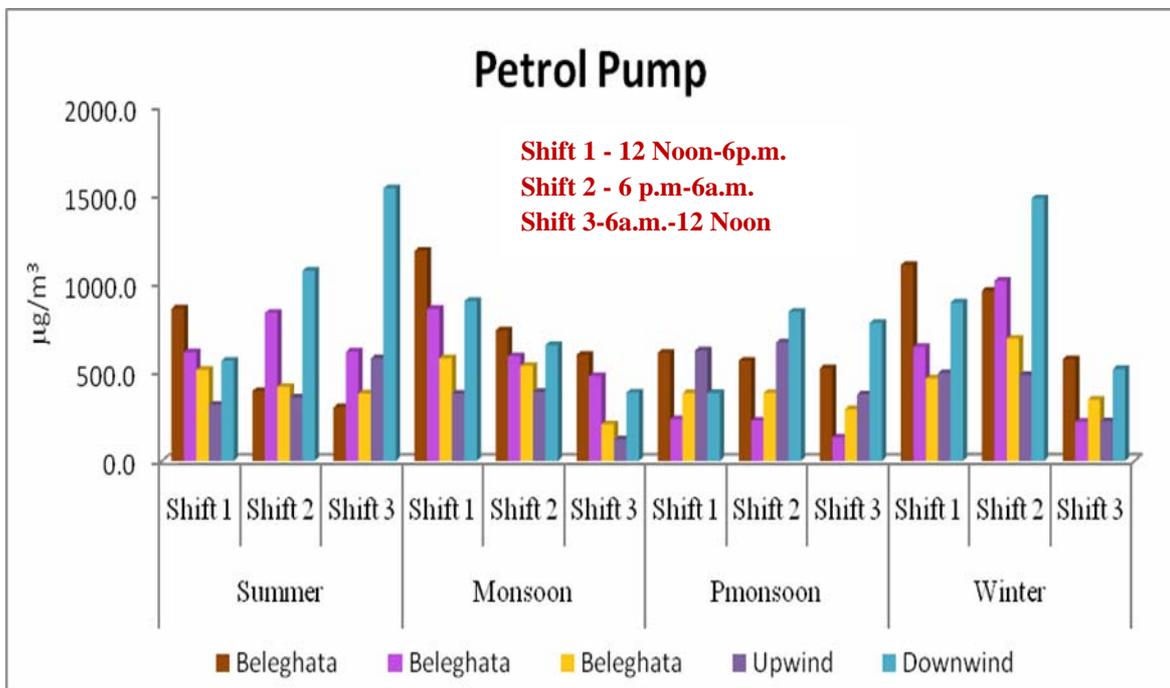


Figure 5.4: Seasonal and Diurnal Variation of Total Non Carbonyls VOCs Observed at Petrol Pumps

Table 5.7: Seasonal Variation of Carbonyls Observed at Petrol Pumps

Petrol Pump		Belegkata	Bose Pukur	Theatre Road	Upwind	Downwind
Summer	Shift 1	859.2	612.6	512.6	315.9	564.8
	Shift 2	394.1	834.5	417.0	357.4	1072.0
	Shift 3	302.0	616.0	380.4	578.7	1537.0
Monsoon	Shift 1	1184.8	856.8	578.9	379.5	900.6
	Shift 2	735.7	590.5	535.5	389.1	652.8
	Shift 3	597.6	477.7	205.8	121.5	385.5
Pmonsoon	Shift 1	609.1	236.0	381.6	623.0	382.1
	Shift 2	564.6	227.1	383.3	667.9	840.7
	Shift 3	522.1	130.7	291.1	374.7	777.9
Winter	Shift 1	1104.4	642.8	464.8	495.5	893.1
	Shift 2	959.3	1015.4	688.8	483.9	1480.4
	Shift 3	573.4	219.9	344.9	223.3	517.1



Residential Cum Commercial Areas

The Total Non Carbonyl VOCs concentrations observed ranged from 43.0 $\mu\text{g}/\text{m}^3$ at Dunlop during monsoon to 546.1 $\mu\text{g}/\text{m}^3$ at Alipore during Post monsoon in Residential cum commercial areas. At Alipore minimum concentration observed was 41.5 $\mu\text{g}/\text{m}^3$ during monsoon. Entally showed a minimum Total Non Carbonyl VOCs concentration of 43.1 $\mu\text{g}/\text{m}^3$ during monsoon and maximum concentration observed (412.0 $\mu\text{g}/\text{m}^3$) during Post monsoon. Total Non Carbonyl VOCs concentration observed at Dunlop ranged from 43.0 $\mu\text{g}/\text{m}^3$ during monsoon to 84.8 $\mu\text{g}/\text{m}^3$ during winter. Seasonal and annual averages of Total Non Carbonyl VOCs at Alipore, Dunlop and Entally are presented in **Table 5.8 and Figure 5.5**.

In case of Carbonyls, the highest concentration found at Entally (1430.1 $\mu\text{g}/\text{m}^3$) during Monsoon while the lowest concentration observed at Dunlop (177.4 $\mu\text{g}/\text{m}^3$) during Post Monsoon. Entally showed the higher concentration of total Carbonyls as compared to Alipore and Dunlop. At Entally and Dunlop the concentration of total Carbonyls varied from 189.3 to 1430.1 $\mu\text{g}/\text{m}^3$ and 177.4 to 972.4 $\mu\text{g}/\text{m}^3$ respectively. Total Carbonyls concentration range at Alipore was 246.6 to 781.4 $\mu\text{g}/\text{m}^3$. (**Table 5.9 & Figure 5.7**).

Table 5.8: Seasonal Variation of Total Non Carbonyls VOCs Observed at Residential Cum Commercial Locations

Seasons	Sampling Locations	1	2	3
		12:00 - 6:00pm	6:00pm-6:00am	6:am-12 noon
Summer	Dunlop	56.4	61.3	60.0
	Entally	51.3	51.5	52.2
	Alipore	56.9	43.2	66.1
	Upwind	56	62	58
	Downwind	87	113	72
Monsoon	Dunlop	55.6	43.0	52.0
	Entally	74.7	43.1	75.7
	Alipore	44.3	49.7	41.5
	Upwind	49	64	51
	Downwind	71	96	91
Post Monsoon	Dunlop	77.7	51.9	45.0
	Entally	103.3	61.0	412.0
	Alipore	129.3	546.1	385.9
	Upwind	89	114	100.7
	Downwind	123	145	111
Winter	Dunlop	84.8	58.0	69.0
	Entally	85.6	55.6	45.5
	Alipore	107.0	140.0	98.0
	Upwind	79	132	121
	Downwind	117	178	124

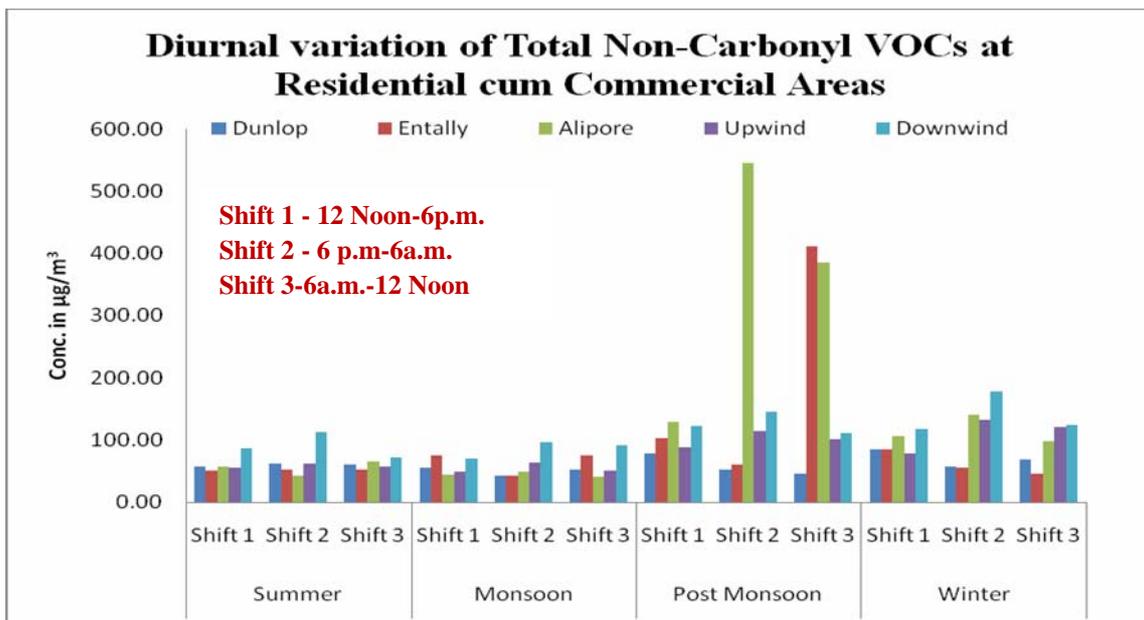


Figure 5.6: Seasonal and Diurnal Variation of Total Non Carbonyls VOC Observed at Residential Cum Commercial Locations

Table 5.9: Seasonal Variation of Carbonyls Observed at Residential Cum Commercial Locations

	Residential	Alipur	Dunlop	Entally	Upwind	Downwind
Summer	Shift 1	706.1	828.5	510.8	315.9	564.8
	Shift 2	453.1	384.1	496.6	357.4	1072.0
	Shift 3	554.8	483.4	794.2	578.7	1537.0
Monsoon	Shift 1	781.4	972.4	1430.1	379.5	900.6
	Shift 2	590.2	418.6	741.7	389.1	652.8
	Shift 3	451.2	594.6	382.3	121.5	385.5
Pmonsoon	Shift 1	483.7	481.8	669.0	623.0	382.1
	Shift 2	246.6	353.5	633.6	667.9	840.7
	Shift 3	429.6	177.4	189.3	374.7	777.9
Winter	Shift 1	374.6	614.9	671.5	495.5	893.1
	Shift 2	646.5	298.5	218.4	483.9	1480.4
	Shift 3	363.8	405.6	398.2	223.3	517.1

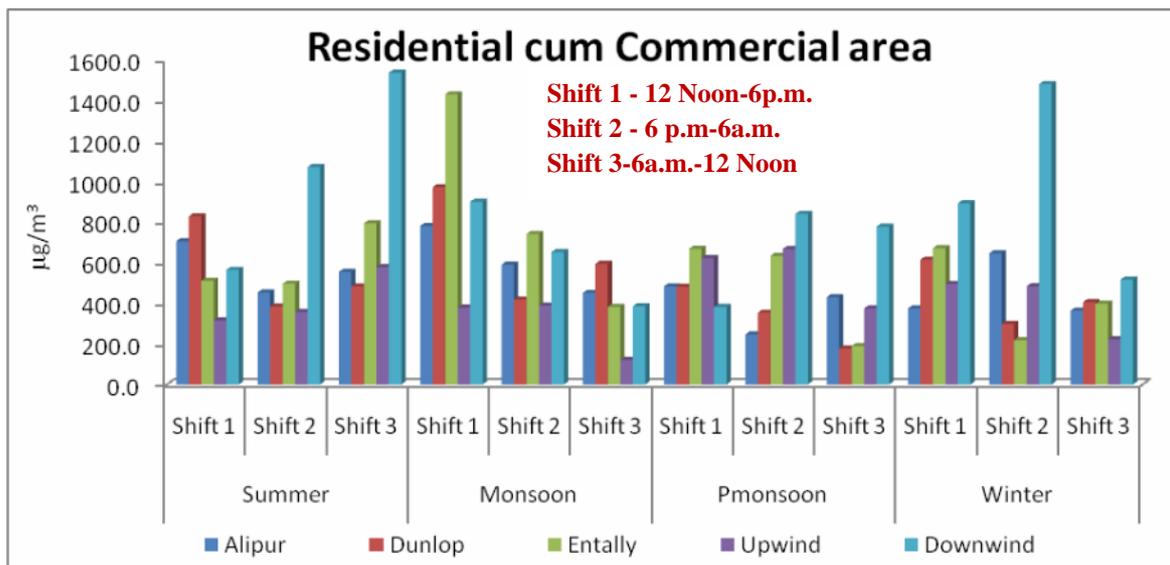


Figure 5.7: Seasonal Variation of Total Carbonyls at Residential Cum Commercial Locations

Traffic Intersection

Total Non Carbonyl VOCs concentration at Rash Behari was observed to be in the range of $255.6 \mu\text{g}/\text{m}^3$ during monsoon to $668.9 \mu\text{g}/\text{m}^3$ during winter. At ShyamBazar which is located at Northern side of Kolkata minimum concentration of $177.6 \mu\text{g}/\text{m}^3$ was observed during summer and maximum concentration of $745.2 \mu\text{g}/\text{m}^3$ found during post-monsoon which was also maximum observed concentration for all the traffic intersections (**Table 5.10 & Figure 5.8**). At Park Street the maximum concentration of $472.2 \mu\text{g}/\text{m}^3$ was observed during summer and minimum of $28.3 \mu\text{g}/\text{m}^3$ during monsoon which was lowest observed concentration for traffic intersections.

The Highest concentration of Carbonyls found at Rash Behari during Summer ($1985.4 \mu\text{g}/\text{m}^3$) while the lowest concentration observed at Shyam Bazar ($325.1 \mu\text{g}/\text{m}^3$) during Postmonsoon. At ShyamBazar and Park Street the concentration range was found to be 325.1 to $1361.9 \mu\text{g}/\text{m}^3$ and 413.8 to $1680.3 \mu\text{g}/\text{m}^3$ respectively. The concentration of total Carbonyls at Rash Behari varied from 354.1 to $1985.4 \mu\text{g}/\text{m}^3$ (**Table 5.11 & Figure 5.9**).

Table 5.10: Seasonal Variation of Total Non Carbonyl VOCs Observed at Traffic Intersections

Seasons	Sampling Locations	1	2	3
		12:00 - 6:00pm	6:00pm-6:00am	6:am-12 noon
Monsoon	Park Street	297.3	28.2	262.6
	RasBehari	329.7	317.2	255.6
	Shyam Bazar	344.5	545.6	395.0
	Upwind	49	64	51
	Downwind	71	96	91
Post Monsoon	Park Street	257.3	404.5	244.9
	RasBehari	465.3	373.3	312.1
	Shyam Bazar	485.8	557.3	745.2
	Upwind	89	114	100.7
	Downwind	123	145	111
Summer	Park Street	367.9	472.2	345.8
	RasBehari	573.9	490.0	663.4
	Shyam Bazar	607.7	177.6	433.4
	Upwind	56	62	58
	Downwind	87	113	72
Winter	Park Street	401.8	467.0	379.0
	RasBehari	488.0	668.9	350.5
	Shyam Bazar	535.8	364.3	450.0
	Upwind	79	132	121
	Downwind	117	178	124

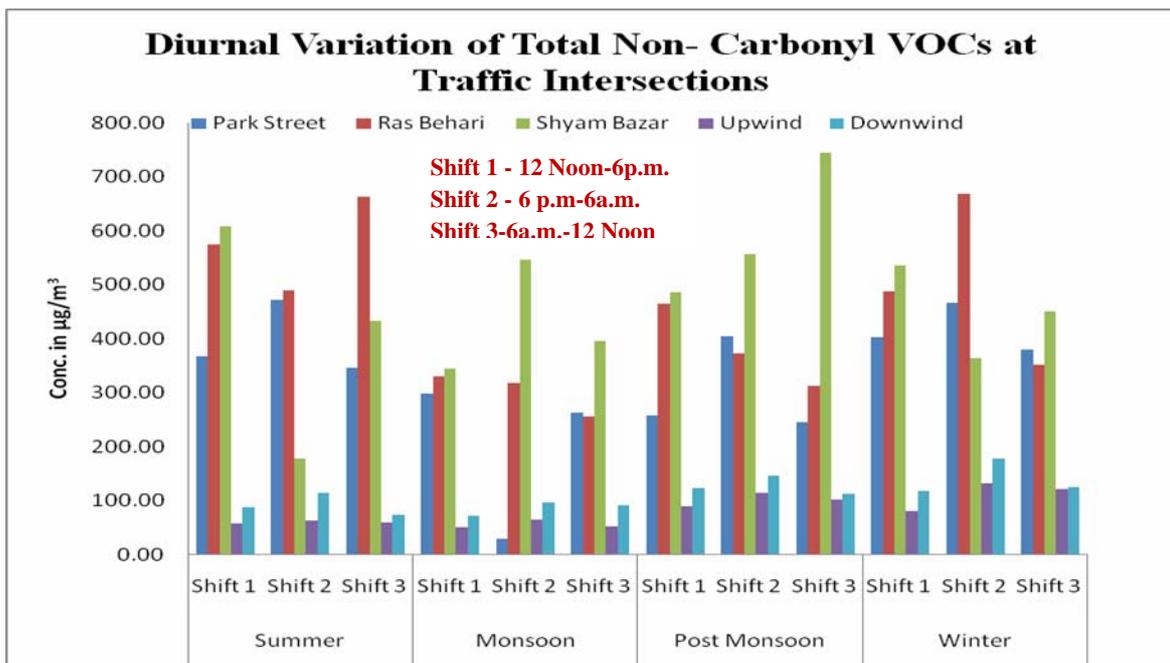


Table 5.11: Seasonal Variation of Carbonyls Observed at Traffic Intersections

Traffic Intersection		parkstreet	Rashbihari	shyambazar	Upwind	Downwind
Summer	Shift 1	839.9	1985.4	1361.9	315.9	564.8
	Shift 2	547.3	419.5	480.5	357.4	1072.0
	Shift 3	1024.2	879.3	1310.8	578.7	1537.0
Monsoon	Shift 1	1687.1	815.3	1004.2	379.5	900.6
	Shift 2	635.1	675.6	1178.0	389.1	652.8
	Shift 3	442.6	1277.6	872.8	121.5	385.5
Pmonsoon	Shift 1	767.9	354.1	475.7	623.0	382.1
	Shift 2	413.8	606.1	325.1	667.9	840.7
	Shift 3	545.1	702.4	775.8	374.7	777.9
Winter	Shift 1	1112.0	1730.5	743.3	495.5	893.1
	Shift 2	599.5	755.7	1246.9	483.9	1480.4
	Shift 3	1680.3	1154.2	694.2	223.3	517.1

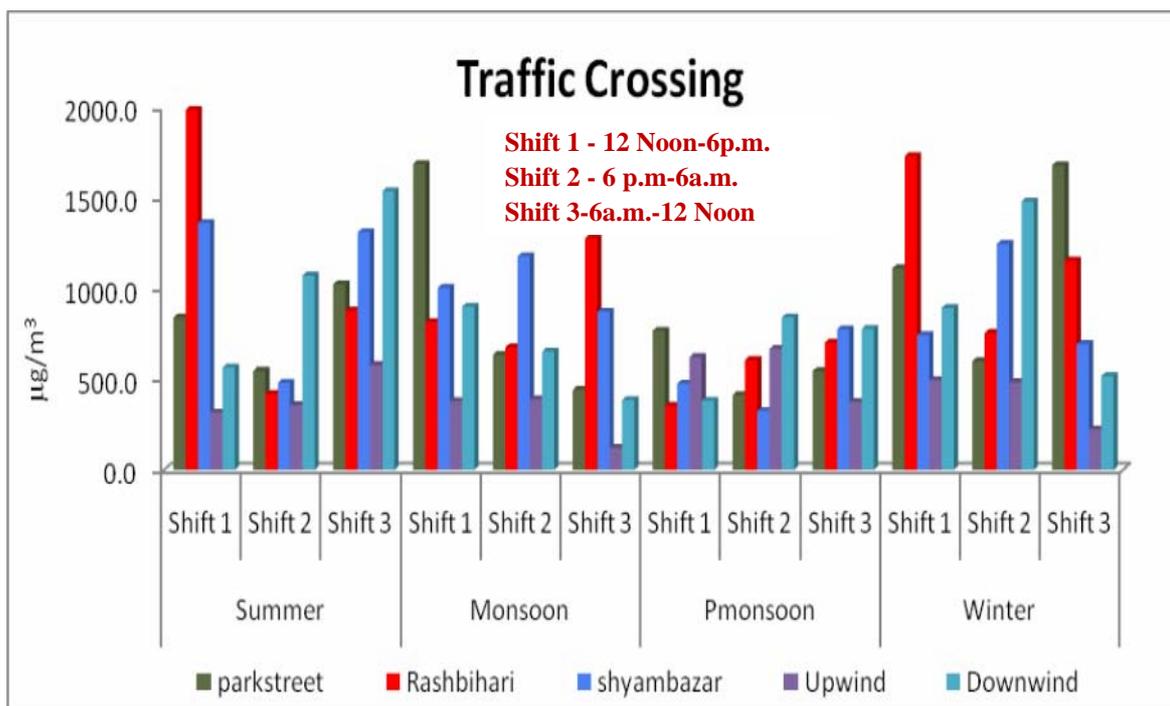


Figure 5.9: Seasonal Variation of Total Carbonyls at Traffic Intersections

In urban air of Kolkata high values of aldehydes have been observed (Tables 5.5, 5.7, 5.9 and 5.11). This may be due to oxidation of VOCs as discussed in Chapter 2 Section 2.3.4.

The following contour diagrams describe the special distribution of Total Carbonyl (**Figure 5.10 to 5.13**) and Total Non Carbonyl VOCs (**Figure 5.14 to 5.17**) during each season at different period of day.

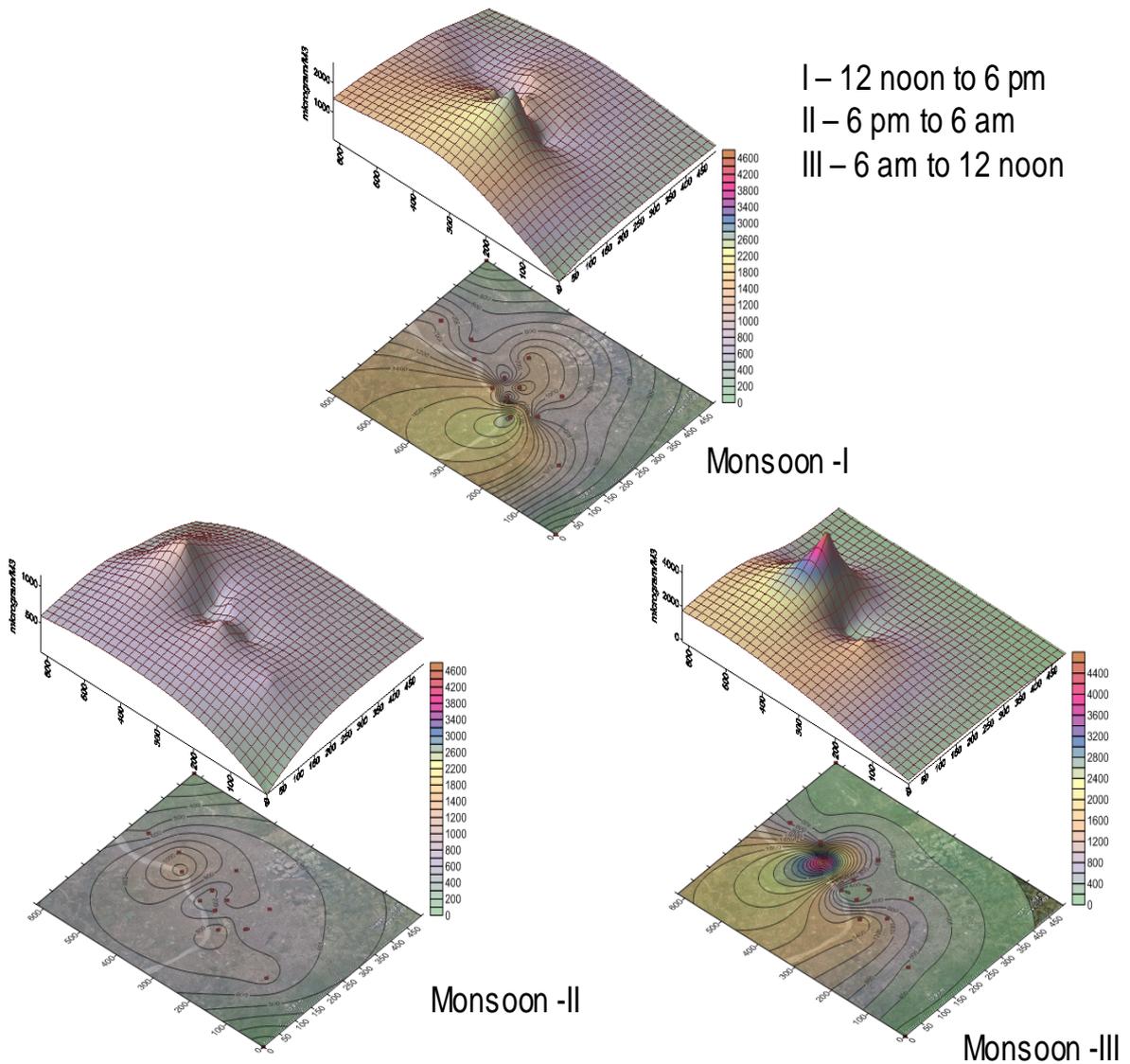


Figure 5.10: Seasonal Diurnal Contour of Total Carbonyl for Kolkata (Monsoon)

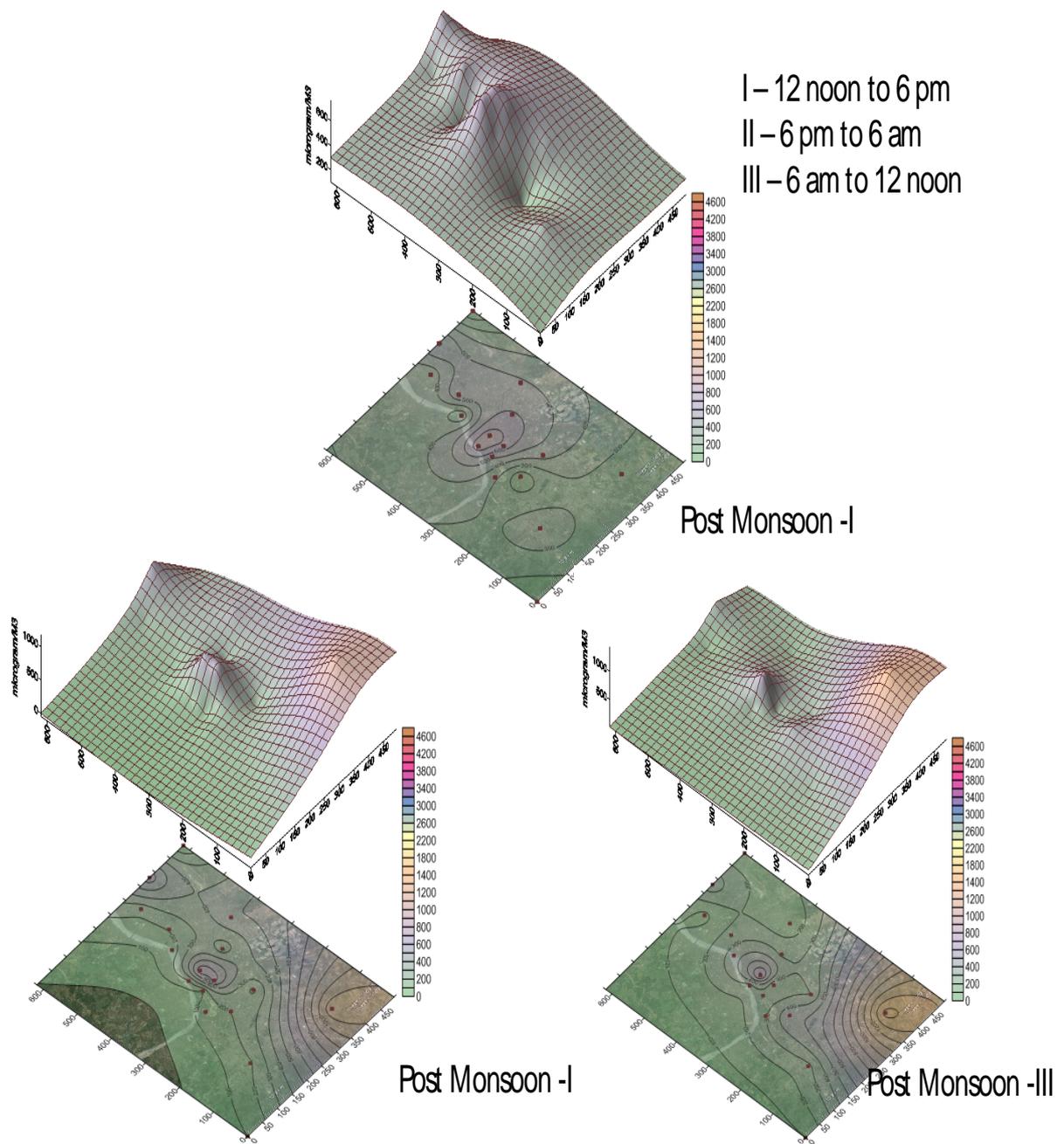


Figure 5.11: Seasonal Diurnal Contour of Total Carbonyl for Kolkata (Post Monsoon)

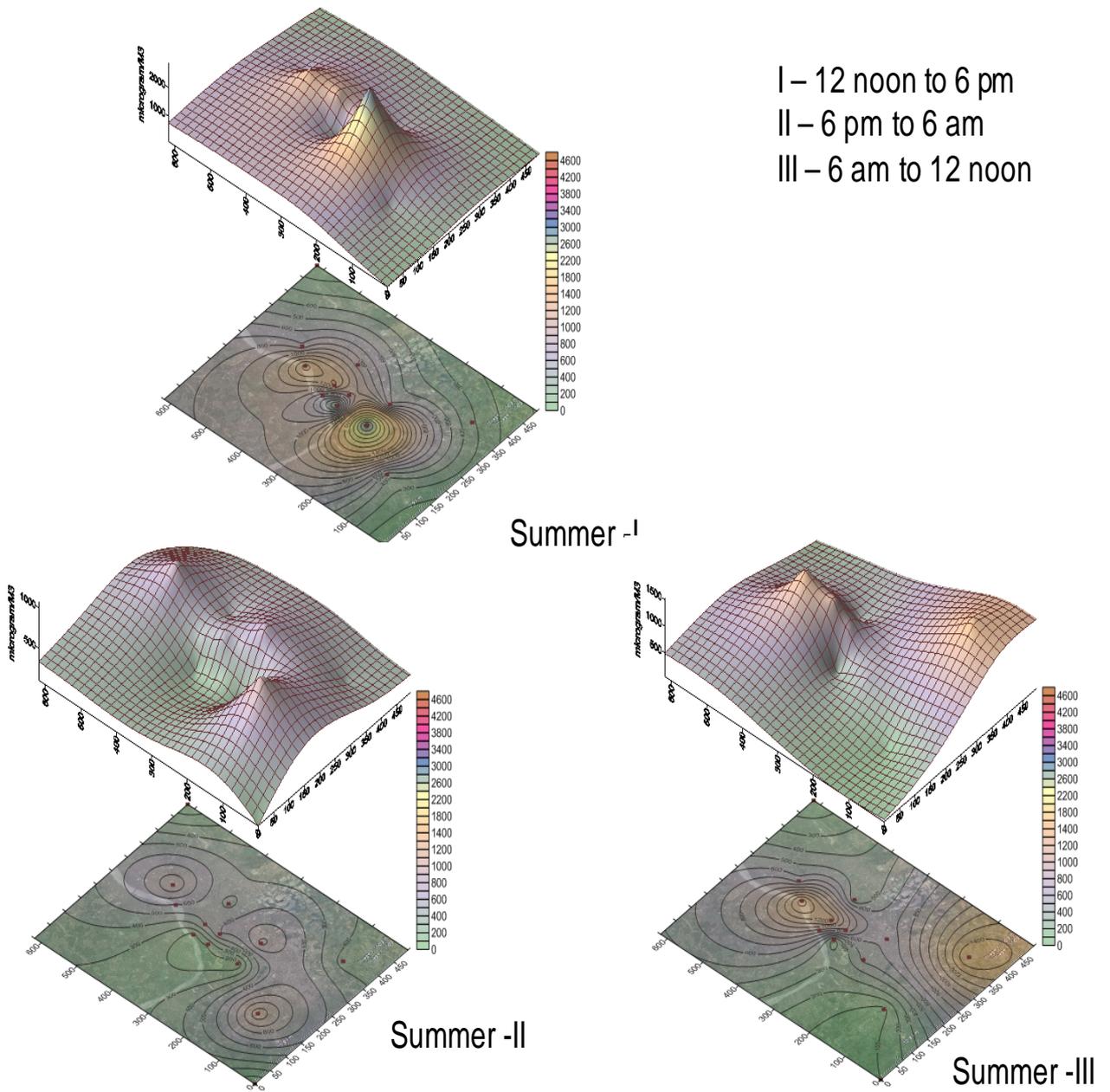


Figure 5.12: Seasonal Diurnal Contour of Total Carbonyl for Kolkata (Summer)

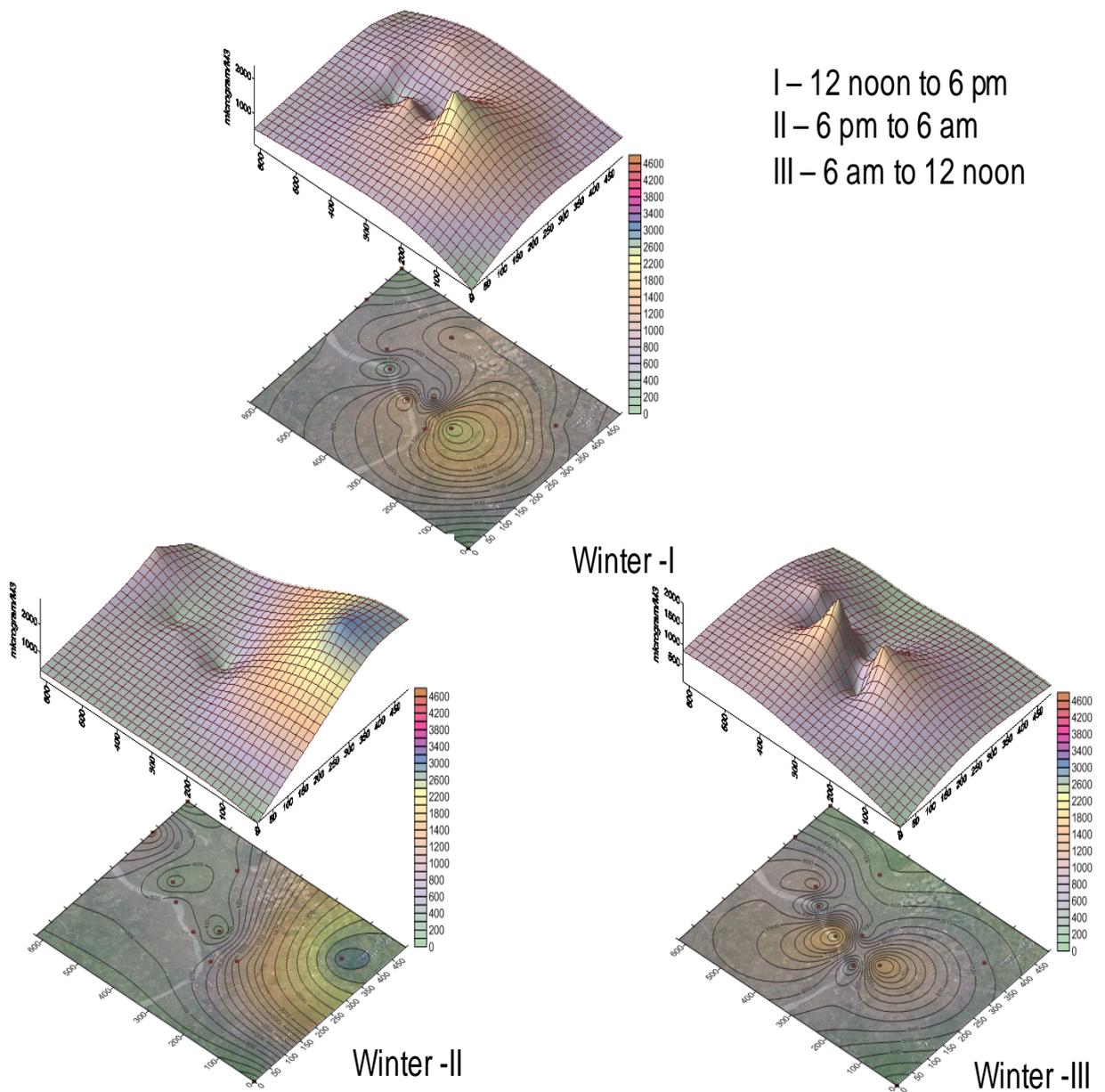


Figure 5.13: Seasonal Diurnal Contour of Total Carbonyl for Kolkata (Winter)

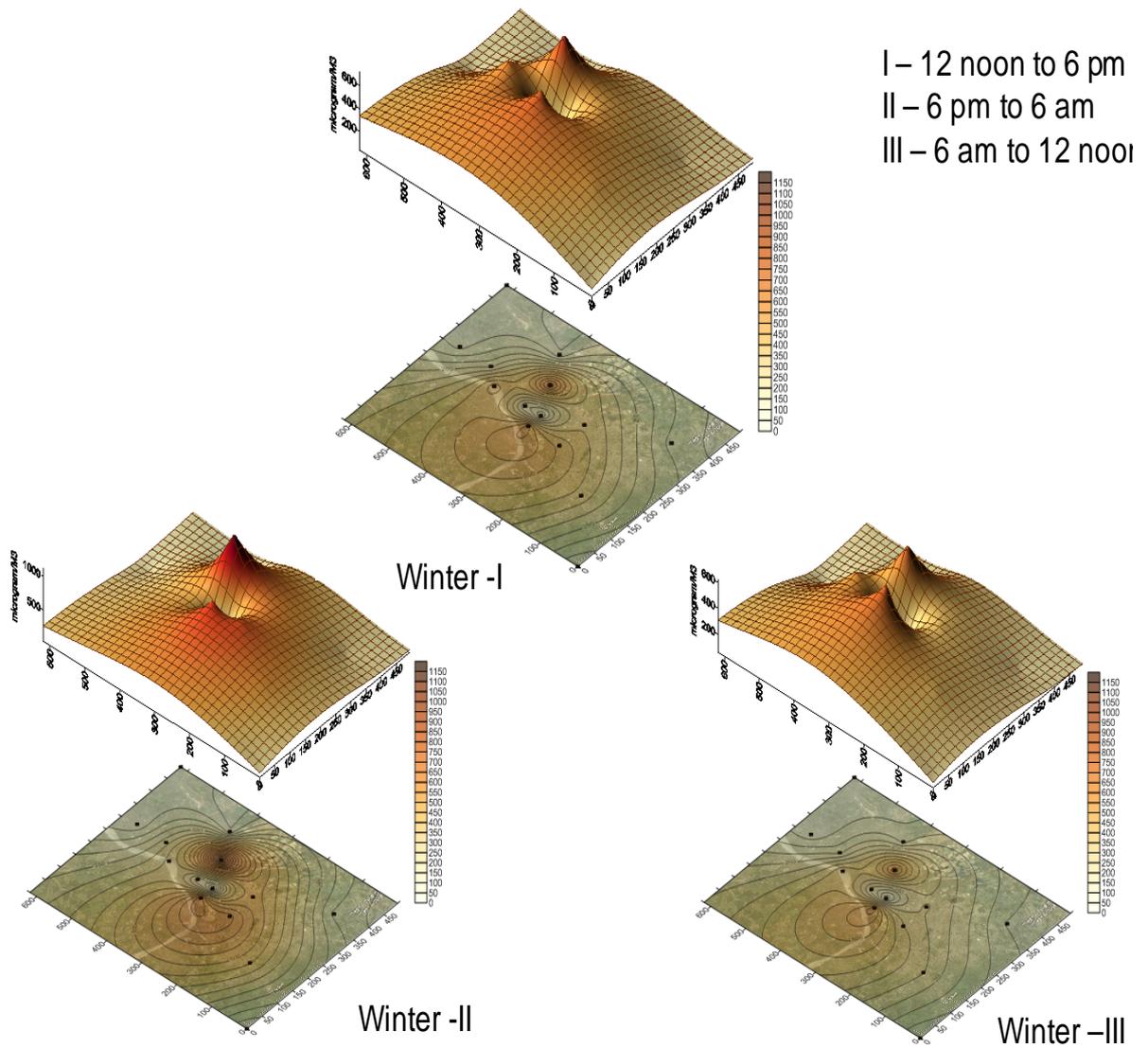


Figure 5.14: Seasonal Diurnal Contour of Total Non Carbonyl VOCs (Winter)

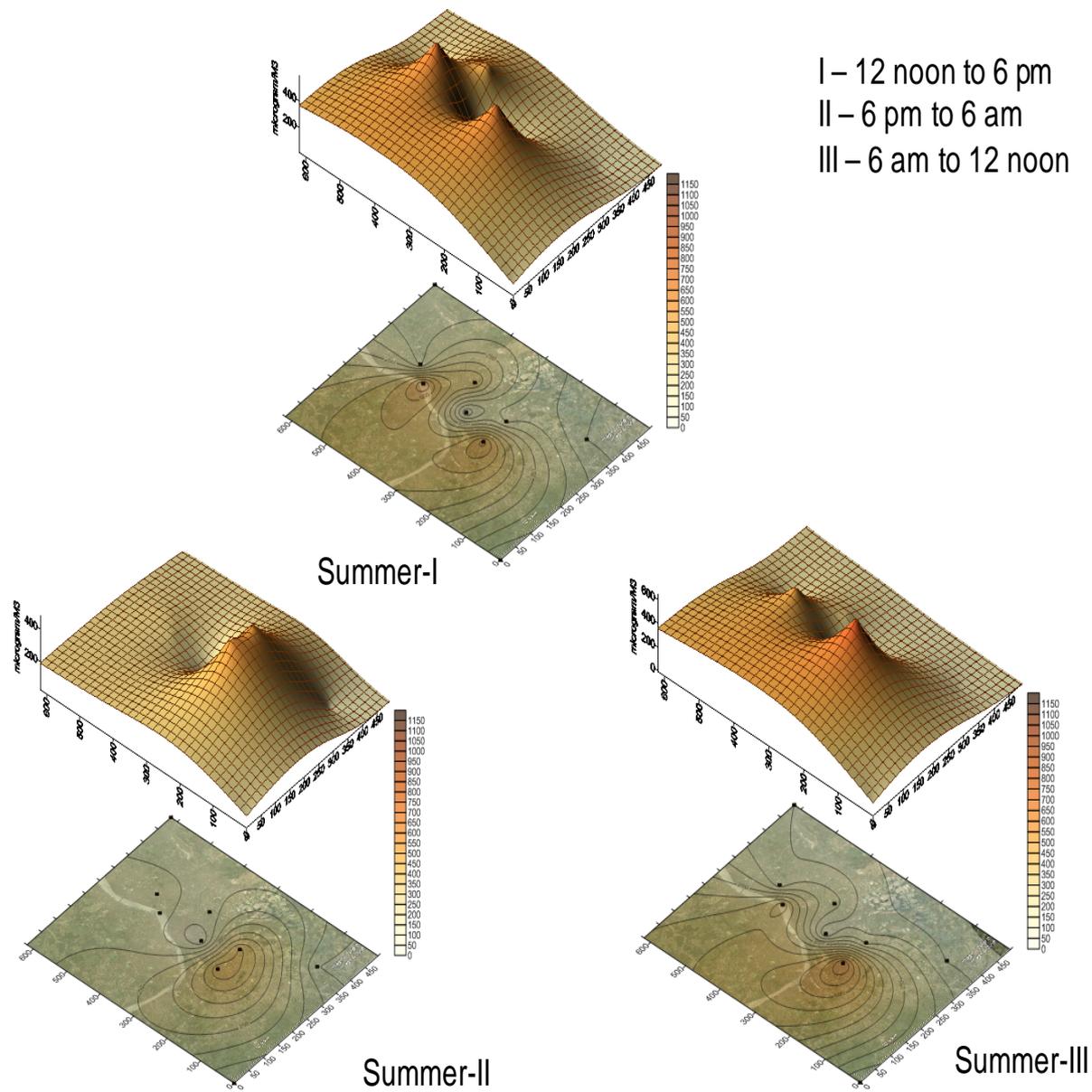


Figure 5.15: Seasonal Diurnal Contour of Total Non Carbonyl VOCs (Summer)

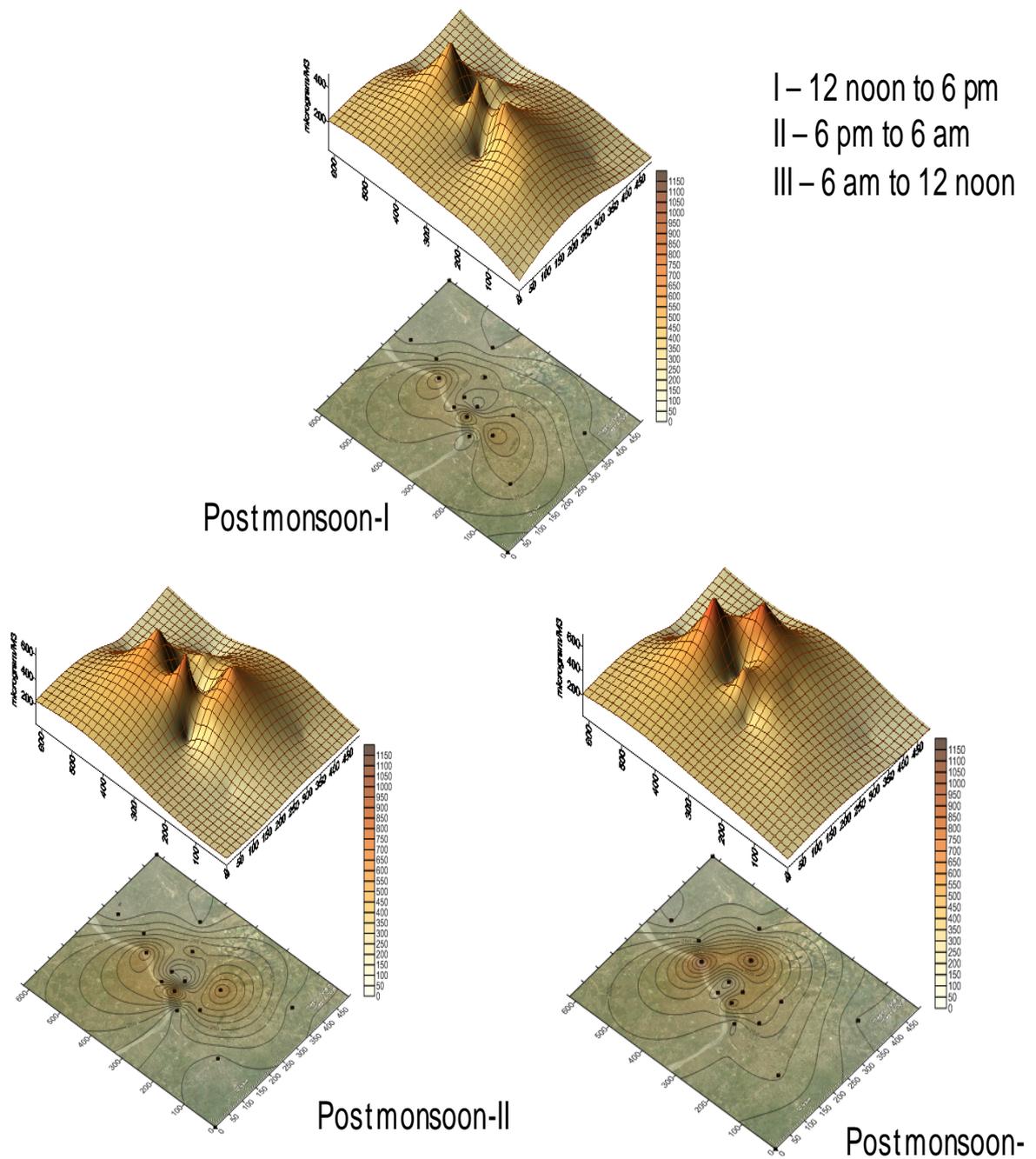


Figure 5.16: Seasonal Diurnal Contour of Total Non Carbonyl VOCs (Post Monsoon)

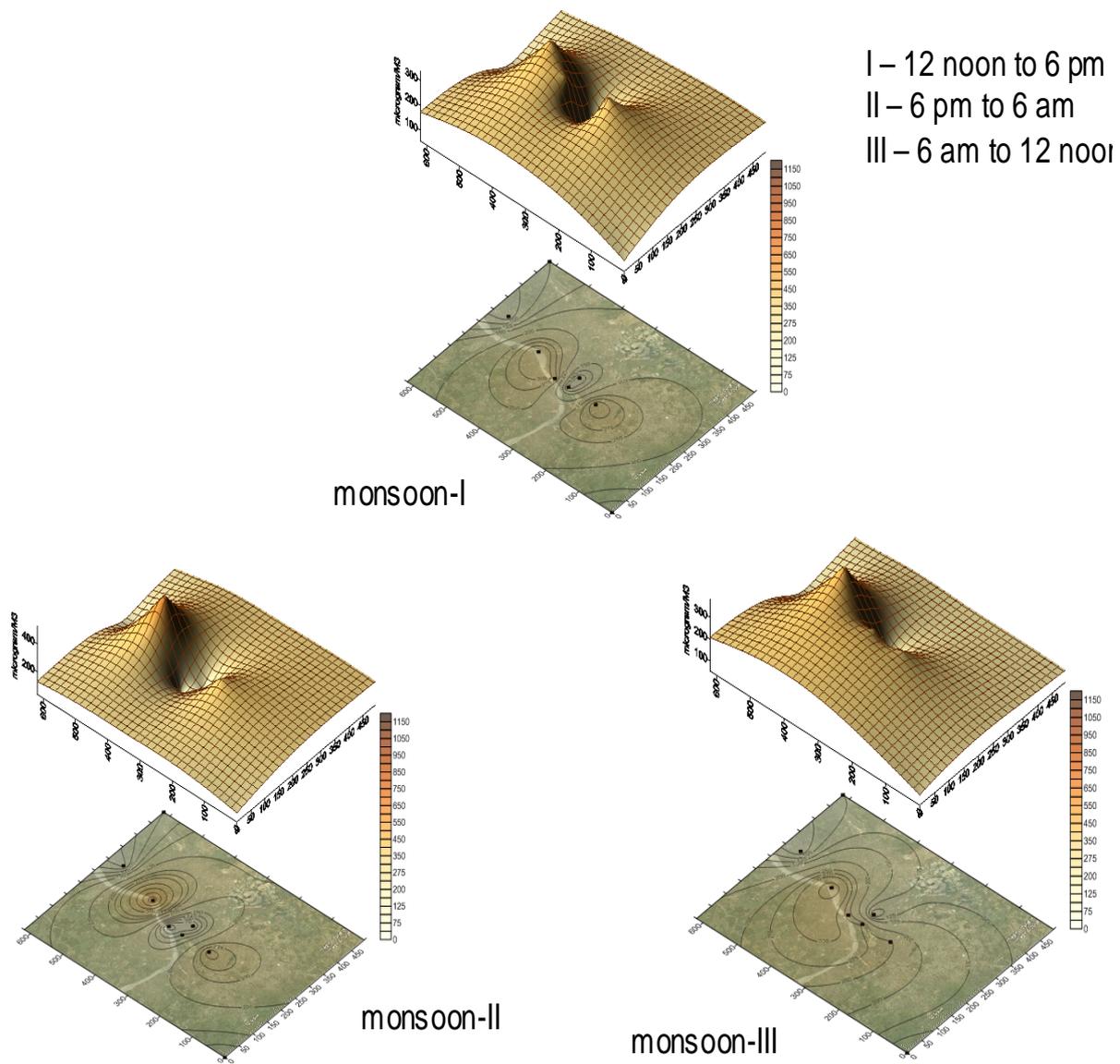


Figure 5.17: Seasonal Diurnal Contour of Total Non Carbonyl VOCs (Monsoon)

5.1.2 Effects of Festival season on mixing ratios of VOCs

The festival season in Kolkata was covered separately. **Figure 5.18 and 5.19** depict species wise and total carbonyl VOC level pre and post festival season. Except at Cossipore, Baithakkhana (both industrial locations) and Theater road (Petrol Pump) at all the locations the total carbonyl VOC level was found to be more in post festival season compared to pre-festival season although the levels of total non carbonyl VOCs do not vary significantly. The increase in total carbonyl VOCs level varied from 27% in Bosepukur to 170% in Alipur. Comparison of levels of individual VOCs during pre and post festival season m, & p-tolualdehyde level was found to have increased 62 and 36 time respectively. The other components have increased 1 to 5 times.

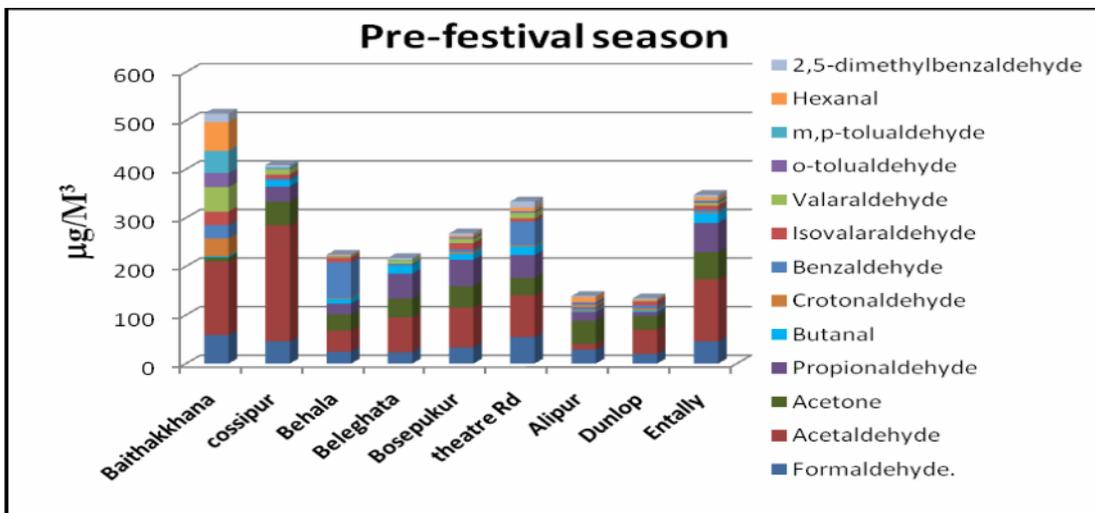


Figure.5.18: Species Wise and Total Carbonyl VOC Level During Pre Festival Season

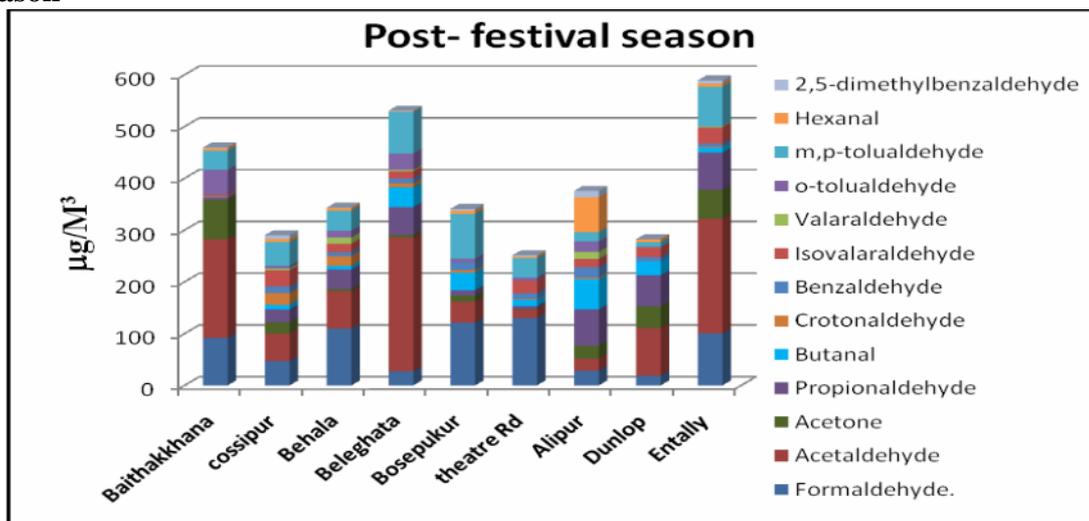
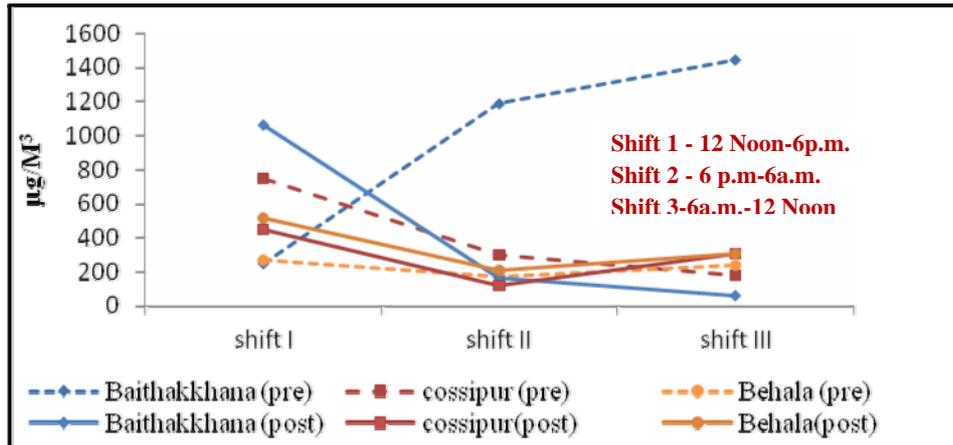


Figure.5.19: Species Wise and Total Carbonyl VOC Level during Post Festival Season

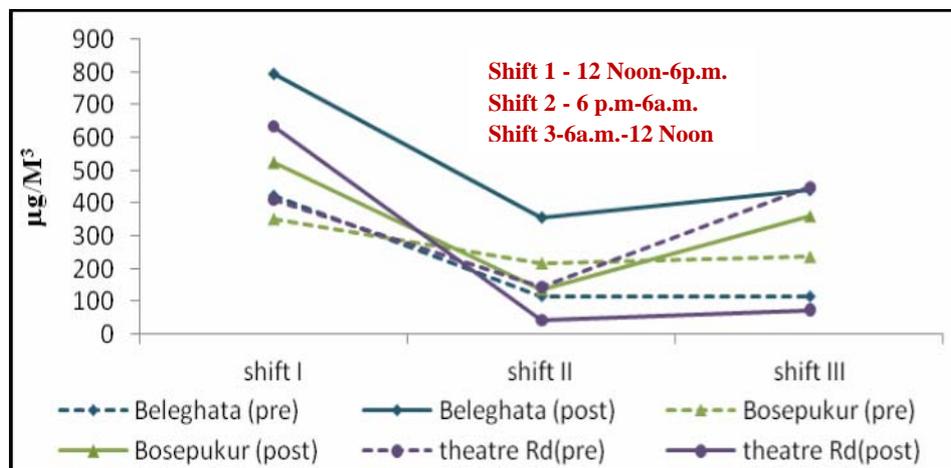
Diurnal variation: Figure 5.20 represent the difference in diurnal variation of total carbonyl VOCs level pre and post festival season. Overall average diurnal trend (lower at night time and higher in daytime) was not found to have altered during pre and post season. The total carbonyl VOC levels have been found to increase in many case and decrease in a few case at the Petrol pump and Industrial locations. There are different specific major sources of carbonyls at these sites depending upon the activities prevalent in these areas. During the festival season, the number of cars on the road is markedly decreased due to long holiday-closure in school, colleges, and other institution as a result refueling also decreases. Also the small scale industries operating within the city are closed a major part during this period. The units which are operating do not do so in full capacity during this period. Total carbonyl VOC levels observed at these locations represent the mixed effect of change in regular activity and special activities of this season; as a result no clear trend is observed. However total carbonyls VOC levels have increased in all instances from pre to post festival season at all the locations. There is no specific source (other than city background) of carbonyls in these areas and it can be inferred that the special activities during the festival season has increased the total carbonyl VOC level in these area.

Immediate effect of fireworks on VOC levels:

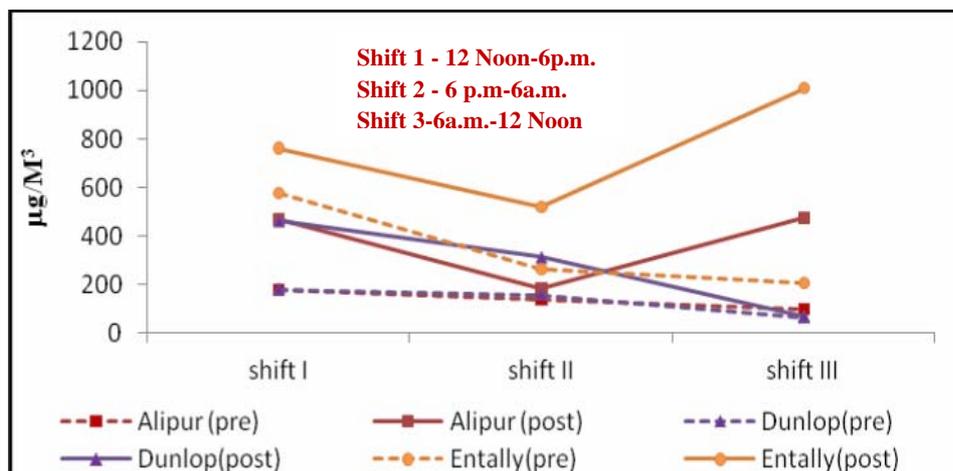
Figure 5.21& 5.22 compares respectively the average level of individual and sum of the quantified VOCs both non carbonyls and carbonyls in air on the night of Diwali with the same on the night before. The total carbonyl VOC levels are found to increase significantly on Diwali night as compared to the previous night. The total non carbonyl VOCs quantified was also found to be high on the Diwali night but not significantly. The contours in figure... depict the level of total non carbonyl VOCs and carbonyl compounds estimated in city air during the study. The average level for all the VOCs, Carbonyl and non carbonyl, were found to be elevated except naphthalene which found to decrease by 32%. Carbonyls are found to be more affected by the event than non-carbonyl VOCs. The increase in average level of carbonyls varied from 10% for benzaldehyde to 407% for acetone whereas among non-carbonyl VOCs the average level increased from 5% for styrene to 81% for toluene.



a) Industrial Locations



b) Petrol Pumps



c) Residential Cum Commercial Locations

Figure.5.20: Diurnal Variation of Total Carbonyls VOCs During Pre and Post Festival Season

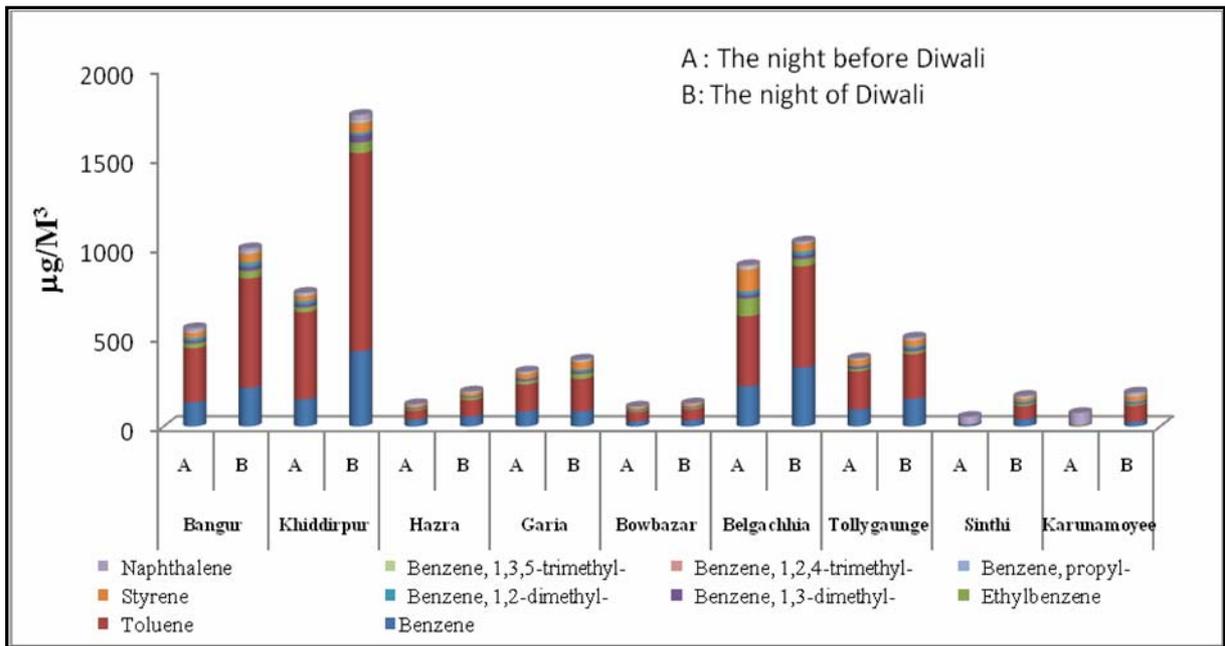


Figure.5.21: Average Level of Individual Non Carbonyl VOCs in Air on The Night of Diwali & The Night Before

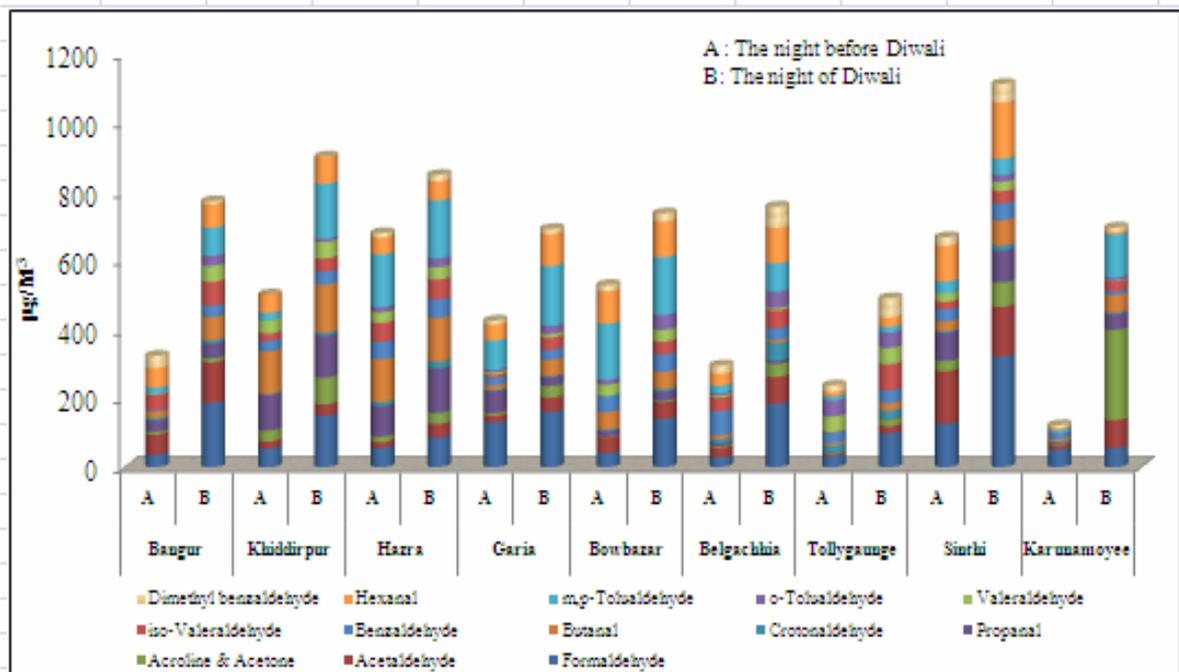


Figure.5.22: Average Level of Individual Carbonyl VOCs in Air on The Night of Diwali & The Night Before

5.1.3 Status of NO₂ at ambient air of Kolkata:

The present studies are mainly focused on volatile organic pollutants and lower atmospheric Ozone in Kolkata's ambient air. However NO₂ concentration is closely related with Ozone formation chemistry so NO₂ was also monitored alongside of ozone. The following figures (**Figure 5.23 to 5.26**) depict the seasonal as well as diurnal distribution of NO₂ concentration in different category of sites. It is observed that the average level of NO₂ is quite low in all Kolkata air. The level is consistently lower than 80 µg/M³ which is the permissible limit of NO₂ (24 hr Average); (National Ambient Air Quality standard, CPCB, 2009)

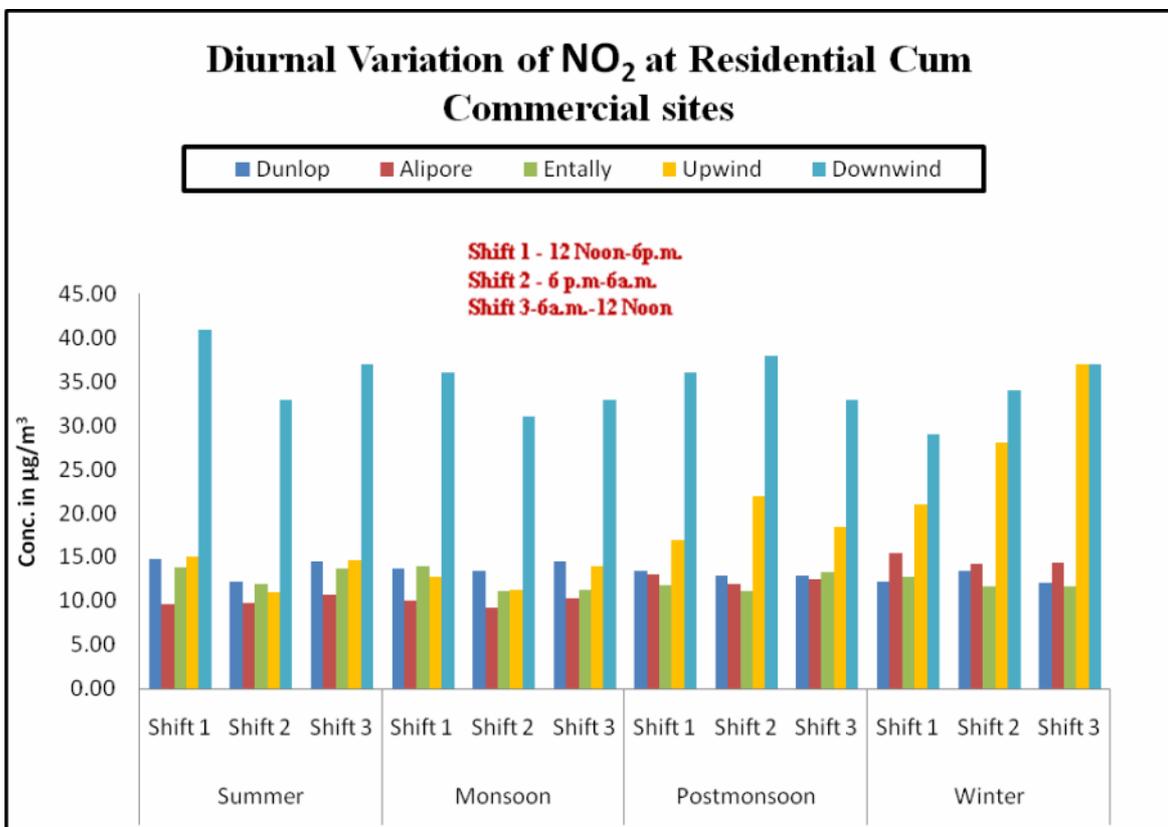


Figure 5.23: Diurnal Distribution of NO₂ in Residential Cum Commercial Location

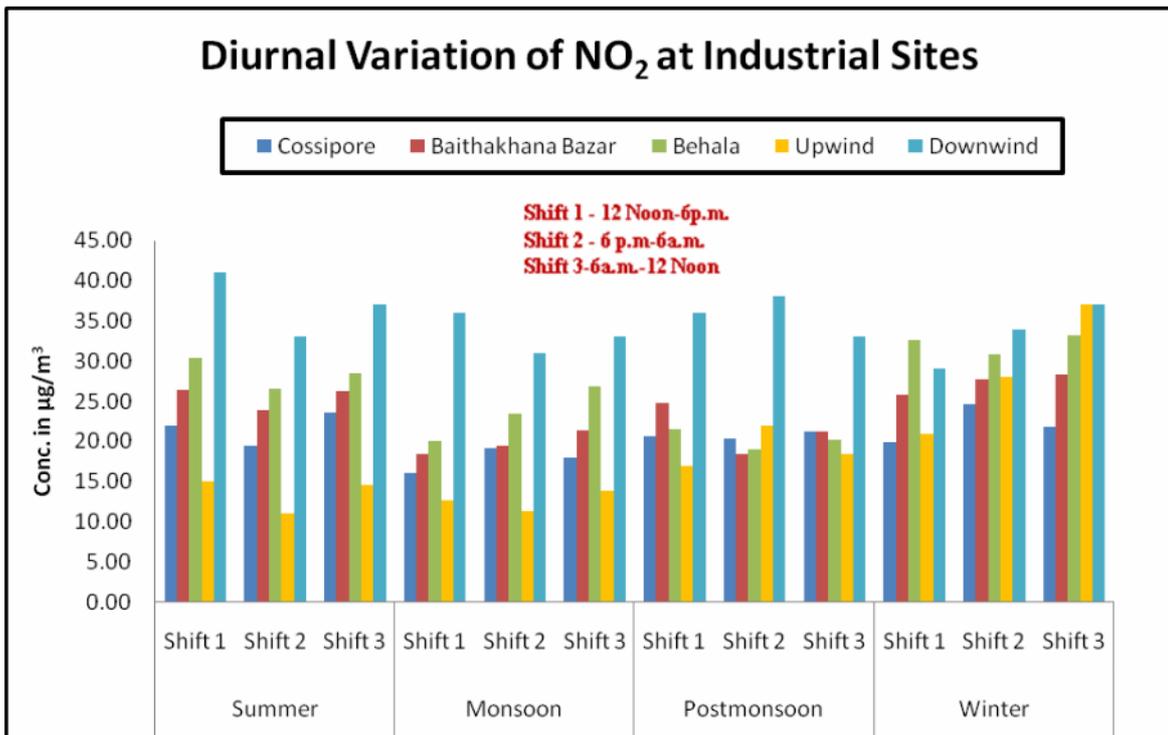


Figure 5.24: Diurnal Distribution of NO₂ in Industrial Location

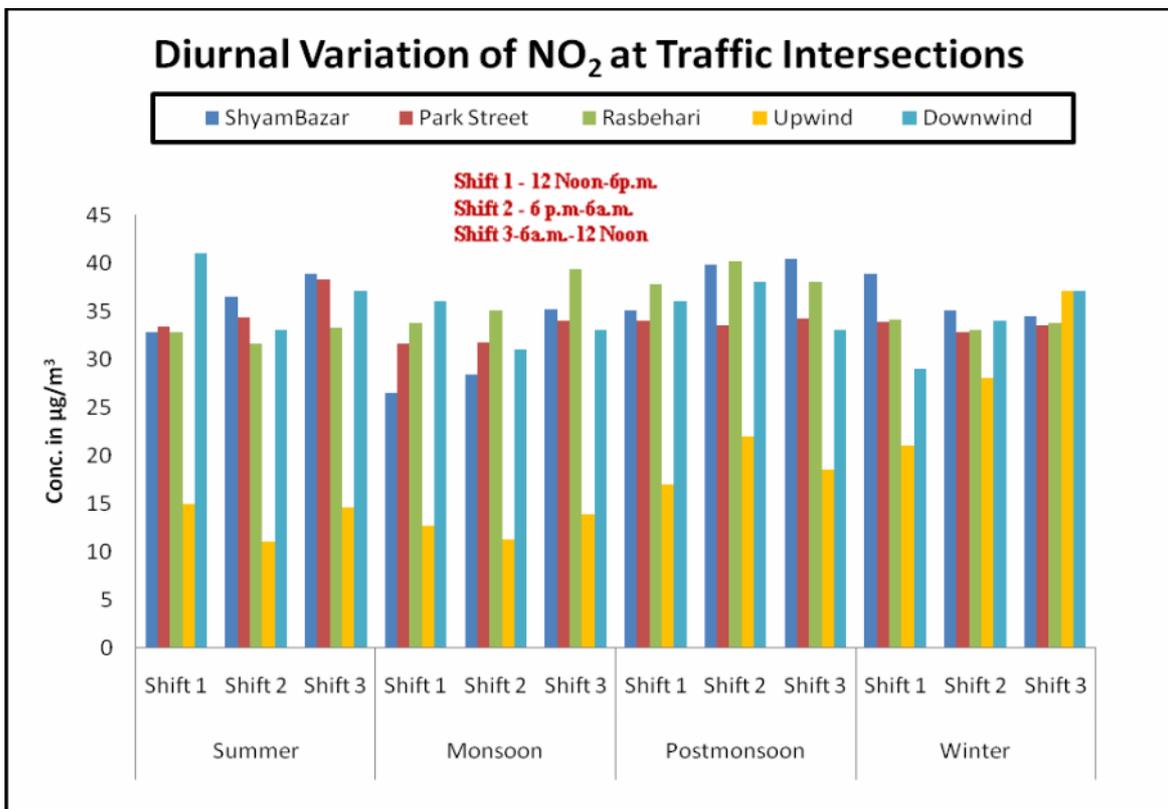


Figure 5.25: Diurnal distribution of NO₂ in Traffic Intersection

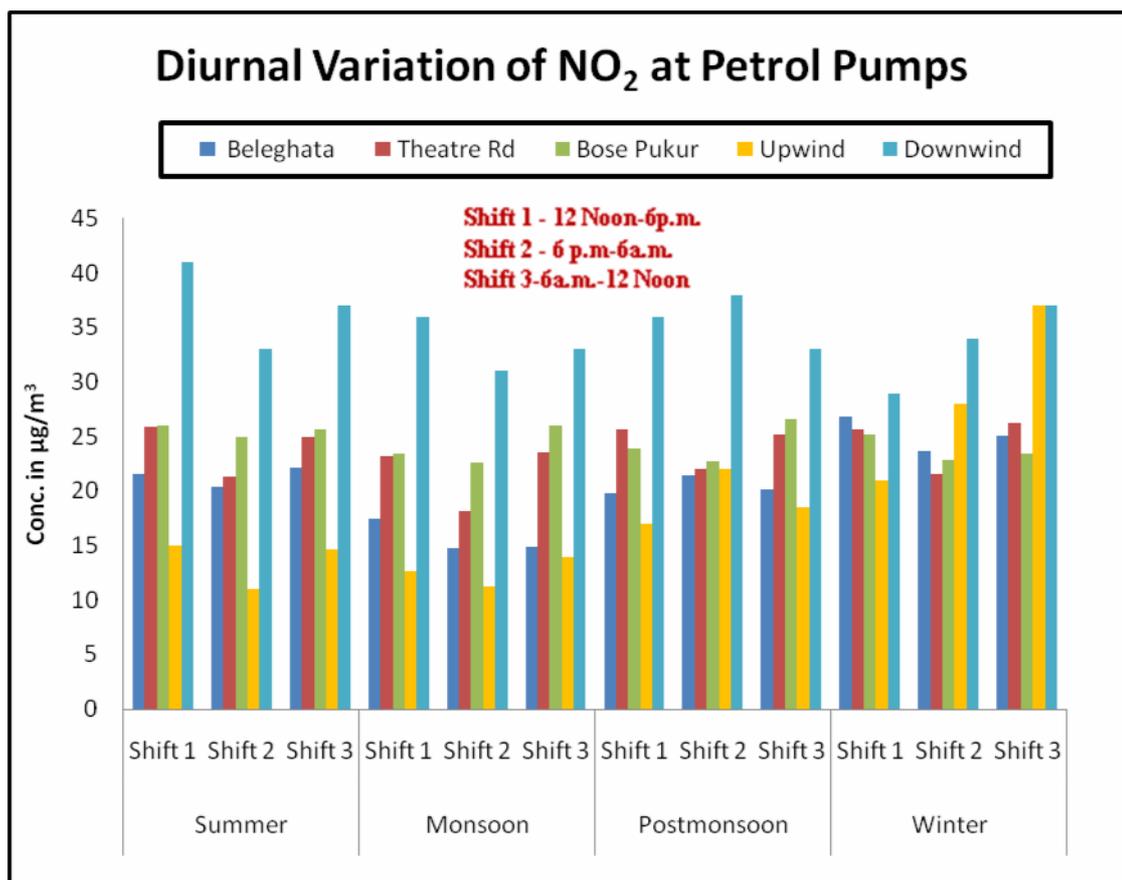


Figure 5.26: Diurnal Distribution of NO₂ in Petrol Pumps

5.1.4 Status of Ozone concentration in ambient air of Kolkata

Monitoring of ambient ozone was done at all the selected sampling locations on 24 hourly basis for all the months. The following figures (**Figure 5.27 to 5.30**) show the monthly diurnal variation of ozone concentration at all the sites during the study period.

Percentile distribution of hourly concentration of ozone (**Figure 5.31 to 5.34**) shows that from November to May 95 percentile values crossed 100 µg/m³ at residential areas. At industrial locations excepting at Behala 100 µg/m³ was never exceeded. At Behala this concentration was exceeded 5 percent times during July and December to March. At traffic intersections only at RashBehari crossing in the month of February violation from standard of 100 µg/m³ was observed 5 percent times. At all petrol pumps ozone concentrations exceeded 100 µg/m³ 5 percent times in the month of July.

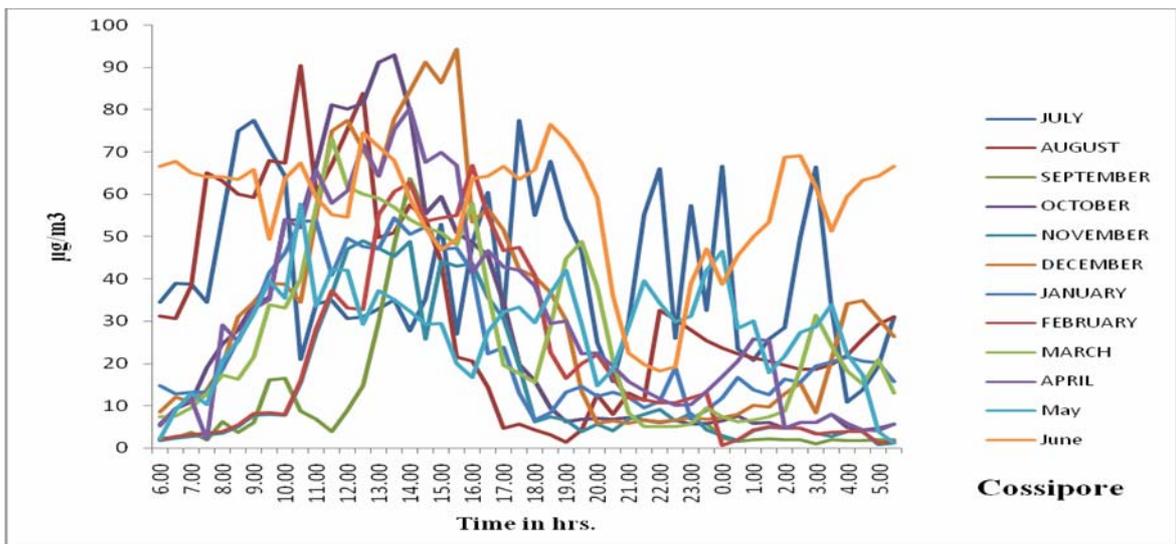
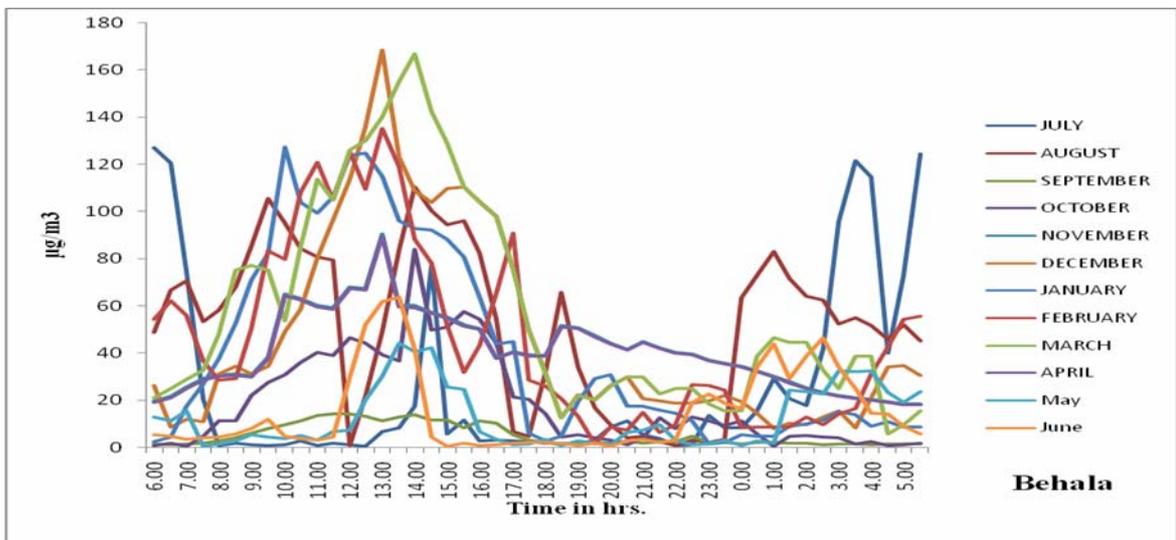
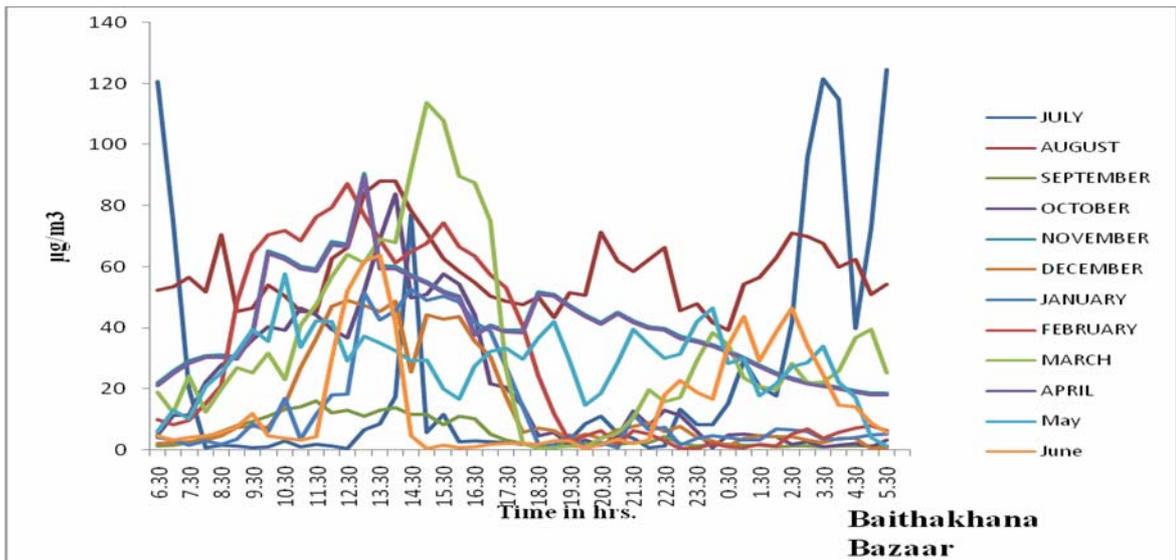


Figure 5.27: Monthly Diurnal Variation of Ozone in Industrial Locations

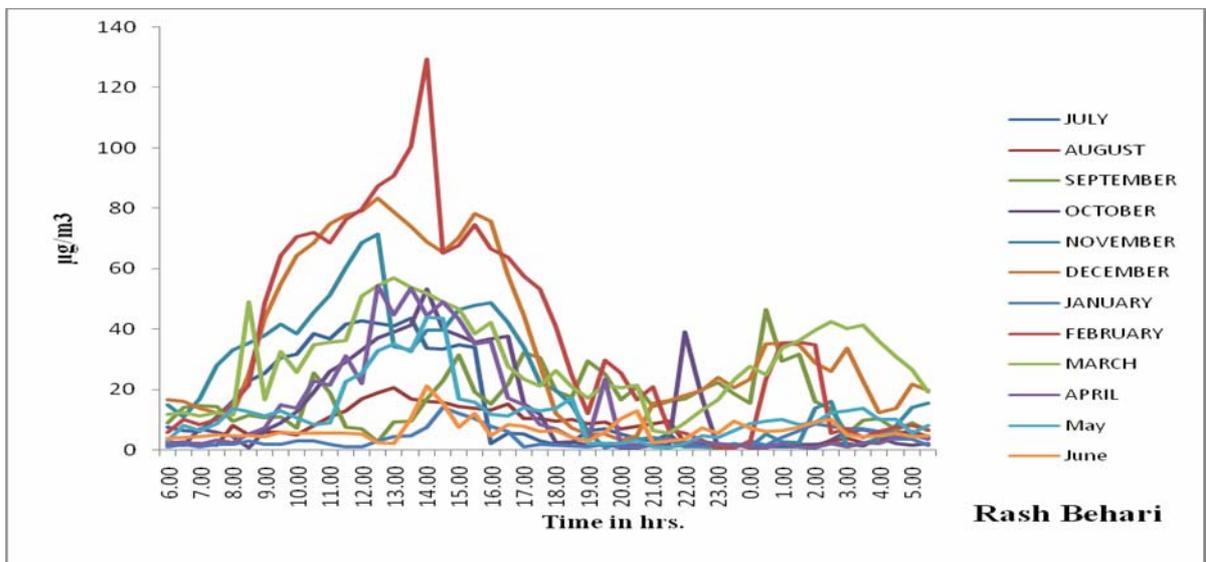
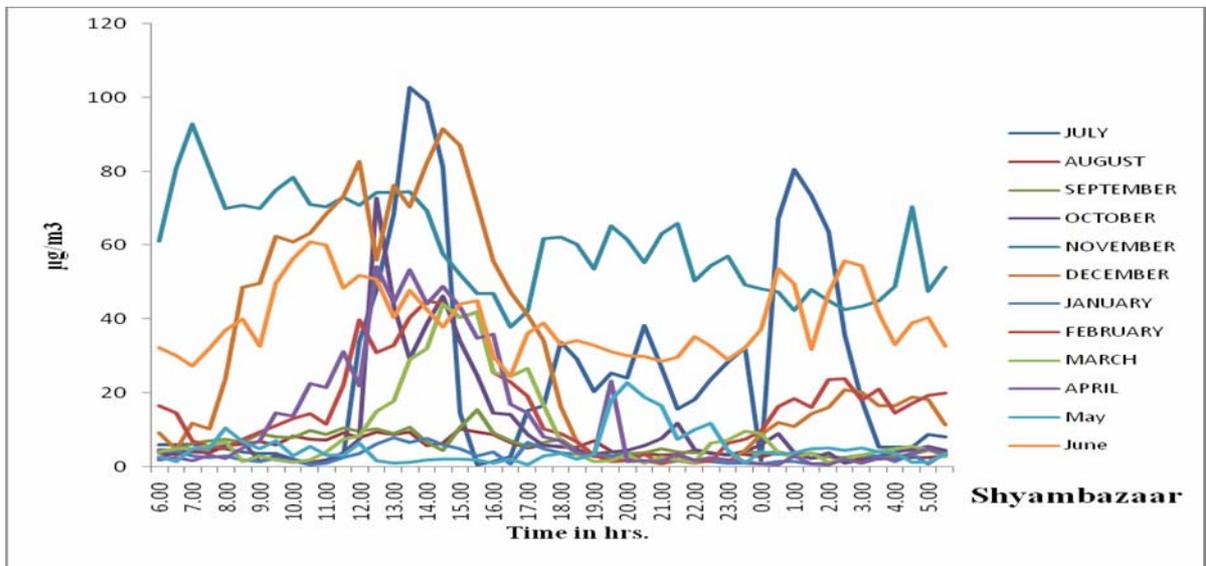
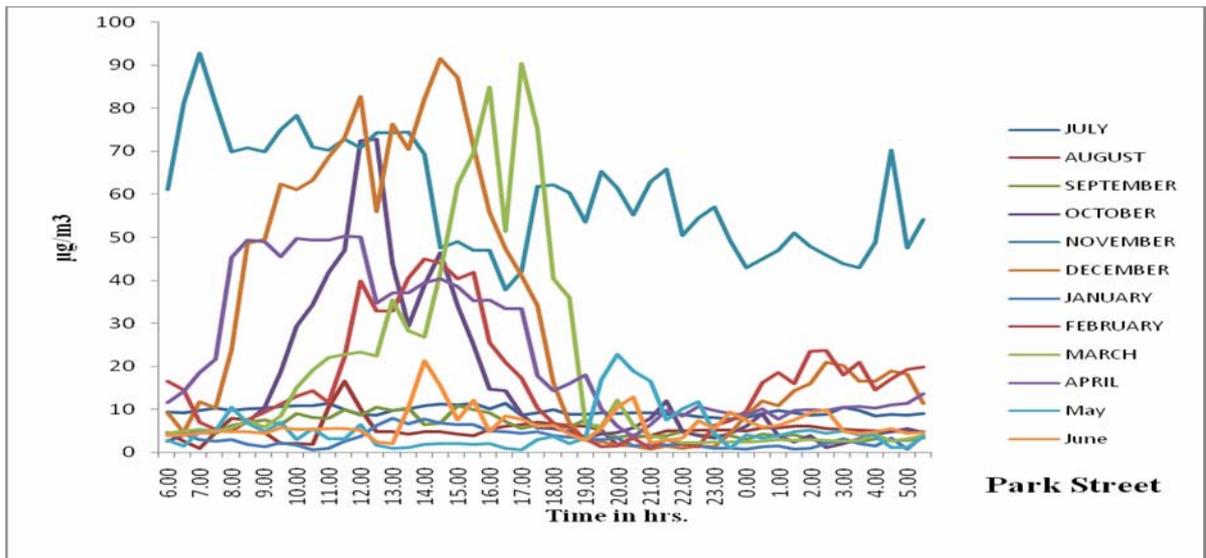


Figure 5.28: Monthly Diurnal Variation of Ozone at Traffic Intersection

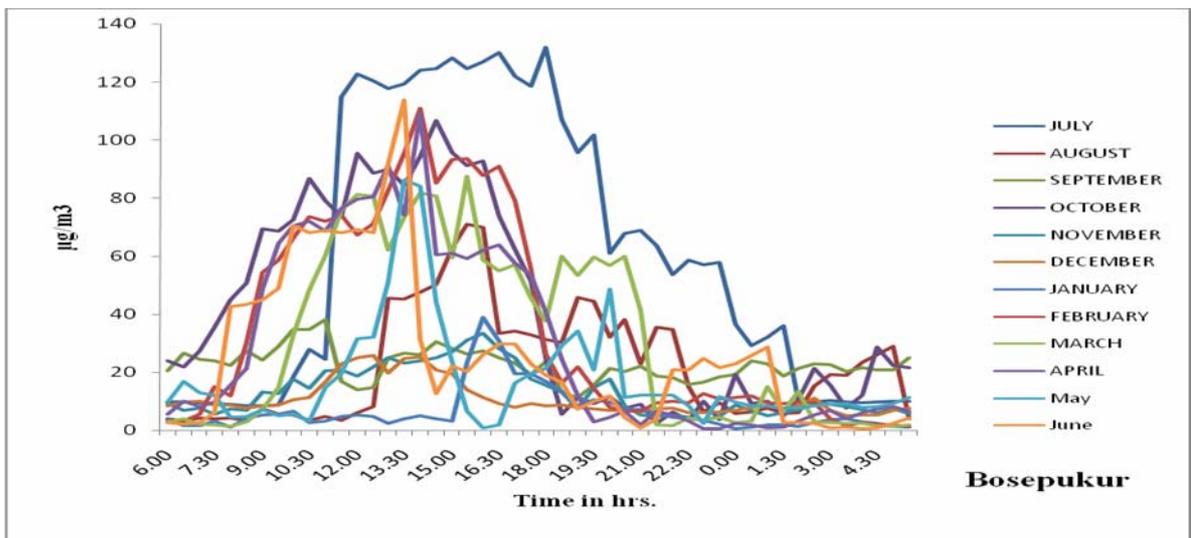
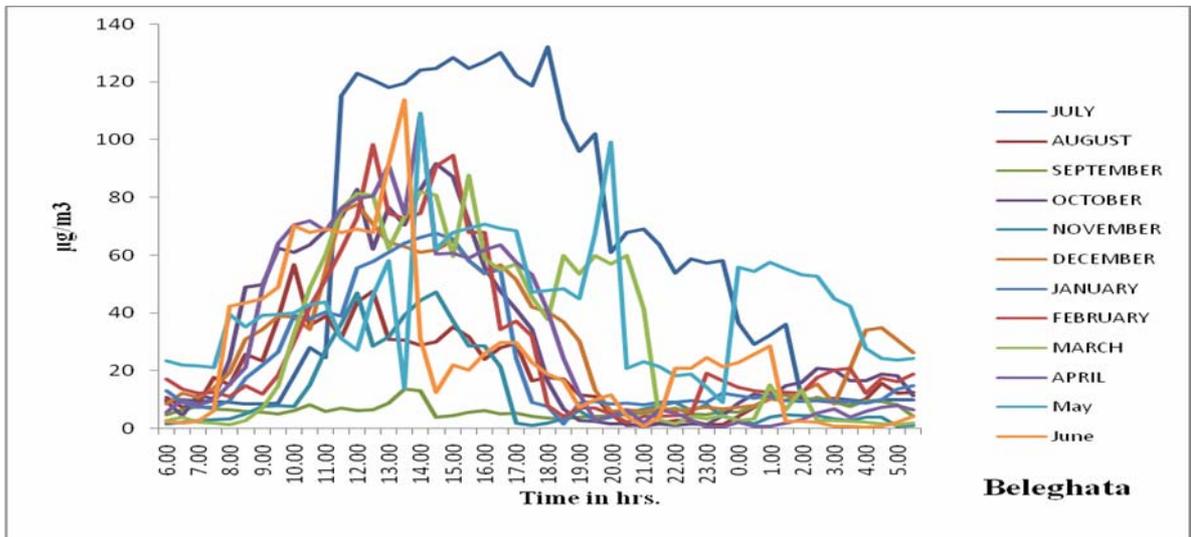
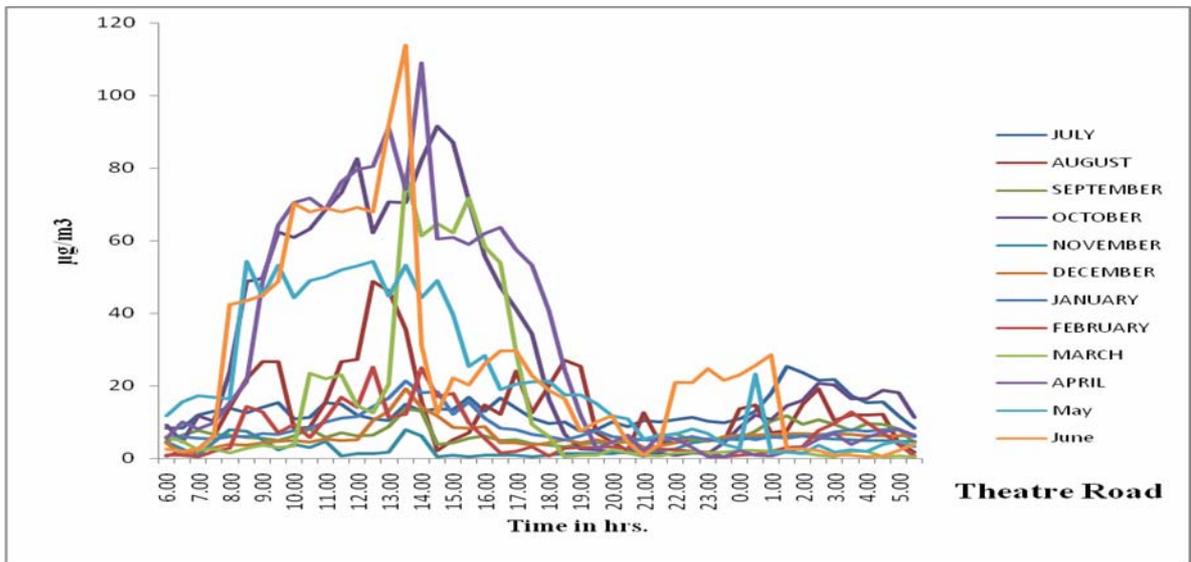


Figure 5.29: Monthly Diurnal Variation of Ozone at Petrol Pumps

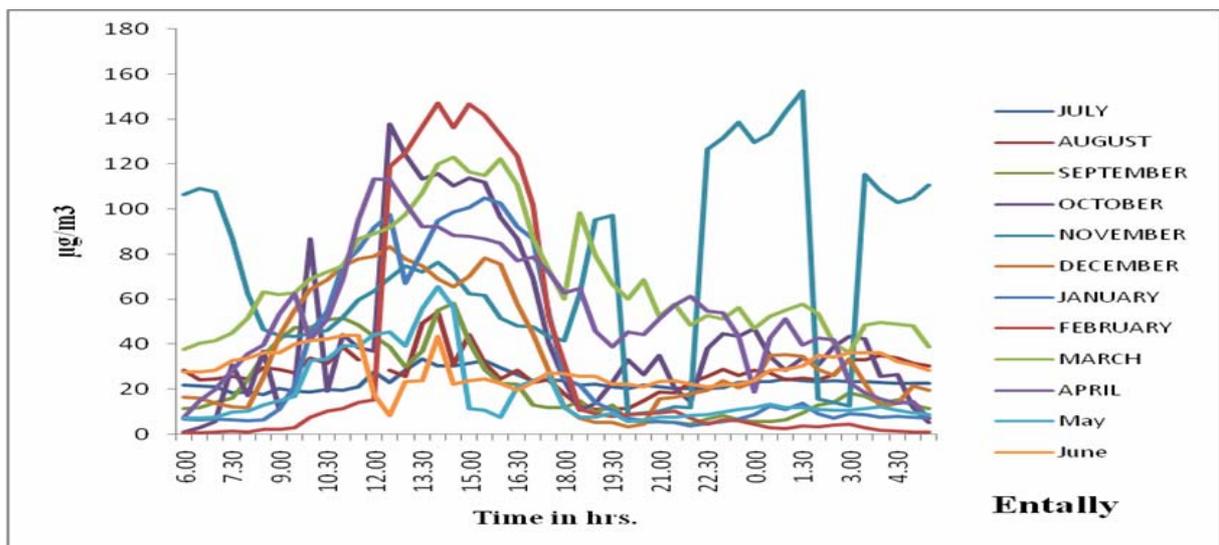
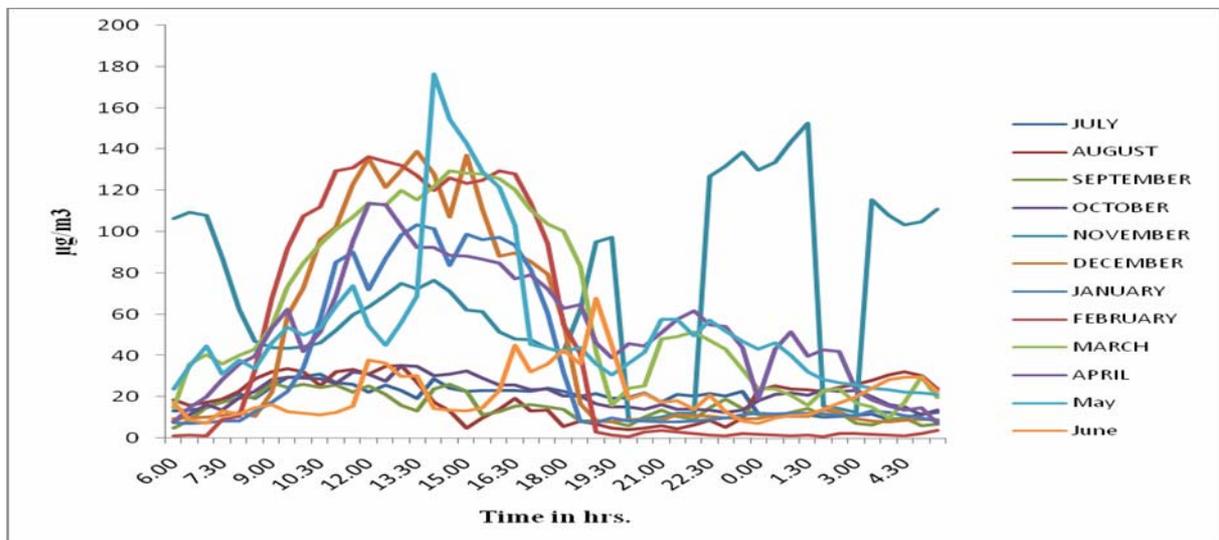
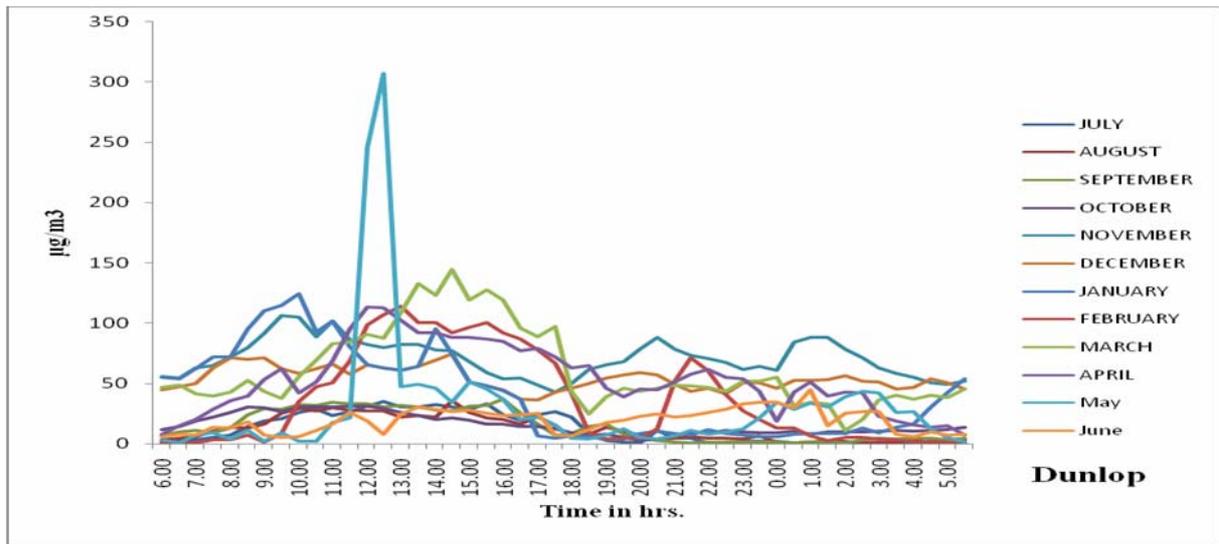


Figure 5.30: Monthly Diurnal Variation of Ozone at Residential Cum Commercial Locations

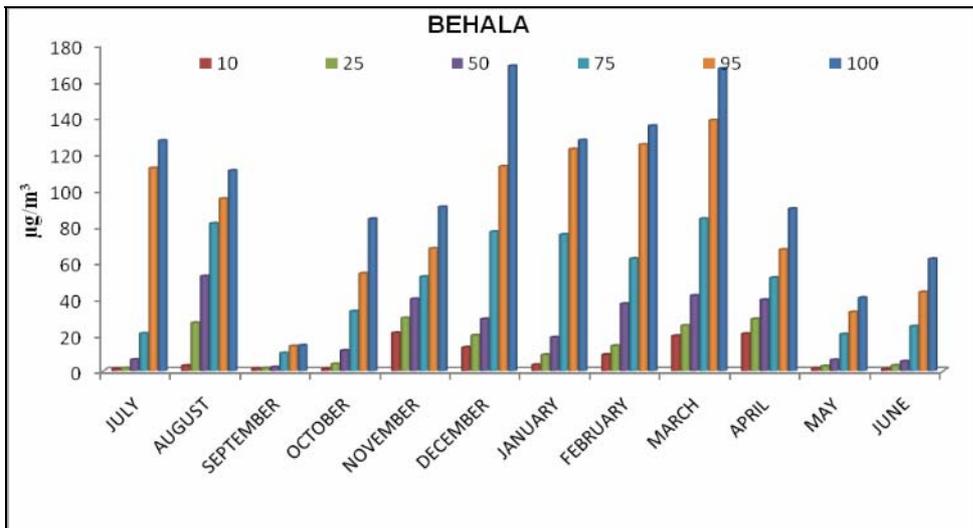
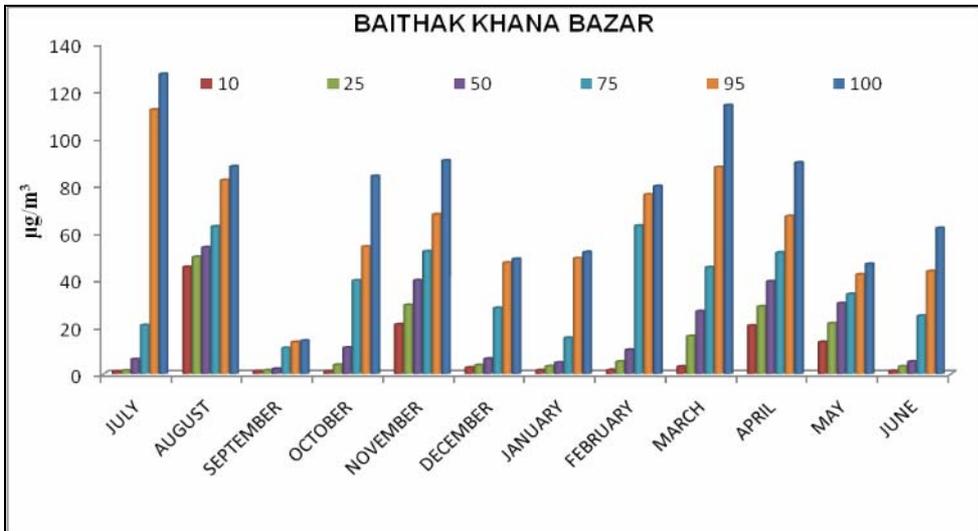
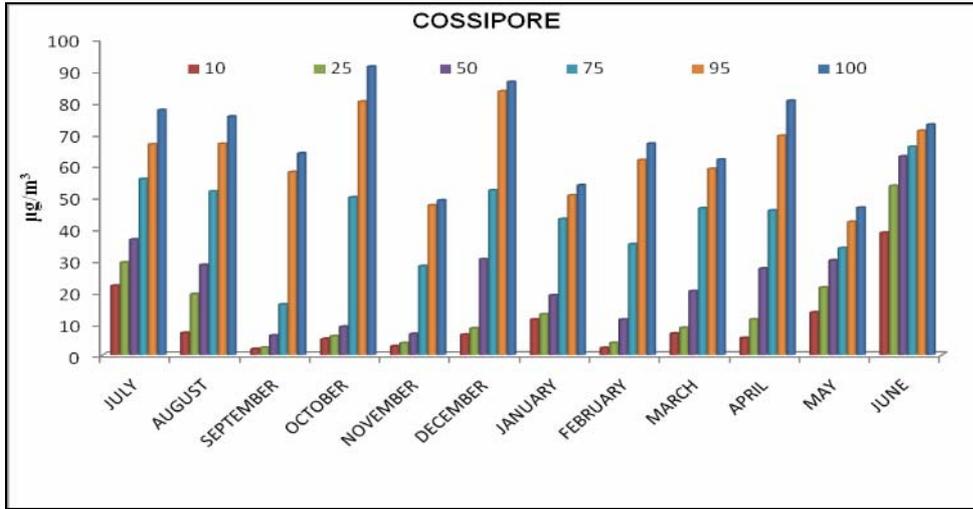


Figure 5.31: Percentile Distribution of Hourly Concentration of Ozone (Industrial Locations)

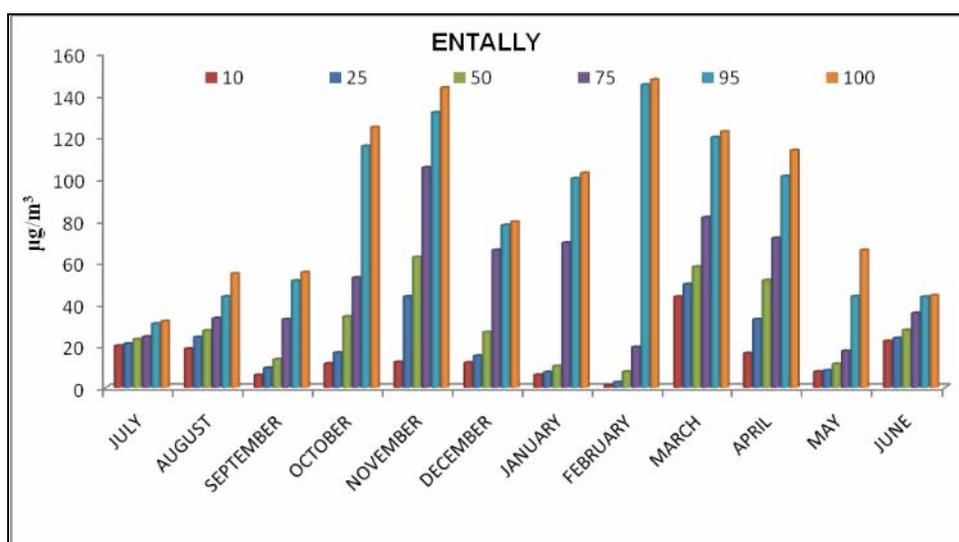
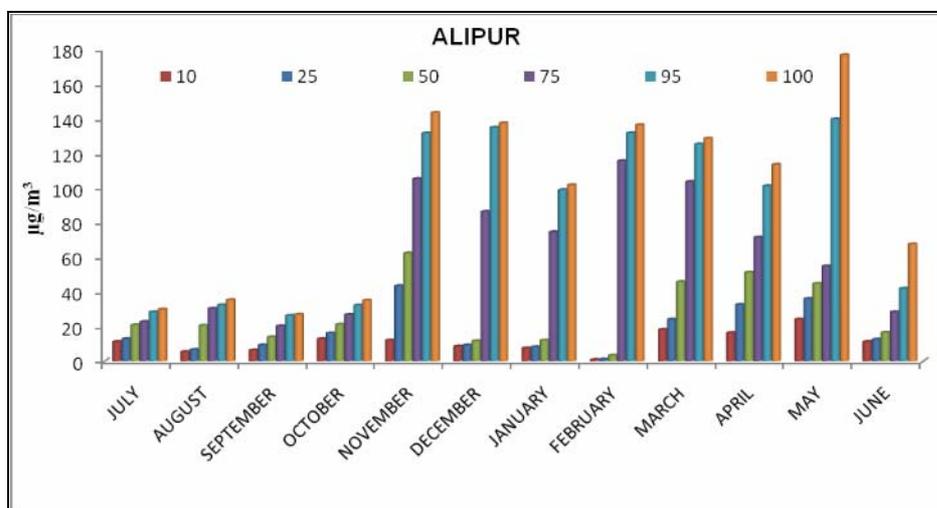
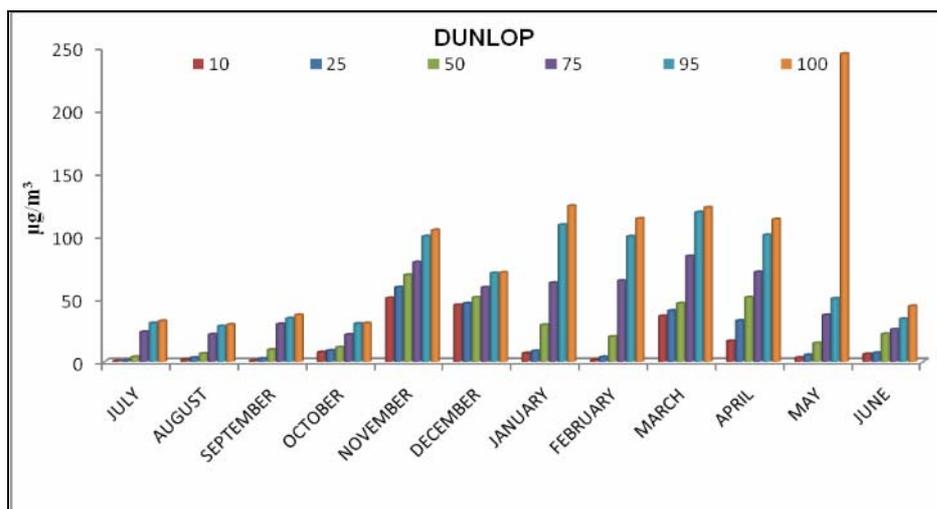


Figure 5.32: Percentile Distribution of Hourly Concentration of Ozone (Residential Cum Commercial Locations)

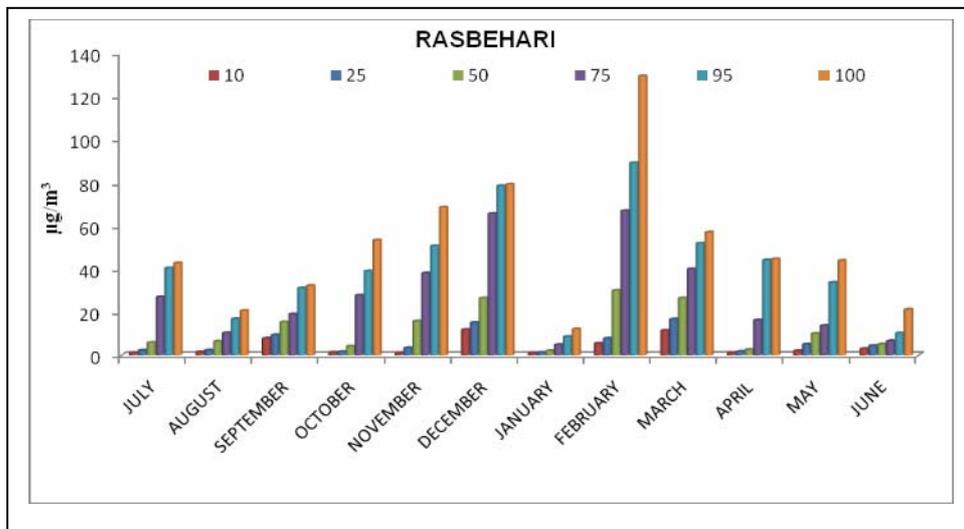
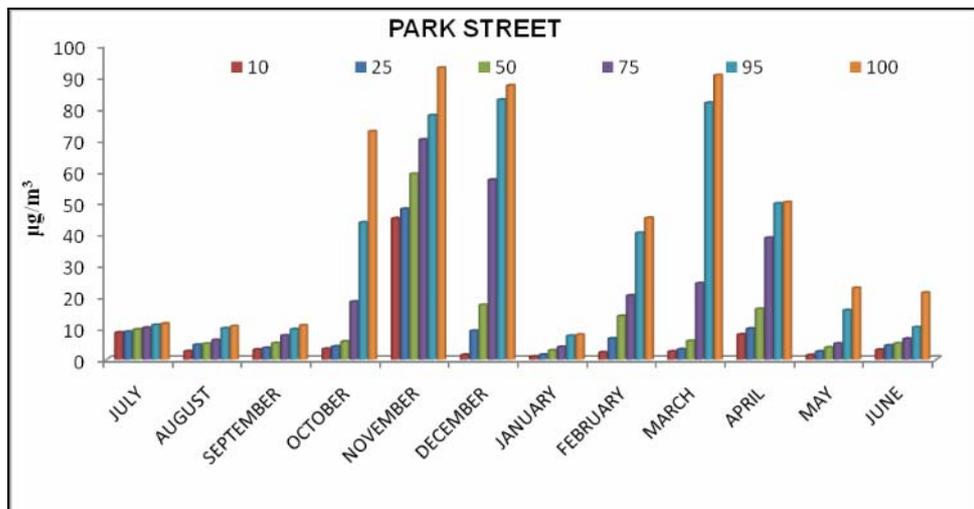
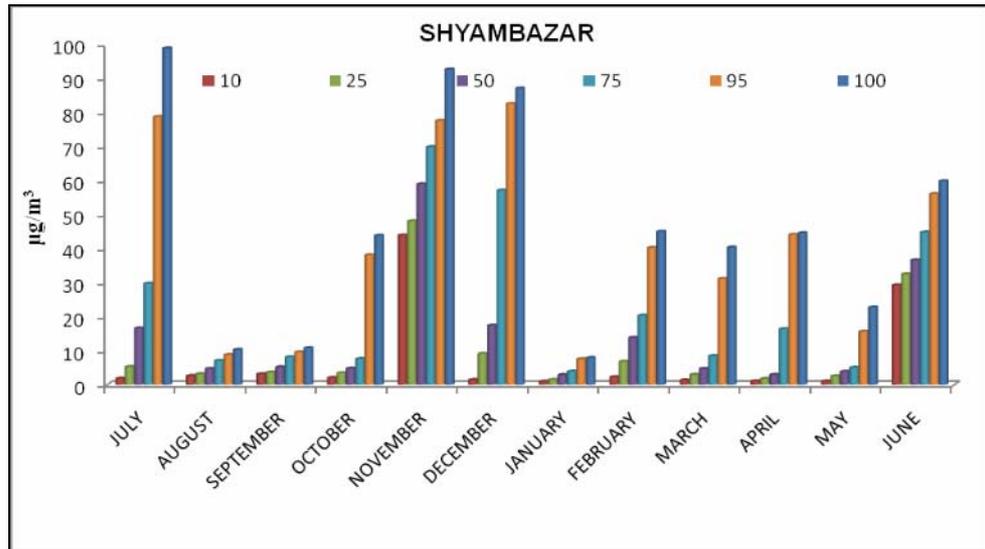


Figure 5.33: Percentile Distribution of Hourly Concentration of Ozone (Traffic Crossings)

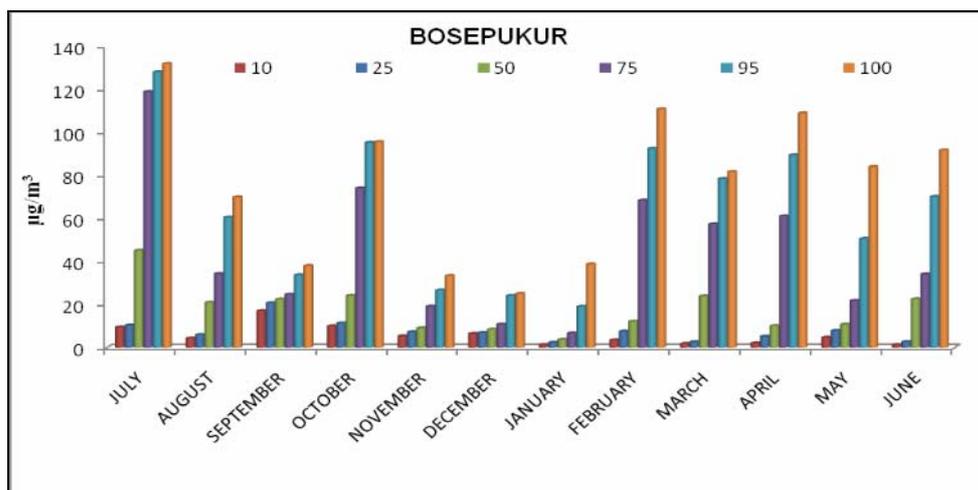
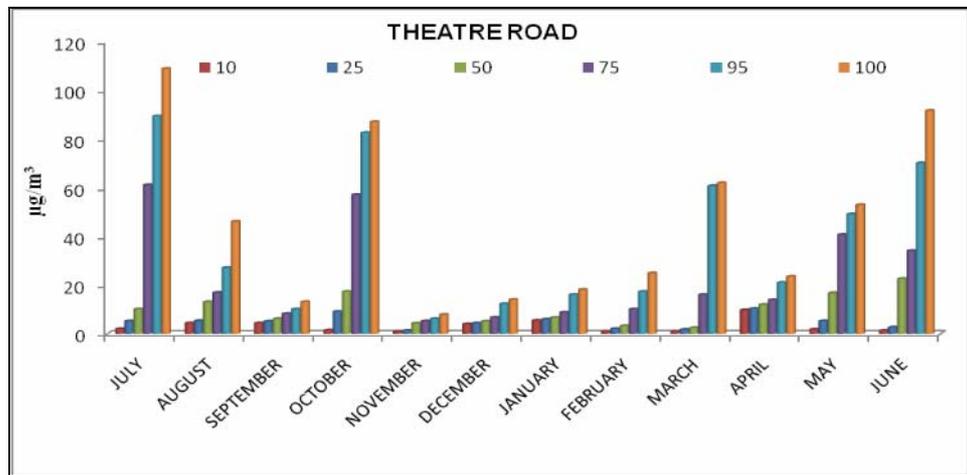
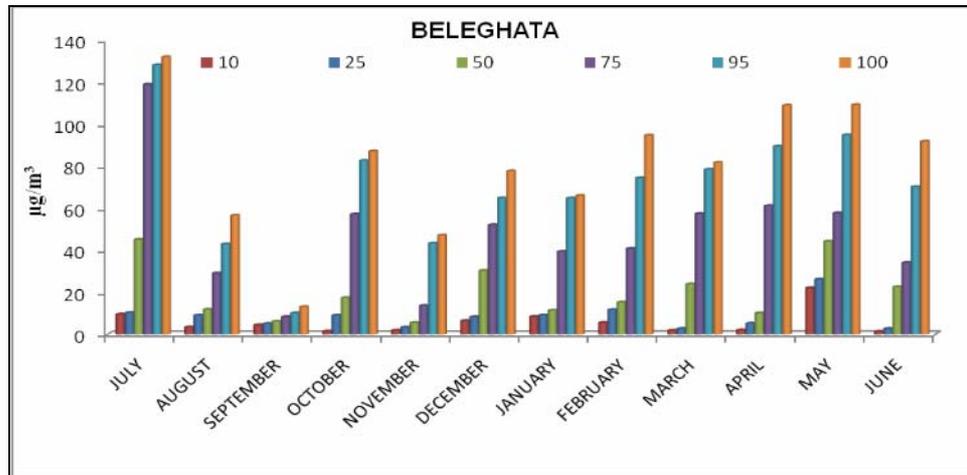


Figure 5.34: Percentile Distribution of Hourly Concentration of Ozone (Petrol Pumps)

5.2 Discussion

VOC/ NO₂ ratios observed in Kolkata are primarily high indicating NO₂ sensitive conditions. High rate of VOC emissions (due to local activity like biomass burning, roadside cooking etc) increases the ratio of VOC to NO₂ and makes NO₂-sensitive conditions more likely.

Instantaneous photochemical ozone formation, P(O₃) can be computed as the O₃ production rate as a function of NO₂ concentration. The chemical production rate of ozone is defined as

$$P(O_3) = d(Ox)/dt \quad \dots\dots\dots(1)$$

Where,

$$Ox = O(1D) + O_3 + NO_2 \quad \dots\dots\dots(2)$$

During the daytime NO₂ can be reasonably assumed to achieve a steady state so that $d(Ox) = d(O_3)/dt$. It is commonly believed that the O₃ production rate increases at low NO₂ until a maximum is reached and then decreases at high NO₂. **Figures 5.35 to 5.38** shows similar behavior for urban air of Kolkata. Negative values of P(O₃) have been observed during 06 pm to 06 am during all seasons.

This behavior occurs because high NO₂ promotes removal of OH radicals by reaction with NO₂ and hence reduces photochemical O₃ formation. In addition to NO₂, P(O₃) is also dependent on VOC reactivity, sunlight, and radical precursors.

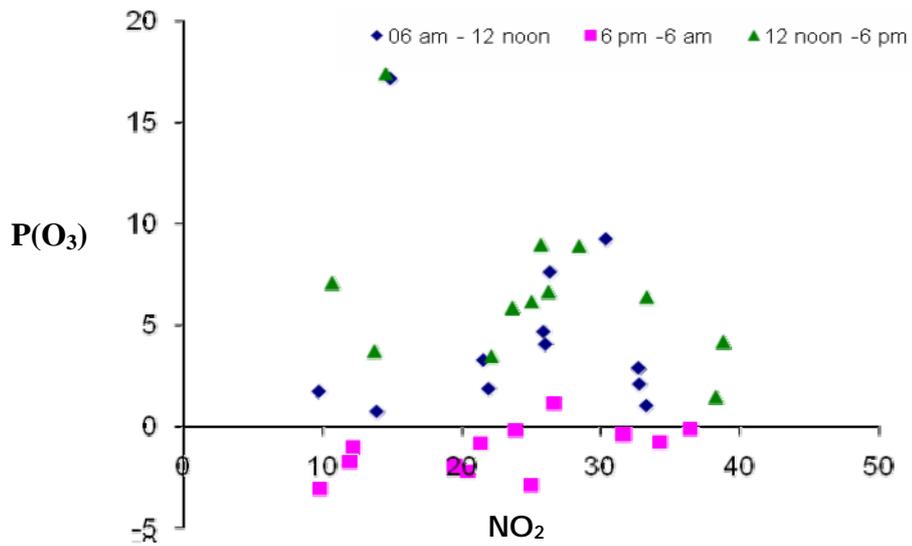


Figure 5.35: Instantaneous Ozone Production in Kolkata With Respect to NO_2 During Summer

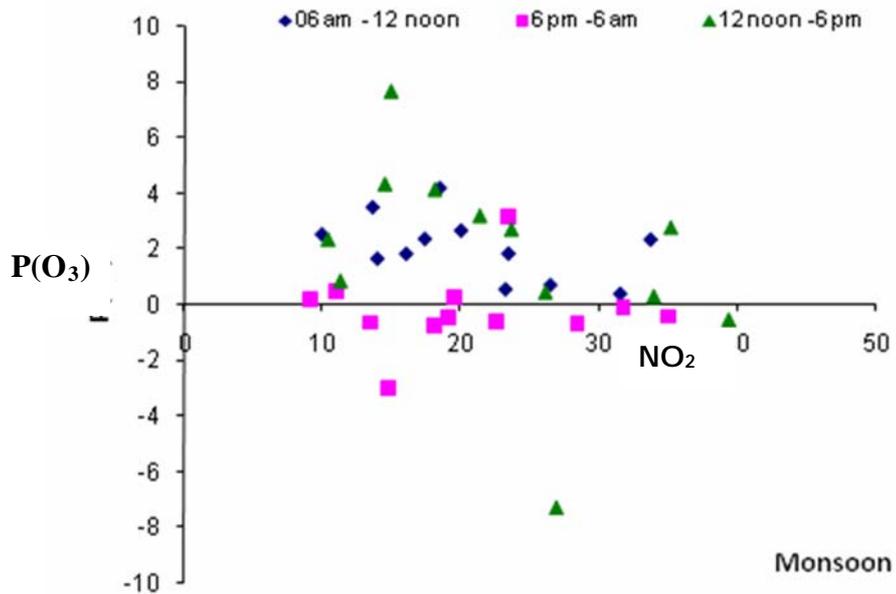


Figure 5.36: Instantaneous Ozone Production in Kolkata With Respect to NO_2 During Monsoon

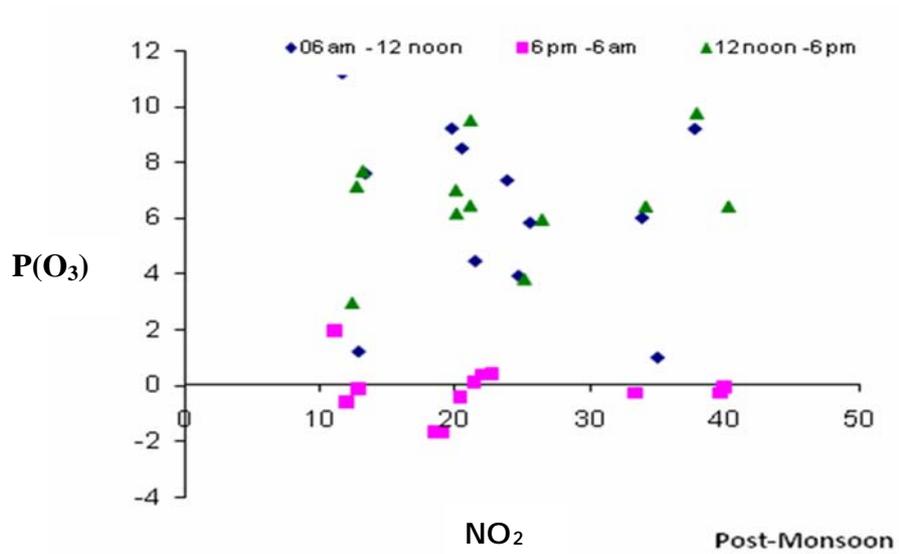


Figure 5.37: Instantaneous Ozone Production in Kolkata With Respect to NO_2 During Post-Monsoon

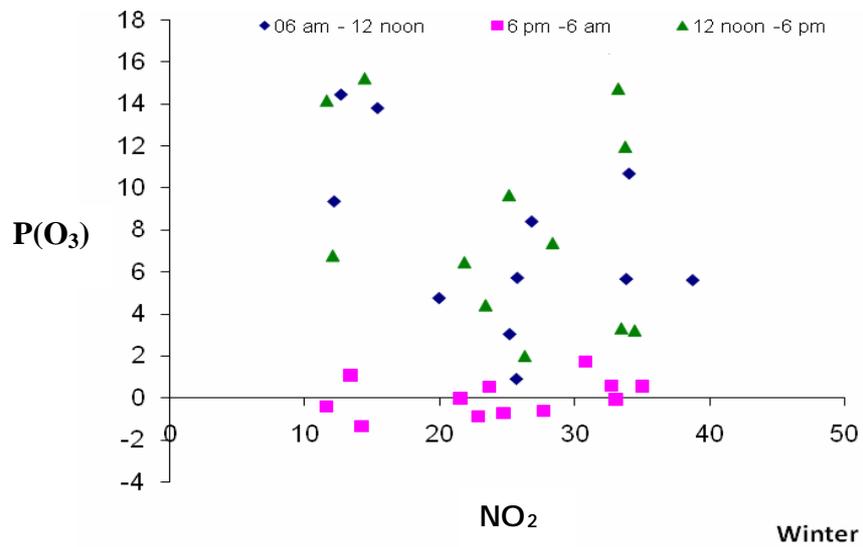


Figure 5.38: Instantaneous Ozone Production in Kolkata With Respect to NO_2 During Winter

Upper Limit MIR Values

The upper limit kinetic and mechanistic reactivities to obtain an estimate of the incremental reactivity in the MIR scale. The incremental reactivities obtained by multiplying the kinetic and mechanistic reactivities derived is in units of moles of ozone formed per mole VOC emitted, but for regulatory applications the appropriate units are grams of O₃ per gram VOC. This conversion is done by multiplying by the ratio of the molecular weight of O₃ to the molecular weight of the VOC. Therefore,

$$\text{Upper Limit MIR (gm O}_3\text{ / gm VOC)} = \text{Upper Limit Kinetic Reactivity} \cdot \text{Upper Limit Mechanistic Reactivity (mol O}_3\text{ / mol VOC)} \cdot \frac{48 \text{ (gm O}_3\text{/ mol O}_3\text{)}}{\text{Mwt}^{\text{VOC}} \text{ (gm/mol)}} \dots\dots (3)$$

For regulatory or life cycle impact assessment applications where NO₂ impacts need to be evaluated using the same scale as VOC impacts, and where the MIR scale is used for evaluating VOC impacts, the NO₂ impacts used should be those derived for the NMIR scale. For the SAPRC-07 reactivity scale given by Carter (2007) the NMIR values of 25.37, 17.24, and 15.85 grams O₃ per gram compound for NO, NO₂, and HONO respectively be added to the MIR values given for the VOCs. **Table 5.28** shows the ozone formation by VOCs observed using MIR values given by SAPRC07.

Table 5.12: Instantaneous Ozone Formation by VOCs Using MIR Values

Compound	MIR	06pm-06am	12 noon-6pm	6am- 12 noon
Toluene	5.2	5.51E-02	1.17E+03	5.55E-02
4-Isopropyltoluene	7	3.94E-02	6.92E+02	6.18E-02
1,3,5-Trimethylbenzene	13.9	3.35E-02	1.27E+02	4.32E-02
p-Xylene	5.69	1.09E-02	4.68E+01	1.06E-02
Ethylbenzene	2.93	9.38E-03	6.59E+01	8.98E-03
Styrene	1.95	5.28E-03	5.18E+01	1.05E-02
Naphthalene	3.24	3.67E-03	1.81E+01	3.23E-03
n-Propylbenzene	1.95	1.90E-03	2.86E+00	4.21E-03
Benzene	0.8	1.79E-03	3.18E+00	1.36E-03
Benzene, 1,3-dimethyl-	7	1.04E-03	3.08E-01	9.63E-04
Benzene, 1,2,4-trimethyl-	11.44	9.89E-04	2.46E-01	1.36E-03

Table 5.12 (contd.): Instantaneous Ozone Formation by VOCs Using MIR Values

Isopropylbenzene	2.43	5.59E-04	2.41E-01	6.33E-04
Benzene, propyl-	8	4.20E-04	2.60E-02	5.12E-04
Benzene, butyl-	8	3.21E-04	1.67E-02	4.06E-04
1-Propene, 1,3-dichloro-,	8	2.74E-04	3.23E+02	3.00E+00
Benzene, 1,2,3,4-tetramet	9.01	1.93E-04	5.05E-03	2.18E-04
Ethene, 1,1-dichloro-	1.69	4.24E-05	9.13E-04	3.30E-05
o- xylene	7.44	2.01E-05	6.01E-05	3.50E-05
m xylene	9.52	1.35E-05	2.47E-05	2.07E-05
p iso propyltoluene	7	8.90E-06	1.36E-05	6.76E-06
methylene chloride	0.04	5.30E-06	6.39E-04	4.27E-06
ethane 11 dichloro	0.07	1.24E-06	2.74E-05	1.67E-06
Chloroform	0.02	7.28E-07	3.05E-05	5.85E-07
Ethane, 1,2-dibromo-	0.1	2.44E-07	1.38E-06	4.18E-07
Ethane, 1,1,1-trichloro-	0.005	3.62E-08	4.88E-07	5.40E-08

MIR values are in gm/gm of VOC

Temporal and spatial variation of NO₂ and observed Ozone concentrations are shown in **Figures 5.39 to 5.41**.

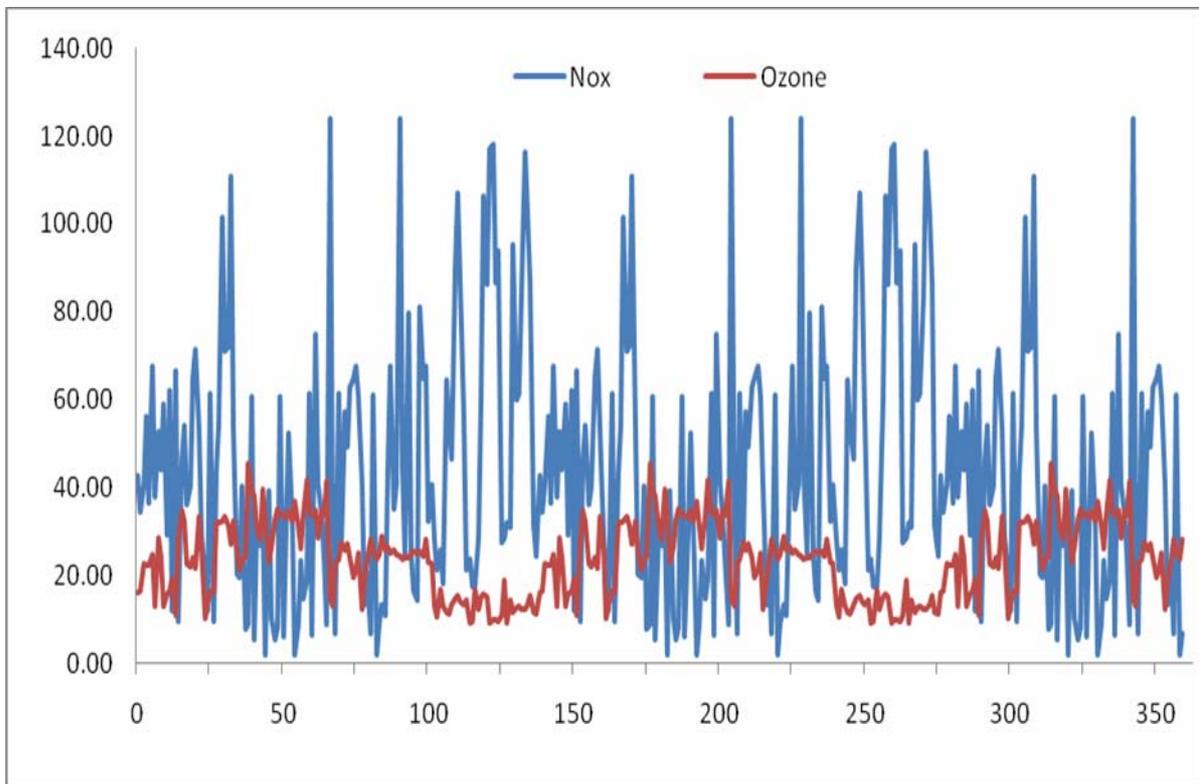


Figure 5.39: Sampling Events in 12 noon to 6 pm During Study Period

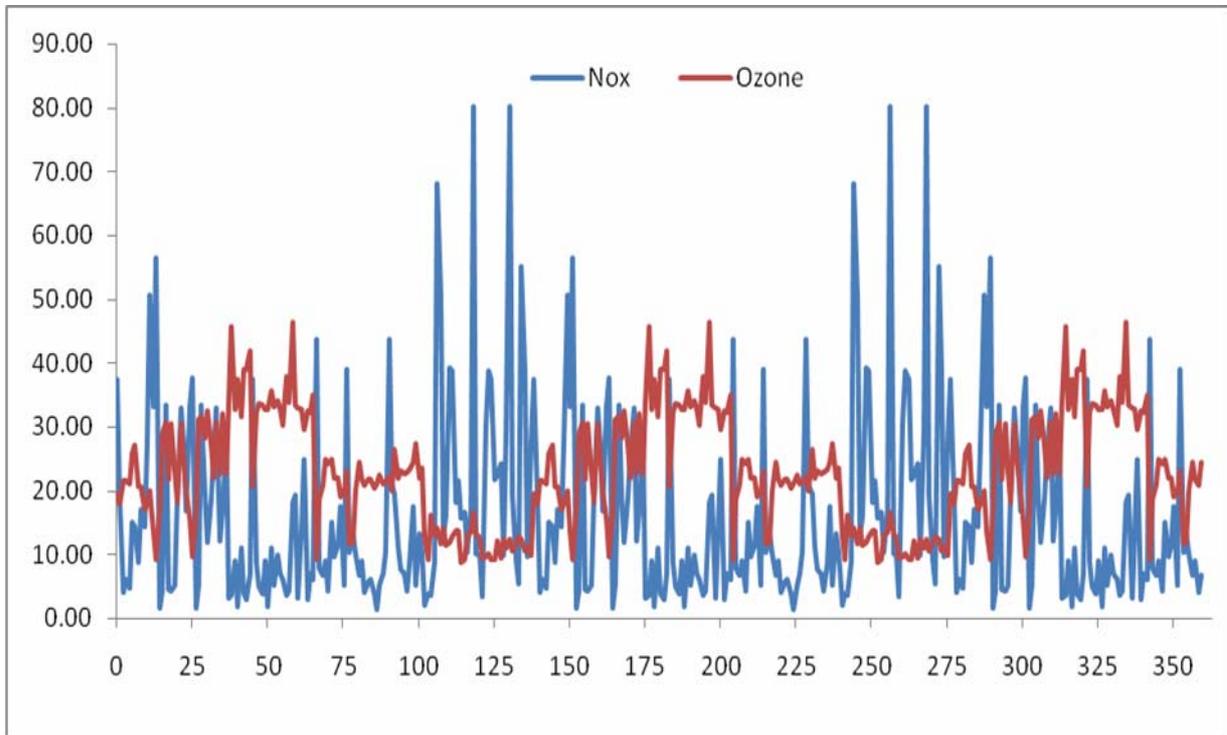


Figure 5.40: Sampling Events in 6 pm to 6 am During Study Period

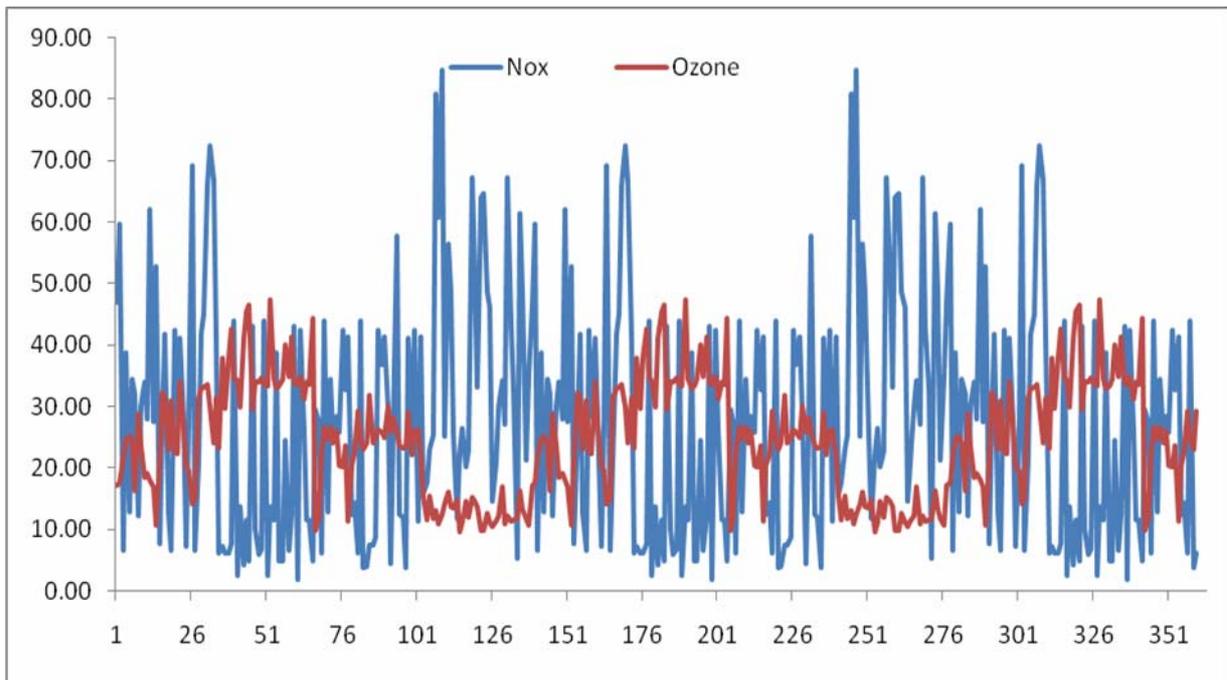


Figure 5.41: Sampling Events in 6 am to 12noon During Study Period

The strong correlation between Ozone, NO₂ and total VOCs (i.e. Carbonyl & Non carbonyl VOCs) is also evident in this study. The diurnal variation of Ozone, NO₂ and total VOCs is graphically represented in **Figures 5.42 to 5.44**.

The maximum carbonyl VOC concentration was observed during 6 pm to 6 am. Maximum concentrations of Carbonyl VOCs and ozone were observed during 12 noon to 6 pm and 6 am to 6 pm. This suggests the same mechanism of formation of non carbonyl VOCs and Ozone.

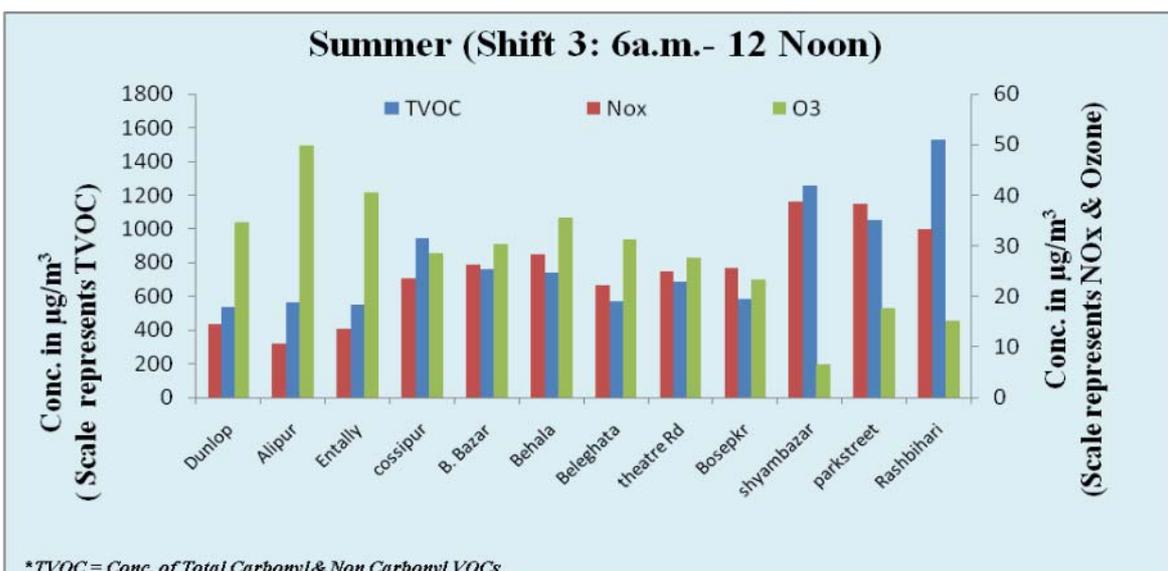
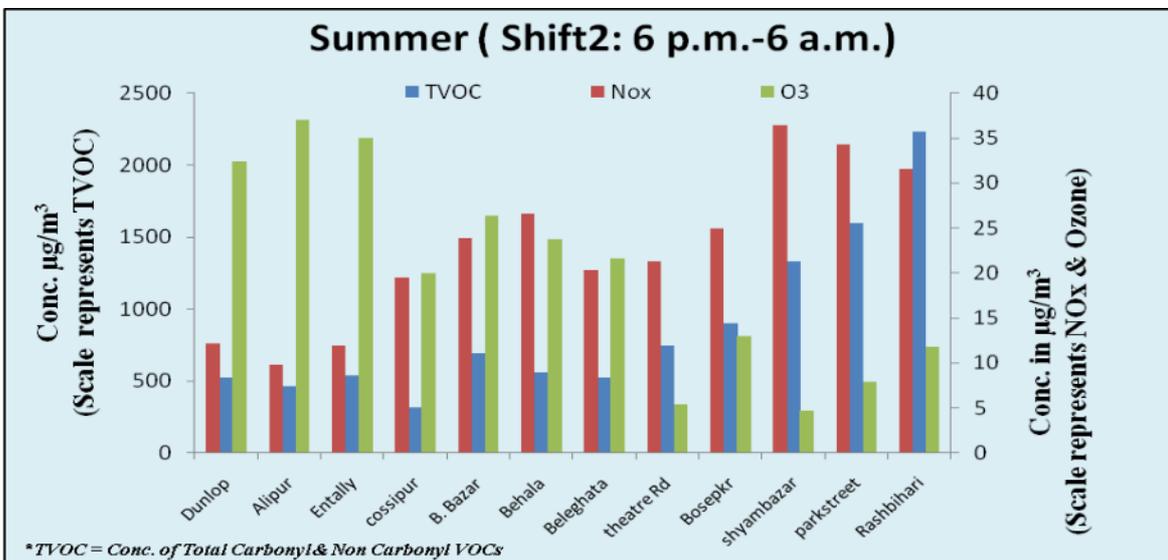
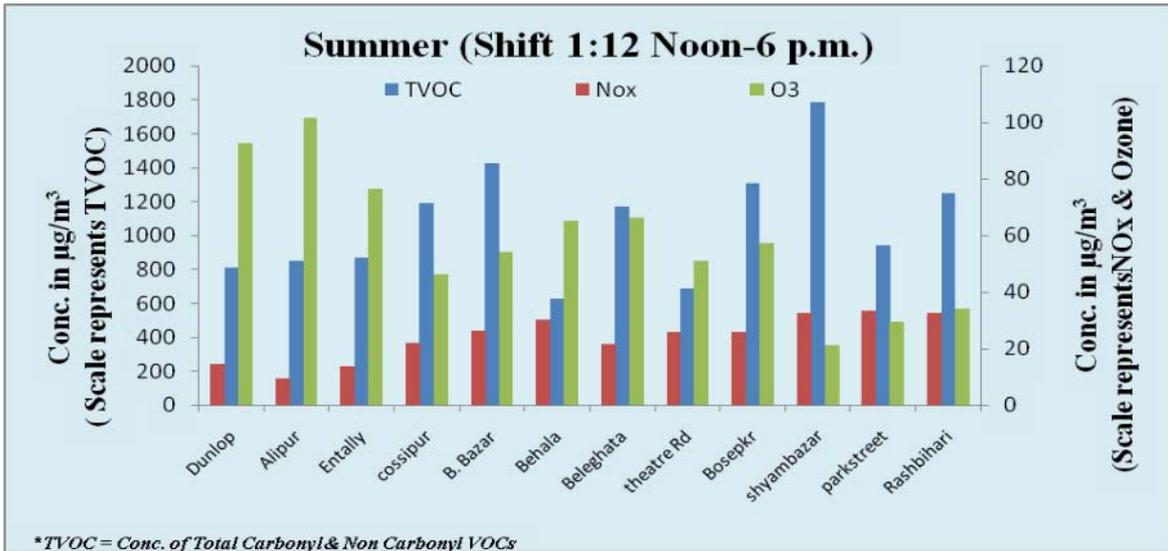


Figure 5.42: Diurnal Variation of TVOC, NO₂ & Ozone During Summer

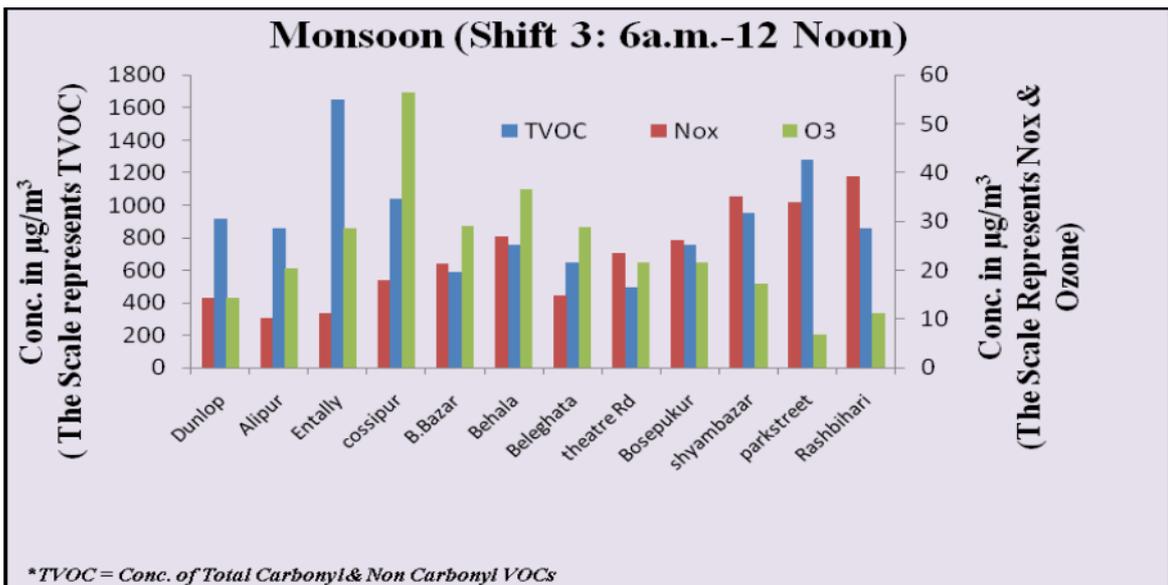
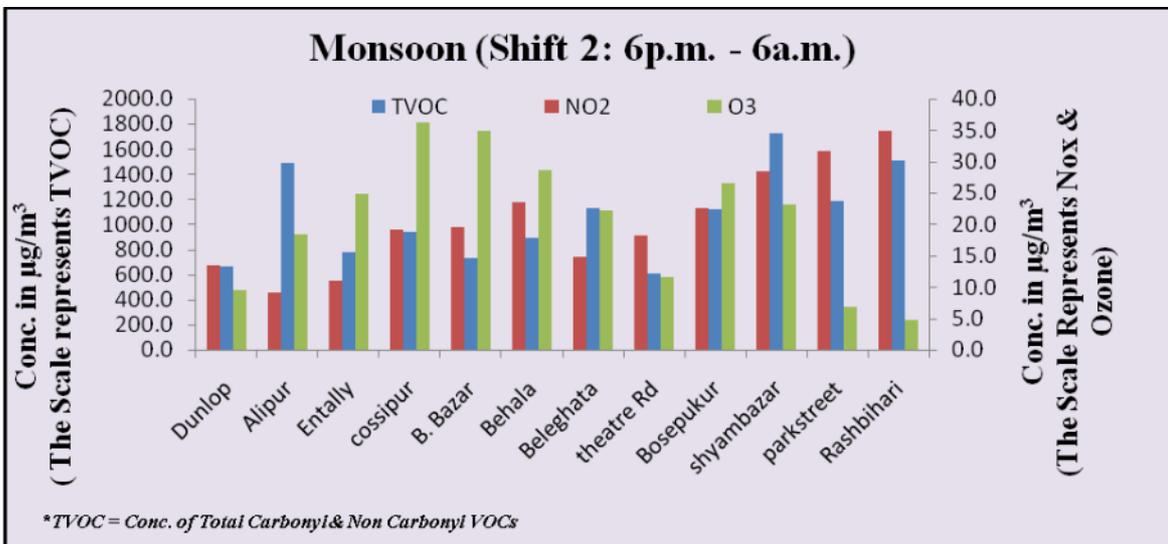
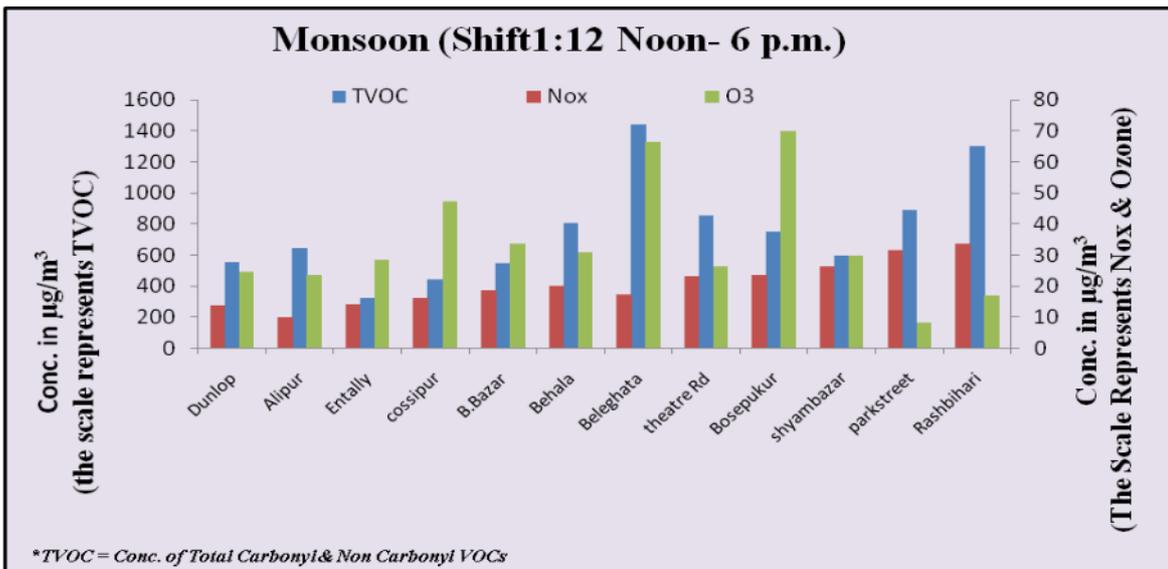


Figure 5.43: Diurnal Variation of TVOC, NO₂ & Ozone During Monsoon

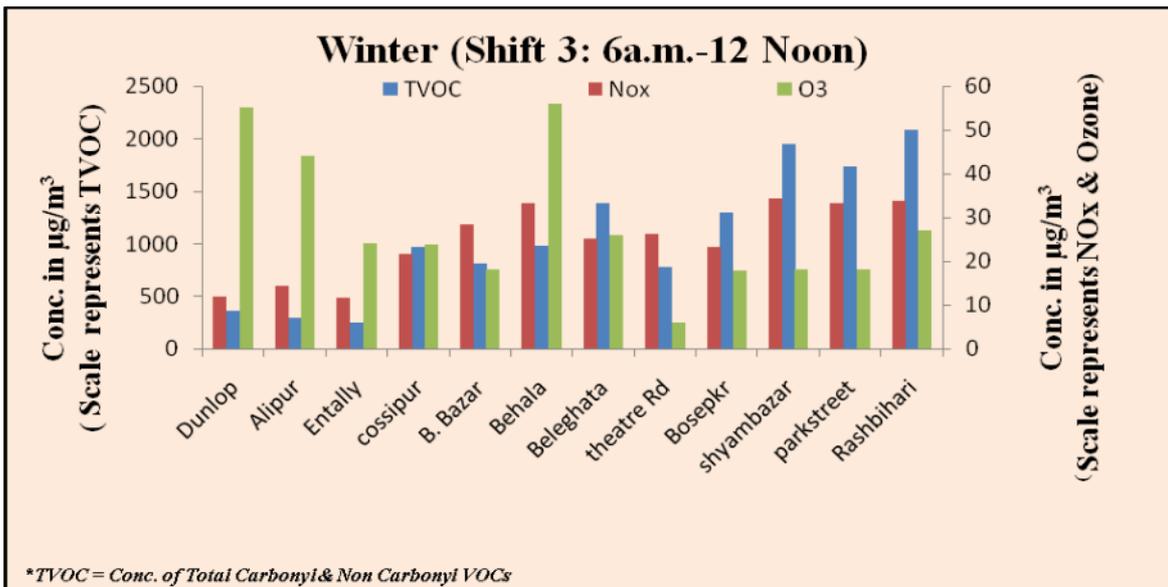
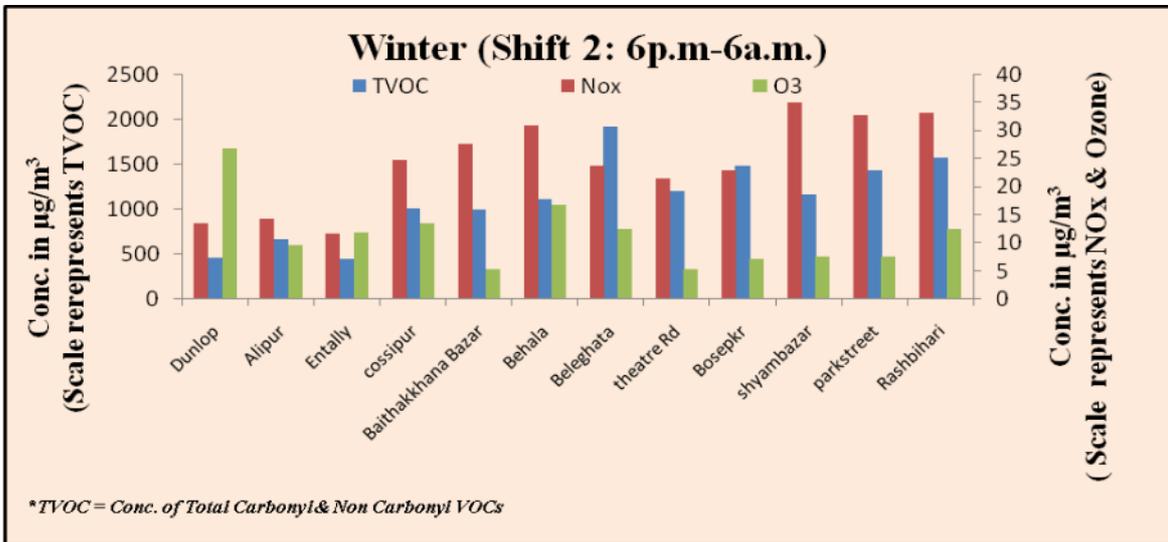
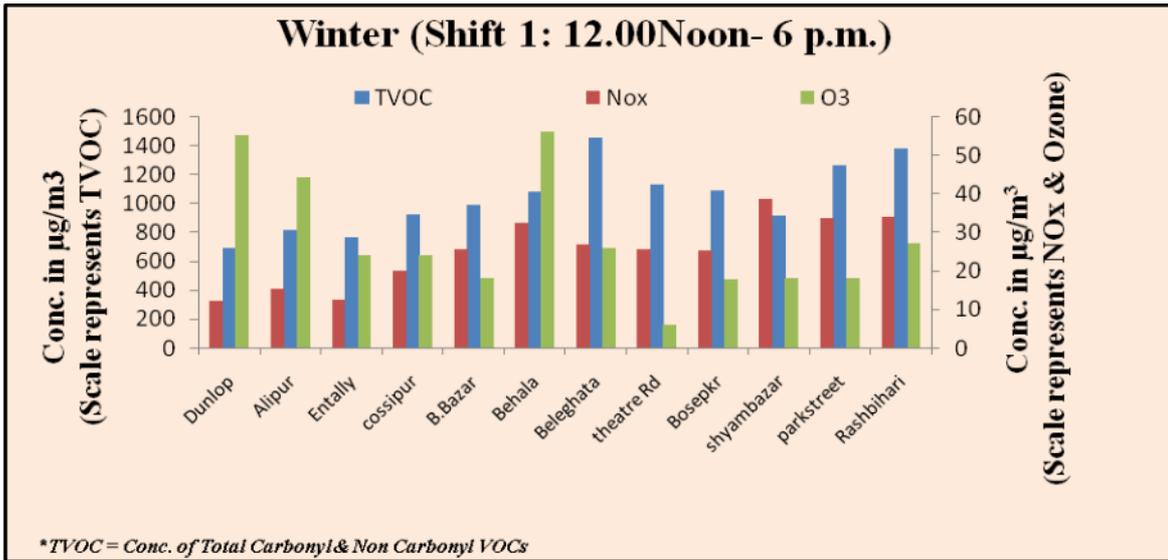


Figure 5.44: Diurnal Variation of TVOC, NO₂ & Ozone During Winter

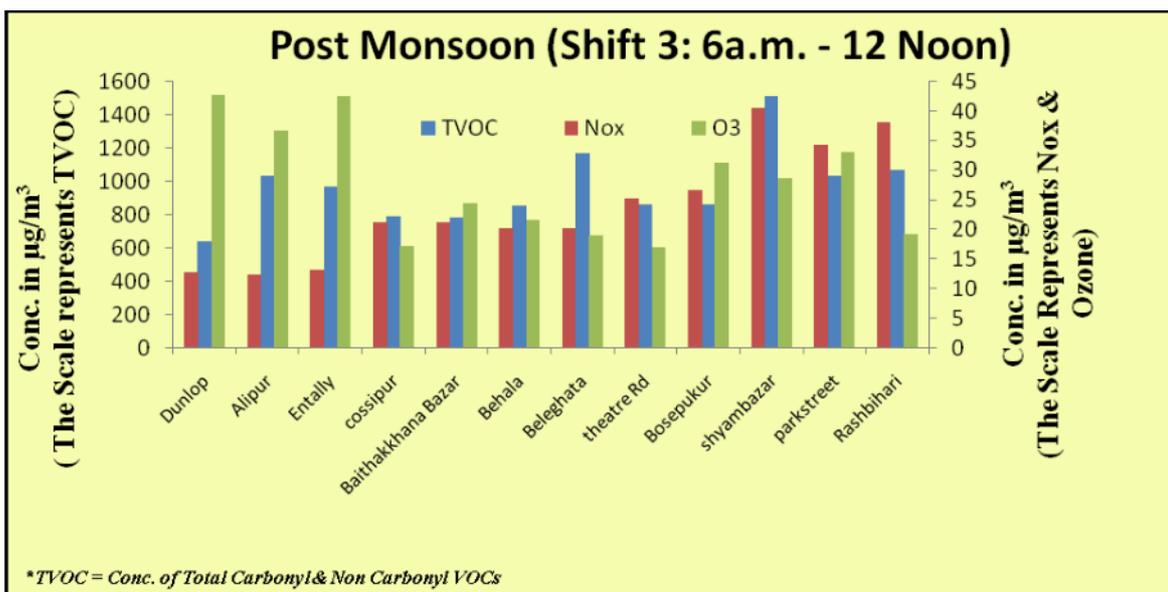
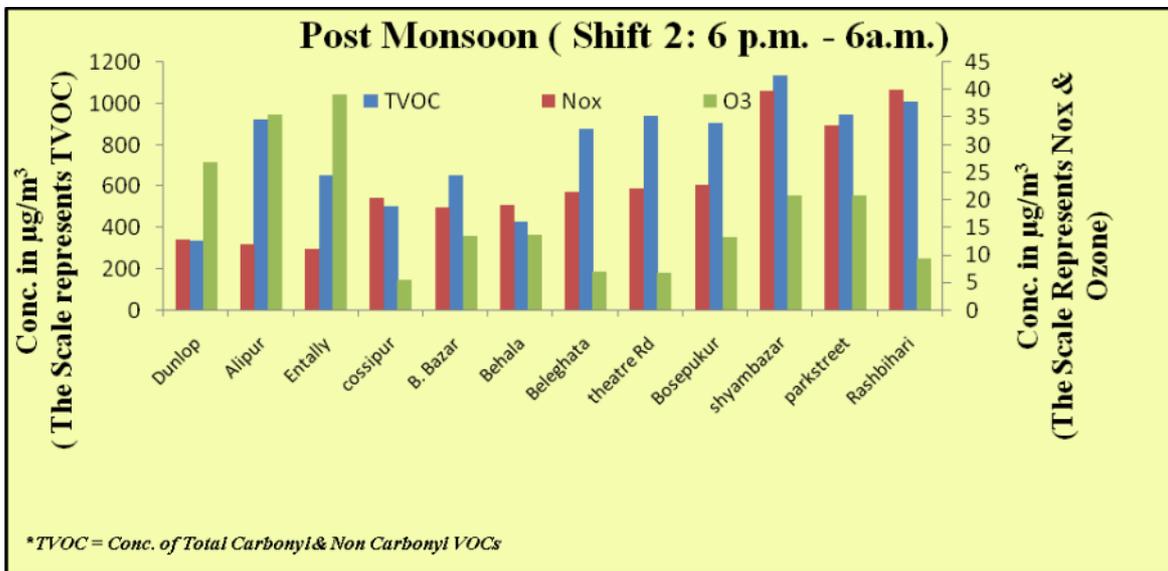
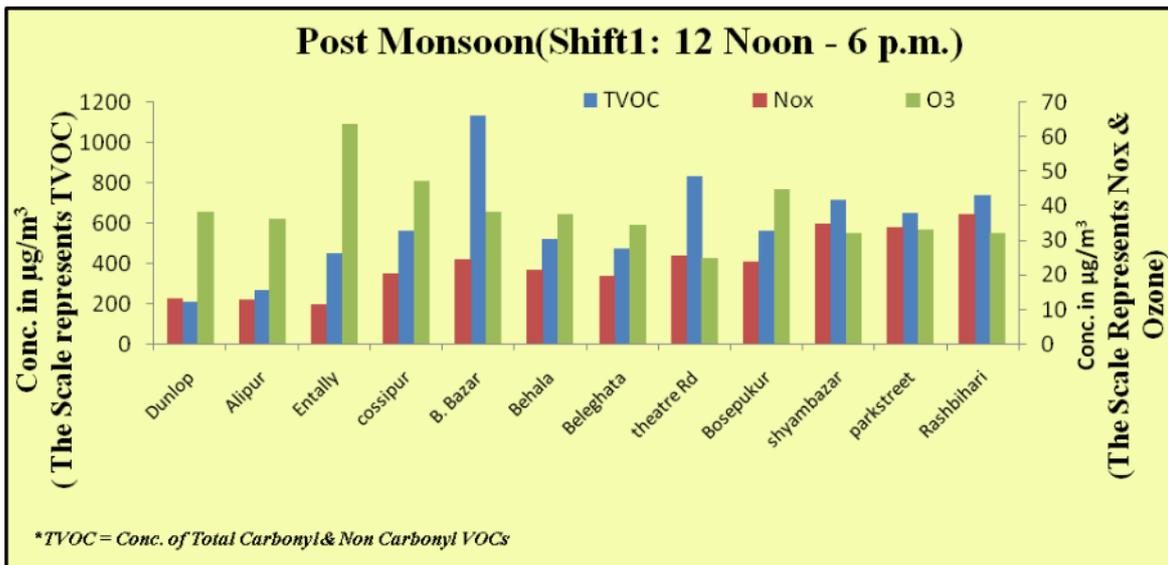


Figure 5.45: Diurnal Variation of TVOC, NO₂ & Ozone During Post-Monsoon

Chapter 6

Source Identification using Receptor Model

6.1 Suitability of Receptor Model

Air quality models offer a useful tool in comprehending these issues. These models evaluate the relationship between air pollutant emissions and their resulting concentration in the ambient air. Commonly used air quality models are: 1) Conceptual Models 2) Emission Models 3) Meteorological Models, 4) Chemical Models, 5) Source Oriented Models and 6) Receptor Models. All of these models have uncertainties associated with them. Chemical transport models, such as Gaussian plume models and gridded photochemical models, begin with pollutant emissions estimates and meteorological observations and use chemical and physical principles to predict ambient pollutant concentrations. Since these models require temporally and spatially resolved data and can be computationally intensive, they can only be used for well-characterized regions and over select time periods. Receptor models, such as Positive Matrix Factorization and Chemical Mass Balance (CMB), source apportionment addresses the problem by statistical inference of source contributions to total pollution from observations of ambient air chemical composition. Mass balance methods of source apportionment use linear models with chemical composition vectors of sources as covariates. Knowledge of meteorological variables is not required but may be used to refine the analysis. Knowledge of emission sources is useful for the interpretation of results from statistical-based receptor models and is required by receptor models that use a mass balance approach. Less data and computational resource requirement by Receptor models as compared to chemical transport models, makes them more convenient tool for evaluation of ambient pollutant concentrations and pollutant emission inventory. However, their utility for reactive air pollutants is uncertain and questionable.

6.2 Chemical Mass Balance Receptor Modeling

Receptor Models use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to the receptor. The particle characteristics must be such that:

- they are present in different source emissions;
- these proportions remain relatively constant for each source type: and
- changes in these proportions between source and receptor are negligible or can be approximated.

Common types of receptor models include:

- Chemical Mass Balance(CMB);
- Principal Component Analysis (PCA, otherwise known as Factor Analysis); and
- Multiple Linear Regression Analysis (MLR).

Descriptions of these models and some of their variations are given in Henry *et al.*(1984) and Hopke (1991). Chemical mass balance is the fundamental receptor model, with all other approaches (including PCA and MLR) based on the use of the mass balance concept.

The **Chemical Mass Balance (CMB)** Receptor Model used by Friedlander, 1973 uses the chemical and physical characteristics of gases and particulate at source receptor to both identify the presence of and to quantify source contributions of pollutants measured at the receptor. The CMB model obtains a least square solution to a set of linear equation, expressing each receptor concentration of a chemical species as a linear sum product of source profile species and source contributions. The fractional amount of each species in the VOC emissions from a given source type is termed as source profile species. The source profile species and the receptor contributions each with uncertainty estimates are input data to the **CMB model**. The output to the model consists of the amount contributed by each source type to each chemical species. The model calculates the contribution from each source and uncertainties of those values. The input data uncertainties are

used to weigh the importance of input data values in the solution and calculate the uncertainties of the source contributions.

6.2.1 CMB Mathematics

The source contribution (S_j) present at a receptor during a sampling period of length T due to a source j with constant emission rate E_j is

$$S_j = D_j \cdot E_j \dots\dots\dots(1)$$

Where,

$$D_j = \int_0^T d[u(t), \sigma(t), x_j] dt \dots\dots\dots (2)$$

is a dispersion factor depending on wind velocity (u), atmospheric stability (σ), and the location of source j with respect to the receptor (x_j). All parameters in Equation 2 vary with time, so the instantaneous dispersion factor, D_j , must be an integral over time period T (Watson, 1979).

Various forms for D_j have been proposed (Pasquill, 1974; Seinfeld and Pandis, 1998; Benarie, 1976), some including provisions for chemical reactions, removal, and specialized topography. None are completely adequate to describe the complicated, random nature of dispersion in the atmosphere. The advantage of receptor models is that an exact knowledge of D_j is unnecessary.

If number of sources, J , exists and there is no interaction between their emissions to cause mass removal, the total mass measured at the receptor, C will be a linear sum of the contributions from the individual sources.

$$C = \sum_{j=1}^J D_j \cdot E_j = \dots\dots\dots (3)$$

Similarly, the concentration of elemental component i , C_i will be

$$C_i = \sum_{j=1}^J F_{ij} \cdot S_j \quad i = 1, \dots, I \dots\dots\dots (4)$$

Where: F_{ij} = the fraction of source contribution S_j composed of element i .

The number of chemical species (I) must be greater than or equal to the number of sources (J) for a unique solution to these equations.

An estimate of the uncertainty associated with the source contributions is an integral part of several of these solution methods. Weighted linear least squares solutions are preferable to the tracer and linear programming solutions because: 1) theoretically they yield the most likely solution to the CMB equations, providing model assumptions are met; 2) they can make use of all available chemical measurements, not just the so-called tracer species; 3) they are capable of analytically estimating the uncertainty of the source contributions; and 4) there is, in practice, no such thing as a “tracer.” The effective variance solution developed and tested by Watson et al. (1984): 1) provides realistic estimates of the uncertainties of the source contributions (owing to its incorporation of both source profile and receptor data uncertainties); and 2) gives greater influence to chemical species with higher precisions in both the source and receptor measurements than to species with lower precisions. The effective variance solution is derived by minimizing the weighted sums of the squares of the differences between the measured and calculated values of C_i and F_{ij} (Britt and Luecke, 1973; Watson et al., 1984). The solution algorithm is an iterative procedure which calculates a new set of S_j based on the S_j estimated from the previous iteration. It is carried out by the following steps expressed in matrix notation. A superscript k is used to designate the value of a variable at the k^{th} iteration.

- Set initial estimate of the source contributions equal to zero.

$$S_j = 0^{k=0} \quad j=1, \dots, J \quad \dots \dots \dots (5)$$

- Calculate the diagonal components of the effective variance matrix, V_e . All off-diagonal components of this matrix are equal to zero.

$$V_{eii}^k = \sigma_{Ci}^2 + \sum(S_j^2) \cdot \sigma_{Fi}^2 \quad \dots\dots\dots (6)$$

- Calculate the k+1 value of S_j

$$S^{k+1} = (F^T (V_e^k)^{-1} F)^{-1} F^T (V_e^k)^{-1} C \quad \dots\dots\dots (7)$$

- Test the (k+1)th iteration of the S_j against the kth iteration. If any one differs by more than 1%, then perform the next iteration. If all differ by less than 1%, then terminate the algorithm.

$$\text{if } |S_j^{k+1} - S_j^k| / S_j^{k+1} > 0.01 \text{ go to step 2} \quad \dots\dots\dots (8)$$

$$\text{if } |S_j^{k+1} - S_j^k| / S_j^{k+1} \leq 0.01 \text{ go to step 5} \quad \dots\dots\dots (9)$$

- Assign the (k+1)th iteration to S_j and S_j. All other calculations are performed with these final values.

$$\sigma_{Sj} = [(F^T (V_e^{k+1})^{-1} F)_{jj}]^{-1/2} \quad j = 1, \dots, J \quad \dots\dots\dots (10)$$

Where: C = (C1...CI) T, a column vector with C_i as the ith component

S = (S1...SJ) T, a column vector with S_j as the jth component

F = an I x J matrix of F_{ij}, the source composition matrix

C_i = one standard deviation precision of the C_i measurement

F_{ij} = one standard deviation precision of the F_{ij} measurement

V_e = diagonal matrix of effective variances

The effective variance solution algorithm is very general, and it reduces to most of the solutions cited above with the following modifications:

- When the σ^{F_{ij}} are set equal to zero, the solution reduces to the ordinary weighted least squares solution.
- When the σ^{F_{ij}} are set equal to the same constant value, the solution reduces to the unweighted least squares solution.

- When a column is added to the F_{ij} matrix with all values equal to 1, an intercept term is computed for the variable corresponding to this column.
- When the number of source profiles equals the number of species ($I=J$), and if the selected species are present only in a single, exclusive source profile, the solution reduces to the tracer solution.
- When the $(F^T(V_e^k)^{-1} F)$ is re-written as $(F^T(V_e^k)^{-1} F - \phi I)$ with “ ϕ ” equal to some non-zero number, known as the smoothing parameter, and “ I ” equal to the identity matrix, the solution becomes the ridge regression solution (Williamson and DuBose, 1983).

Formulas for the performance measures are:

$$\text{Reduced chi square} = \chi^2_{I-J} = \sum_{i=1}^I [(C_i - \sum_{j=1}^J F_{ij}S_j)^2 / V_{eii}] \dots\dots\dots (11)$$

$$\text{Percent Mass} = 100(\sum_{j=1}^J S_j) / C_t \quad \text{where } C_t \text{ denotes the total measured mass}$$

$$\text{R square} \dots\dots = 1 - [(I-J) \chi^2_{I-J} / \sum_{i=1}^I C_i / V_{eii}] \dots\dots\dots (12)$$

$$\text{Modified Pseudo-Inverse Matrix} = (F^T(V_e)^{-1}F)^{-1}F^T(V_e)^{-1/2} \dots\dots\dots (13)$$

The Singular Value Decomposition of the weighted F matrix is given by (Henry, 1992)

$$V_e^{1/2} F = UDV^T \dots\dots\dots (14)$$

Where U and V are $I \times I$ and $J \times J$ orthogonal matrices, respectively, and where D is a diagonal matrix with J nonzero and positive elements called the singular values of the decomposition. The columns of V are called the eigenvectors of the composition and their components are associated with the source types.

CMB model assumptions thus are:

- Compositions of source emissions are constant over the period of ambient and source sampling;
- Chemical species do not react with each other (i.e. they add linearly);
- All sources with a potential for contributing to the receptor have been identified and have had their emissions characterized;
- The number of sources or source categories is less than or equal to the number of species;
- The source profiles are linearly independent of each other; and
- Measurement uncertainties are random, uncorrelated and normally distributed.

The degree to which these assumptions are met in application depends to a large extent on the particle and gas properties measured at source and receptor.

6.2.2 Applicability of Assumption

Applicability of assumption to the present study was examined with regard to assumption 1, source compositions, as seen at the receptor, are known to vary substantially among sources, and even within a single source over an extended period of time. These variations are both systematic and random and are caused by three phenomena:

- a) Transformation and deposition between emissions point and the receptor
- b) Differences in fuel type and operating processes between similar sources or the same source in time
- c) Uncertainties or difference between the source profiles measurement methods.

Literature shows that in a complex urban airshed, which has sources of residual of oil combustion, marine aerosol, steel production, lead smelting, municipal incineration and a continental background aerosol, some source profile were collinear with the measured species. This leads to the average absolute errors of approximately 30% even when coefficients of variations in source profiles reached 50%.

Accordingly to assumption 2, it is necessary to measure source profiles or modify them by some objective method to account for changes in the character between

source and receptor. When profiles are coupled with chemical reaction mechanisms rates, deposition velocities, atmospheric equilibrium, and method to estimate transport and aging time, it is possible to produce aged source profiles which will allow direct attribution of reactive species to sources. This apportionment requires measurement of gaseous as well as particulate species at receptor sites. The present application will result in separating only primary and secondary emitters.

Assumption 3 is a major challenge in application of CMB. Identification of primary contributing species for inclusion in the model in the present work is derived from the observed activities in the area. Literature shows that when actual sources were excluded ratio of measured and calculated concentrations were outside the range of 0.5 to 2.

To examine the validation of CMB in terms of assumption 4, linear independence of source composition needs to be looked into. The degree of co-linearity depends on the number of source categories contributing to influential fitting species, the relative contributions from source types with similar (but not identical) profiles, the variability of species abundances in the profiles, and the relative contribution from each category.

With regard to assumption 5, the true number of individual sources contributing to receptor concentrations is generally much larger than the number of species that can be measured. It is therefore, necessary to group sources into source types of similar composition so that this assumption is met.

Regarding the randomness, normality and the uncorrelated nature of measurement uncertainties that is assumption 6, there are very few results available from verification or evaluation studies. This assumption still requires further evaluation to determine the effects of deviation of errors.

Simulated, ambient concentrations of VOC can provide a means to evaluate the accuracy of CMB as the actual contributions of the VOC sources are known. If same emission source profiles provided to CMB is used to simulate data it will

also possess similar measurement uncertainties as the profiles. This removes this potentially confounding variable from the analysis. Realistic simulated ambient pollutant concentrations have been used to evaluate the ability of receptor models including CMB to apportion sources of NHMC and particulate matter (e.g., Wittig A.E & Allen D.T, 2008, DeCesar and Cooper, 1982; Gerlach et al., 1983; Javitz et al., 1988). The procedure adopted by Wittig A.E & Allen D.T, 2008 has been used here. Concentrations of VOCs are simulated using a simply parameterized photochemical transport model. This approach is favored over simple additive mixtures of sources since it allows for the enrichment of less reactive VOC over time. The photochemical transport model used in this study accounts for the dispersion, dilution and reaction of VOC emitted in various strengths and from different locations to an air mass as it travels downwind. The ambient air quality downwind is simulated using three unsteady batch reactors in series. The simulation begins at 8 am in reactor one. Initial concentration is computed as

$$[C_{i,k,t=0}] = \left\{ [C_{i,k-1,t=1h}] V_{k-1} \frac{A_k}{A_{k-1}} + \sum_{j=1}^J q_{j,k} f_{i,j} / MW_i N_A \right\} V_k^{-1}$$

for $k = 1, \dots, 8$ and $i = 1, \dots, I,$ (15)

where i is the VOC species, j is the source of the VOC, k is the reactor number, $C_{i,k,t=0}$ is the initial concentration of species i in reactor k in mole ccm^{-3} , $C_{i,k,t=1h}$ is the concentration of species i in the prior reactor at the end of 1 h of reaction in mole ccm^{-3} , V_k is the volume of reactor k in cc, A_k/A_{k-1} is the relative surface area of reactors k and $k-1$ and accounts for dispersion, $q_{j,k}$ is the emission rate of VOC from source j within the footprint of reactor k for 1 h in g, $f_{i,j}$ is the fraction of species i in the emissions from source j in gg^{-1} , MW_i is the molecular weight of species i in g mol^{-1} and N_A is Avogadro's number. For reactor one, the value of the $C_{i,k,t=1h}$ upwind concentration is zero. Changing VOC concentration is assumed to be limited by reaction with the OH radical and

is modeled using a batch scheme. Changing concentration of VOC is computed in 0.01 h time steps for 1 h as

$$\frac{d[C_{i,k,t}]}{dt} = k_i[C_{i,k,t}][COH,k] \quad \text{for } k = 1, \dots, 8 \text{ and } i = 1, \dots, I, \dots \dots \dots (16)$$

Where t is time in s, k_i is the rate constant for the reaction of OH with a specific VOC at 298K in mole ccm^{-3} and COH is the OH concentration in mol cm^{-3} . The second hour of the simulation (i.e., starting at 9 am) begins in the second reactor. $C_{i,2}$ initial concentration is computed using Eq. 14 and is now dependent upon the A2/A1 dispersion factor, the final $C_{i,1}$ upwind concentrations in reactor one, the $q_{j,2}$ fresh emissions to reactor two, and the dilution of all sources of NMHC into the new reactor volume. Changing NMHC concentration is again computed in 0.01 h time steps for 1 h using Eq. 15. This sequential process is repeated for all eight trajectory sections. The VOC concentrations computed at the end of the eighth hour in the eighth reactor approximate the air quality at receptor after 8 h of dilution, dispersion and reaction of emissions, and are converted to mass concentration units before being input to CMB.

6.2.3 Source Profiles

Source profiles for use in CMB model in the present study was taken from USEPA Speciate 4.2 the emission sources considered were:

Diesel Internal Combustion Engines: Trucks, off road equipment, stationery engines for pumps and generators.

Petrol Vehicle: Heavy and light duty cars, small engines.

Evaporative Emissions: Hot soak vehicle and asphalt roads, speciate profile was modified with reference to benzene, toluene, ethylbenzene, xylene, propyl benzene, 1,3,5 trimethyl benzene, 1,2,4 trimethyl benzene and naphthalene content. The modification done was based on analysis of petrol samples collected from petrol pumps of IOC, IBP, HPCL and BPCL.

Auto Repair, Degreasing and Dry-cleaning: Vehicle repair garages and shops, stripping and spraying additives. Dry cleaning activity was merged because the profiles were collinear.

Refueling: Refueling petrol and diesel at petrol pumps.

Printing: Large number of printing press in industrial areas mainly small and medium scale is present in Kolkata.

Textile Dyeing and curing: Such units are present in industrial areas in Kolkata

Consumer Products: Car consumer products and personal consumer products like polishes, fresheners, perfumes etc.

Cigarette Smoke: Smoking is widely prevalent in Kolkata.

Naphtha: Naphtha is used as fuel.

Mineral Oil (Kerosene): Mineral Oil (Kerosene) is used as fuel

Table 6.1 gives the species considered in CMB analysis

Table 6.1: Species Considered in CMB Modelling Along with their Sources

Species Name	Diesel exhaust & evaporative	Auto body Repair/ Degreasing	Gasoline	Mineral Spirits	Refueling	Naphtha	Biomass Burning	Printing	Consumer & Commercial Products	Cigarette smoke
1,2,3-trimethylbenzene		√	√	√						
1,2,4-trimethylbenzene (1,3,4-trimethylbenzene)	√	√	√	√	√	√	√	√		√
1,3,5-trimethylbenzene	√	√	√	√	√	√	√	√		√
1,4-diethylbenzene (para)			√				√			
1-Dodecene							√			
2,2,4-trimethylpentane					√					
2,5-Dimethylbenzene	√									
2-chlorotoluene									√	
Benzene	√	√	√		√		√			√
Benzene,1,2,3,4-tetramethyl-				√						
Benzene,1,2,4-trichloro-			√							
Benzene,1-methyl-3-(1-methylethyl)-	√		√	√	√					
Benzene,butyl	√	√		√						
Benzene,propyl-	√	√	√	√	√	√				√
Benzene,secbutyl	√		√							
Chlorobenzene									√	
Chloroform									√	
CIS-1,3-Dichloropropylene									√	
Eicosane								√		
Ethane,1,1,1-trichloro-		√								
Ethylbenzene	√		√		√	√	√	√	√	√
Hexadecane								√		

Table 6.1(contd.): Species Considered in CMB Modelling Along with their Sources

Species Name	Diesel exhaust & evaporative	Autobody Repair/ Degreasing	Gasoline	Mineral Spirits	Refueling	Naphtha	Biomass Burning	Printing	Consumer & Commercial Products	Cigarette smoke
Isomers of xylene		√	√	√	√	√	√	√		√
Isopropylbenzene (cumene)				√		√	√			
Methylene bromide							√			
Naphthalene	√	√	√	√			√	√	√	√
n-Decane	√		√	√	√	√	√			√
n-Dodecane	√			√			√			
n-Eicosane	√									
n-Heneicosane	√							√		
n-Heptadecane	√									
n-Hexadecane	√									
N-hexane		√					√			
n-Nonadecane	√							√		
n-Pentadecane	√									
N-propylbenzene							√	√		
n-Tetradecane	√									
n-Tridecane	√									
n-Undecane	√		√	√			√			
O-dichlorobenzene									√	
P-dichlorobenzene									√	
Perchloroethylene									√	
pisopropyltoluene	√									
Styrene	√		√				√			√
Tetrachloroethylene		√								
Toluene	√	√	√		√	√	√	√	√	√

Table 6.1(contd.): Species Considered in CMB Modelling Along with their Sources

Species Name	Diesel exhaust & evaporative	Autobody Repair/ Degreasing	Gasoline	Mineral Spirits	Refueling	Naphtha	Biomass Burning	Printing	Consumer & Commercial Products	Cigarette smoke
Trichloroethylene		√							√	
Valeraldehyde	√						√			
Tolualdehyde	√						√		√	
Propionaldehyde			√				√			
Isovaleraldehyde	√						√			
Formaldehyde	√		√				√		√	√
Hexaldehyde	√						√			√
Butyraldehyde	√						√			√
Acetaldehyde	√		√				√			√
Acetone	√	√					√	√	√	√
Acrolein (2-propenal)			√							
Benzaldehyde			√				√			

6.3 Results

Overall source contributions to Total VOCs at Kolkata for each site are shown in Figure 6.1 through 6.12.

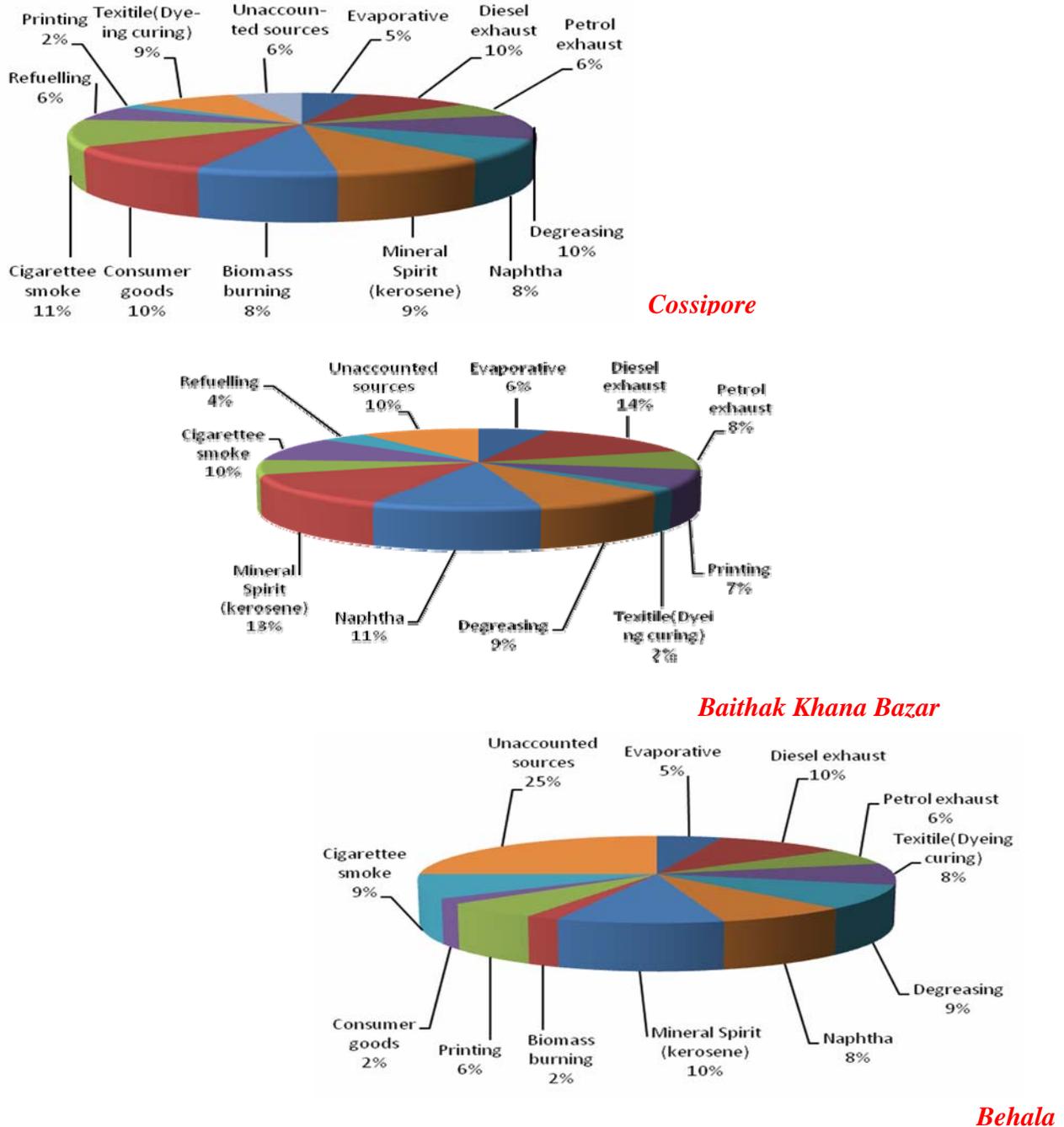
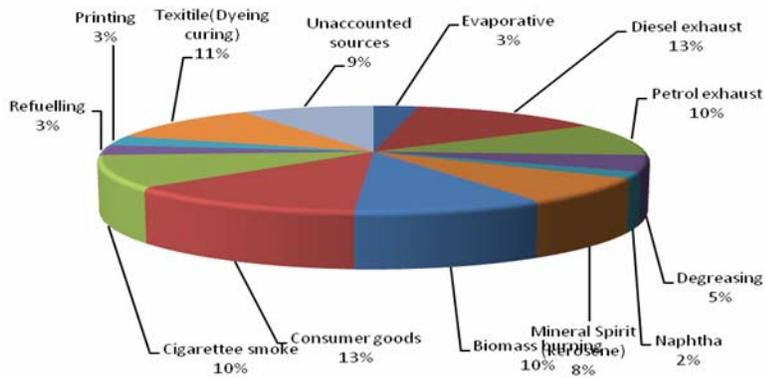
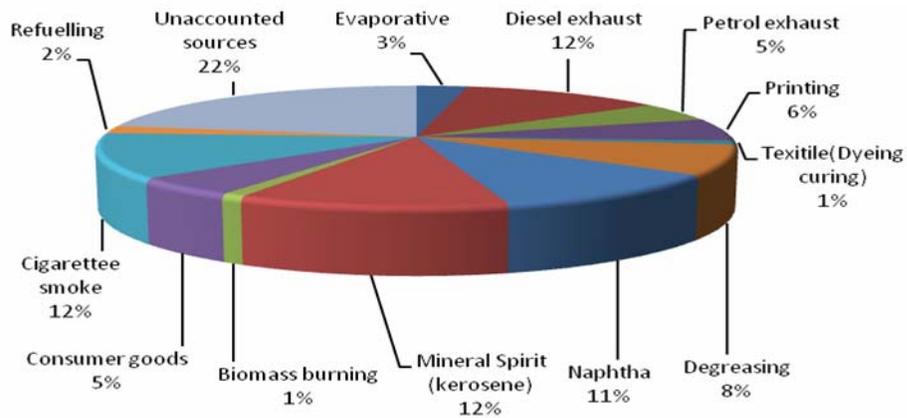


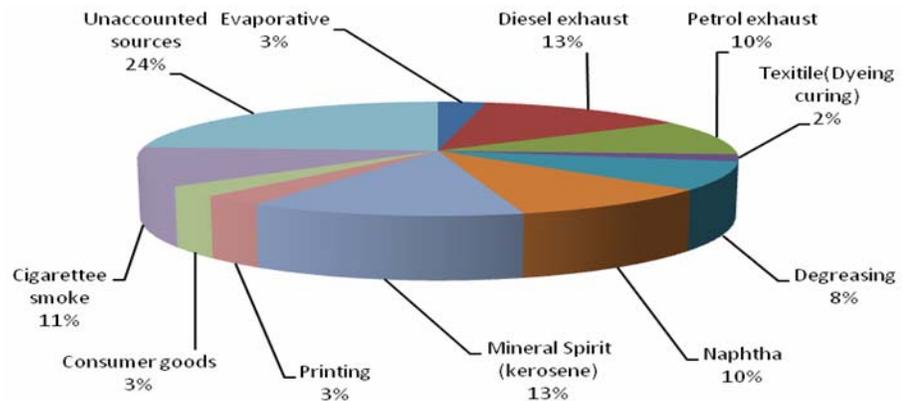
Figure 6.1: Source Contributions to Total VOCs at Kolkata Industrial Sites during Summer



Cossipore

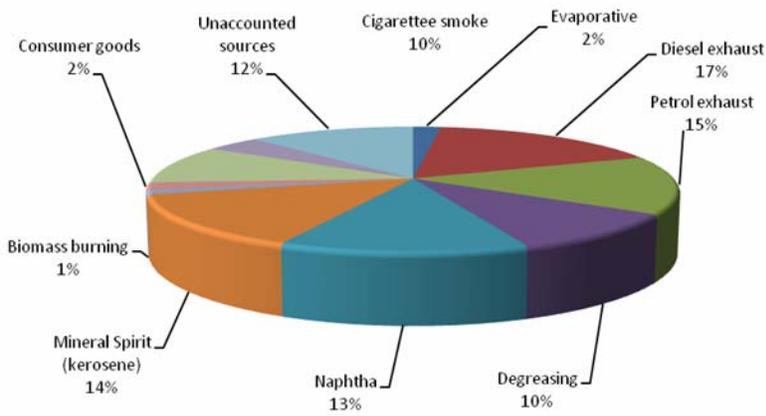


Baithak Khana Bazar

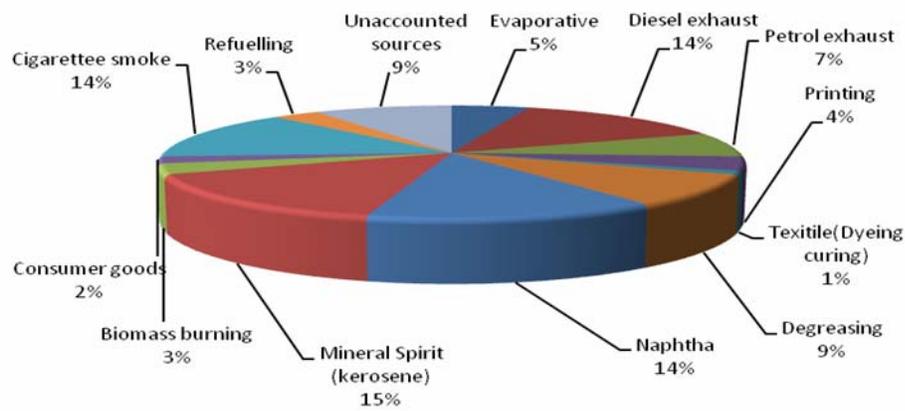


Behala

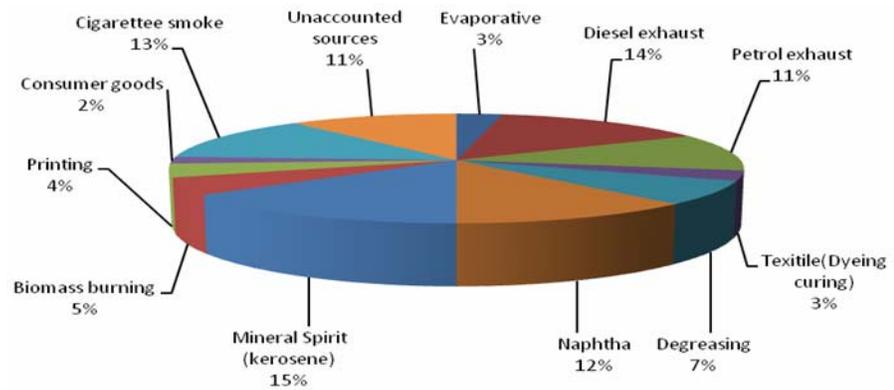
Figure 6.2: Source Contributions to Total VOCs at Kolkata Industrial Sites during Monsoon



Cossipore

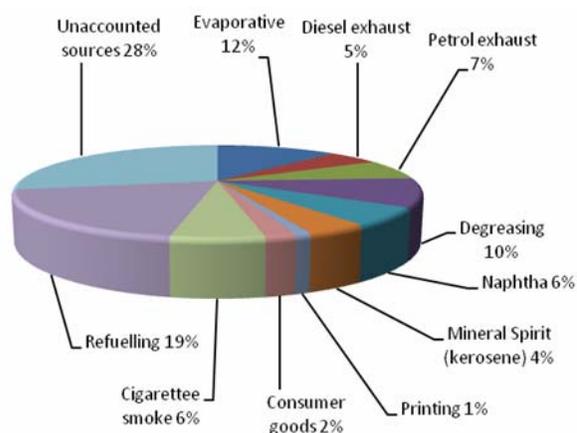


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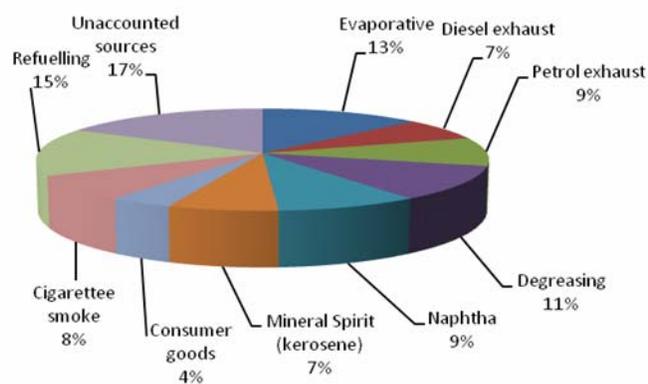


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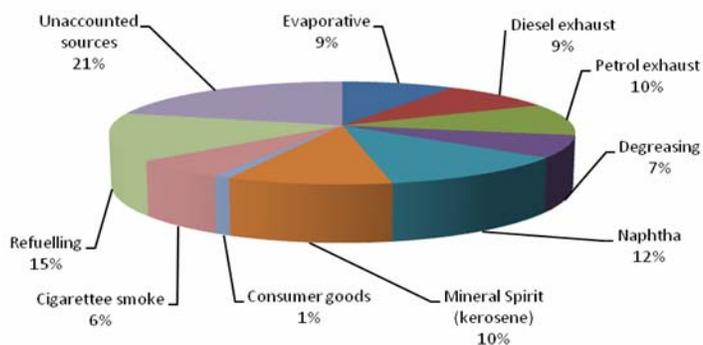
Figure 6.3: Source Contributions to Total VOCs at Kolkata Industrial Sites during Winter



Belegkata

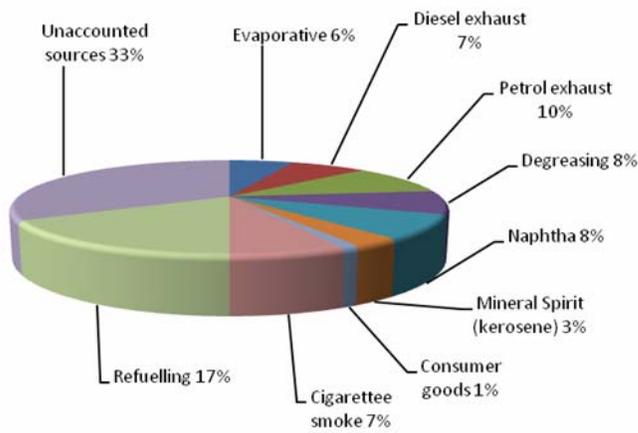


Theatre Road

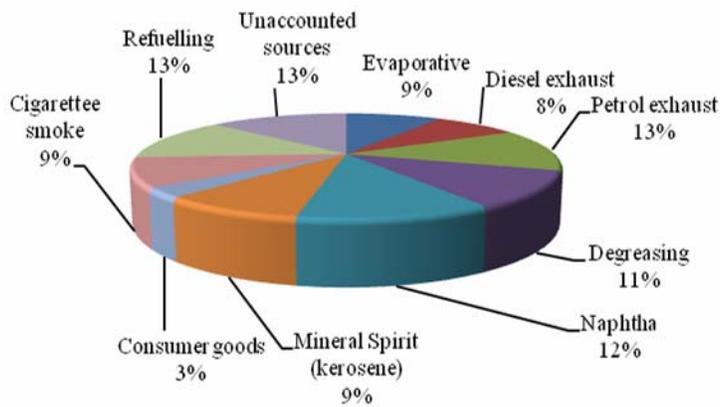


Bosepukur

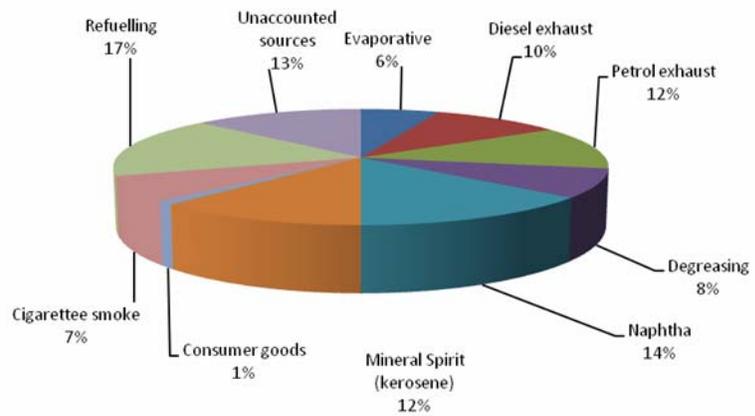
Figure 6.4: Source Contributions to Total VOCs at Kolkata Petrol Pump Locations During Summer



Belegata

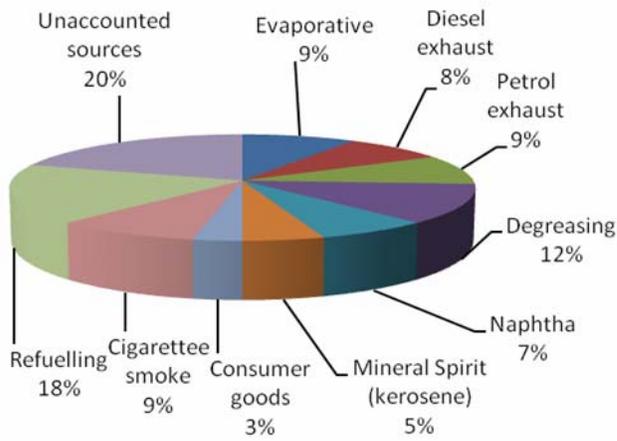


Theatre Road

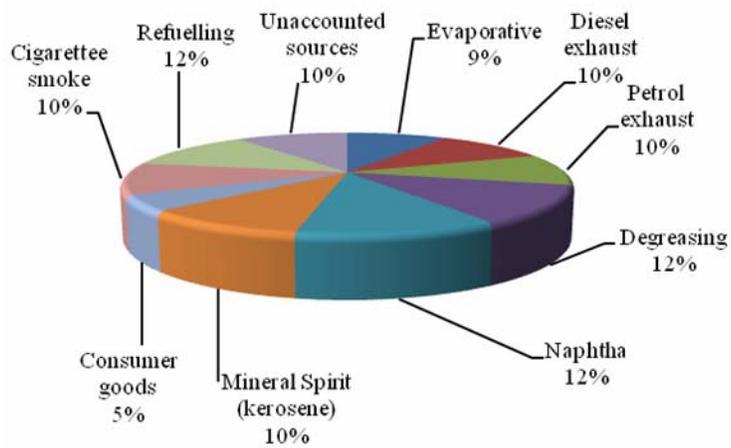


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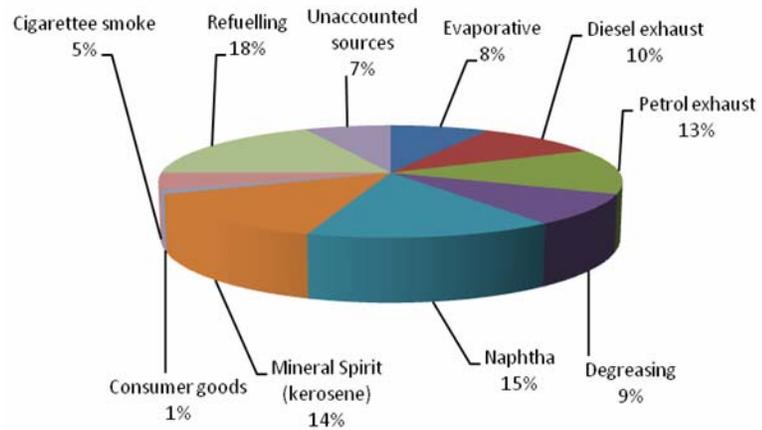
Figure 6.5: Source Contributions to Total VOCs at Kolkata Petrol Pump Locations During Monsoon



Belegkata

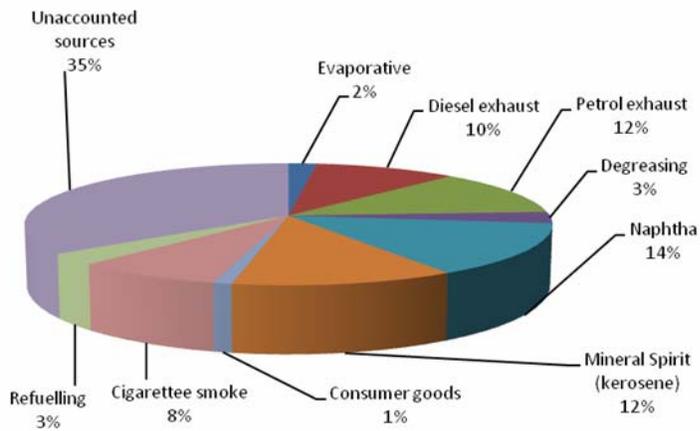


Theatre Road

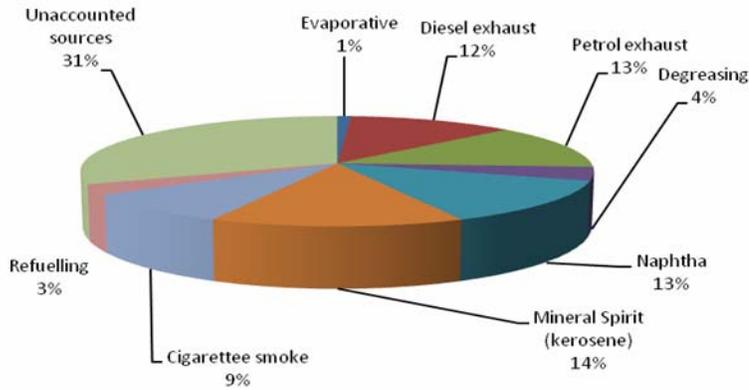


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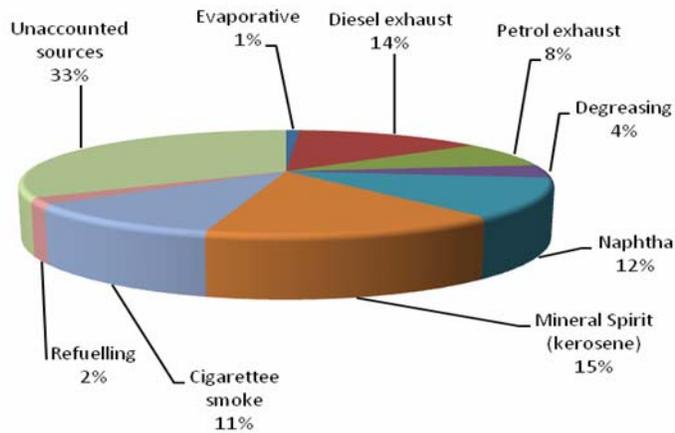
Figure 6.6: Source Contributions to Total VOCs at Kolkata Petrol Pump Locations During Winter



Parkstreet

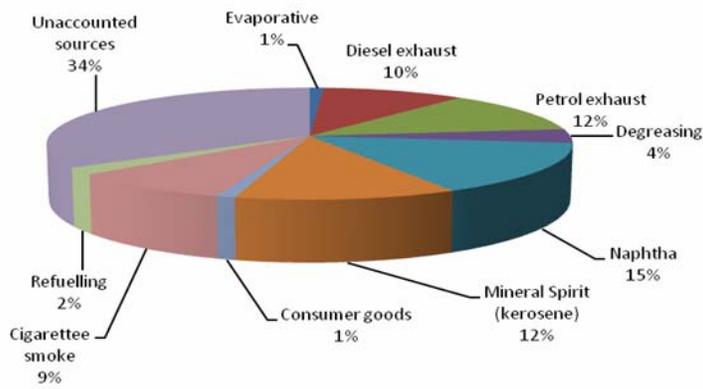


Rashbehari

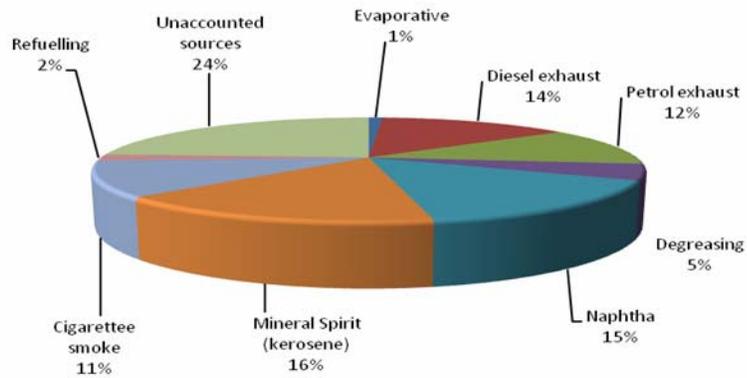


Shyambazar

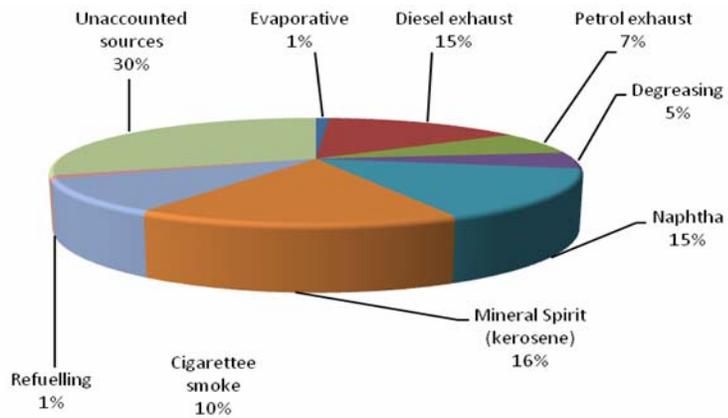
Figure 6.7: Source Contributions to Total VOCs at Kolkata Traffic Crossings Locations During Summer



Parkstreet

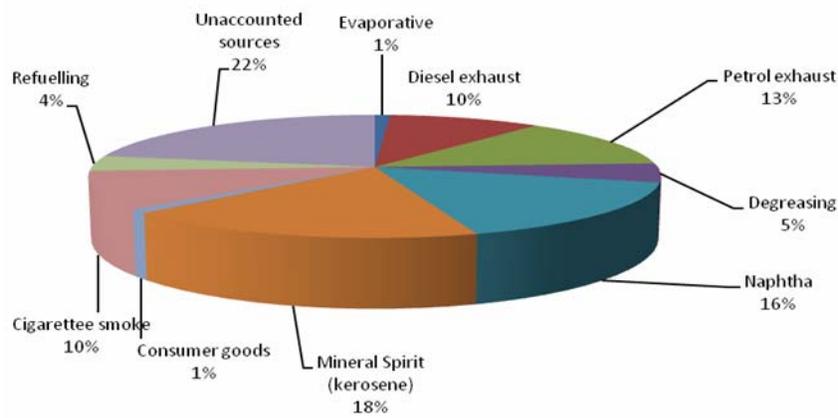


Rashbehari

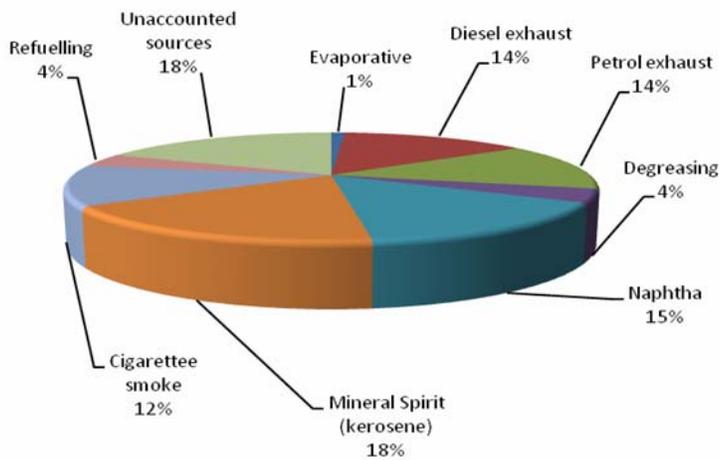


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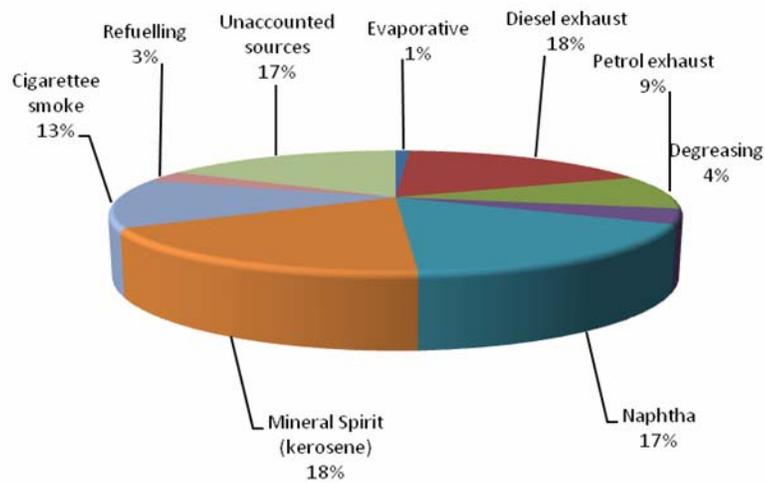
Figure 6.8: Source Contributions to Total VOCs at Kolkata Traffic Crossings Locations During Monsoon



Parkstreet

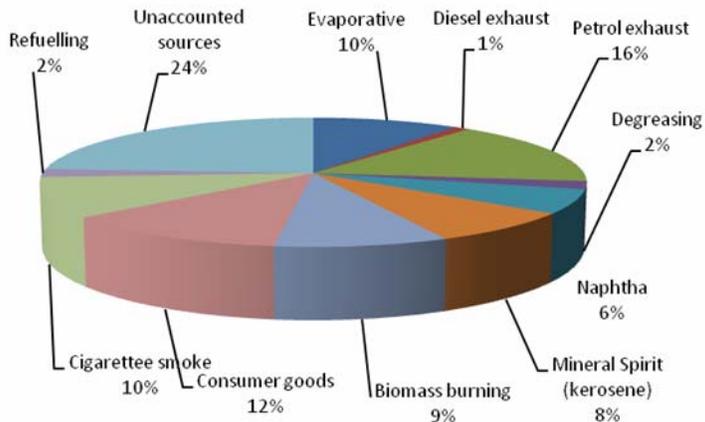


Rashbehari

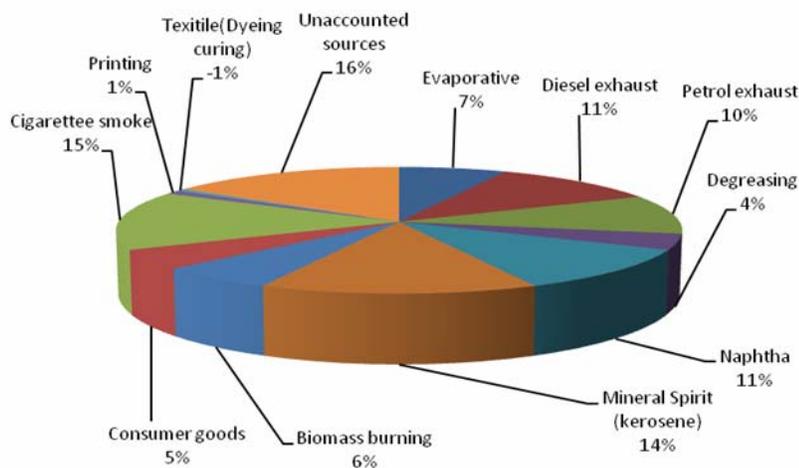


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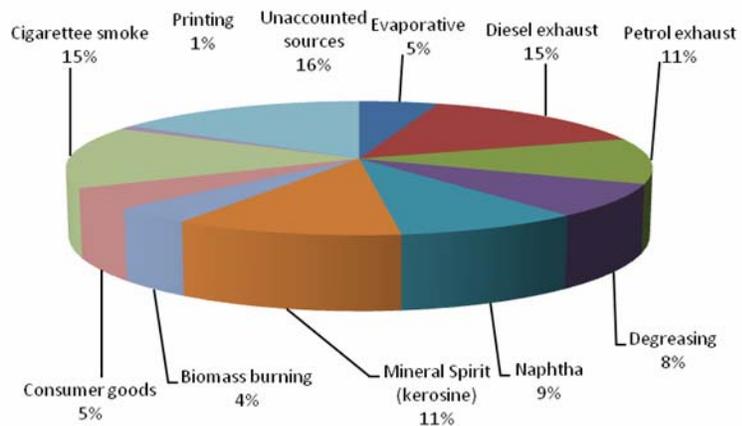
Figure 6.9: Source Contributions to Total VOCs at Kolkata Traffic Crossings Locations During Winter



Alipore

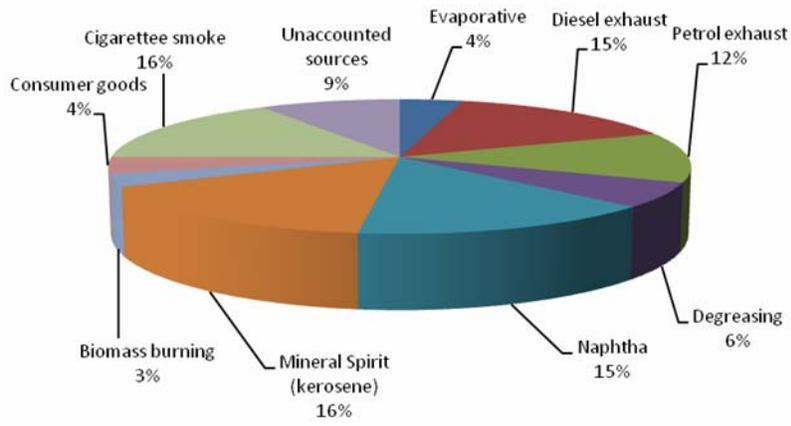
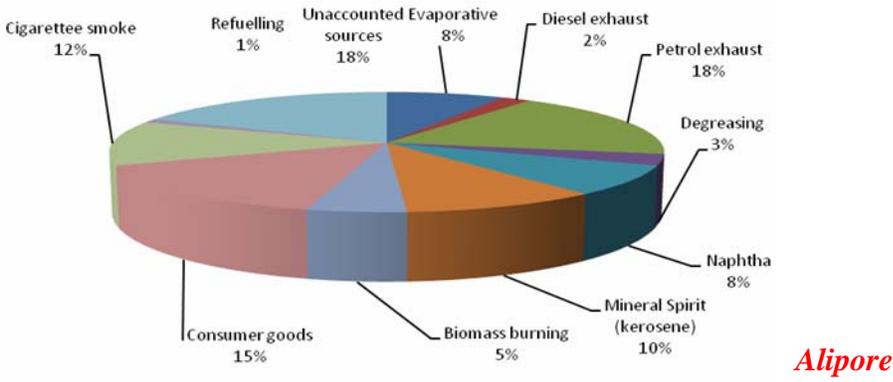


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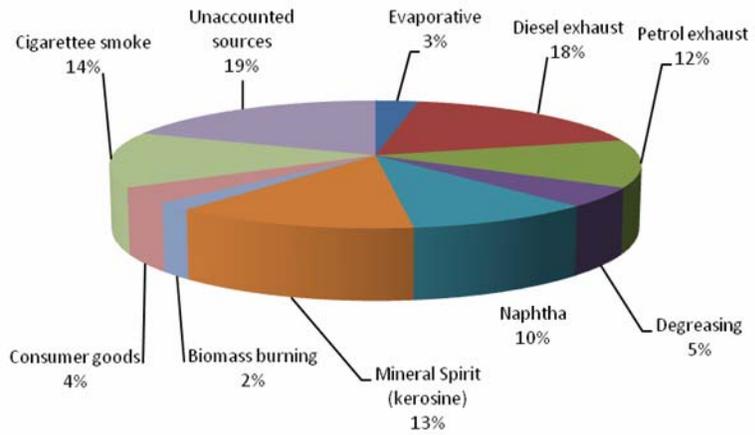


Dunlop

Figure 6.10: Source Contributions to Total VOCs at Kolkata Residential cum Commercial Locations During Summer

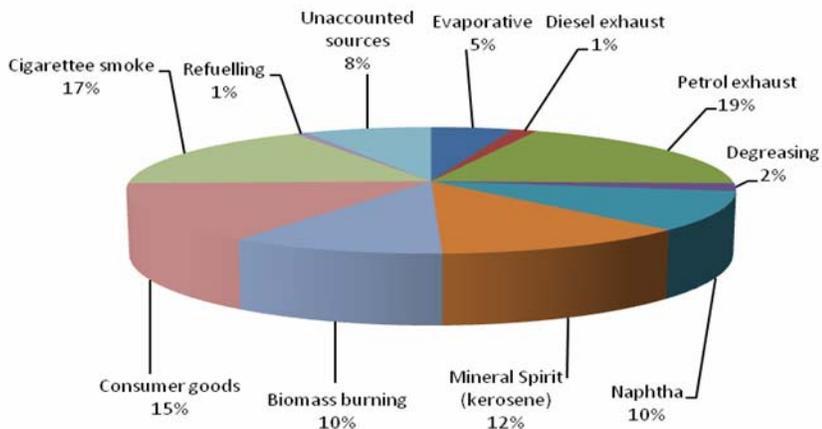


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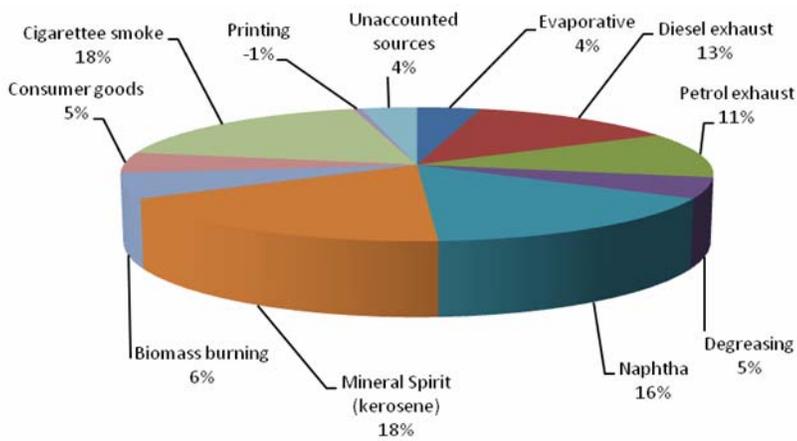


Dunlop

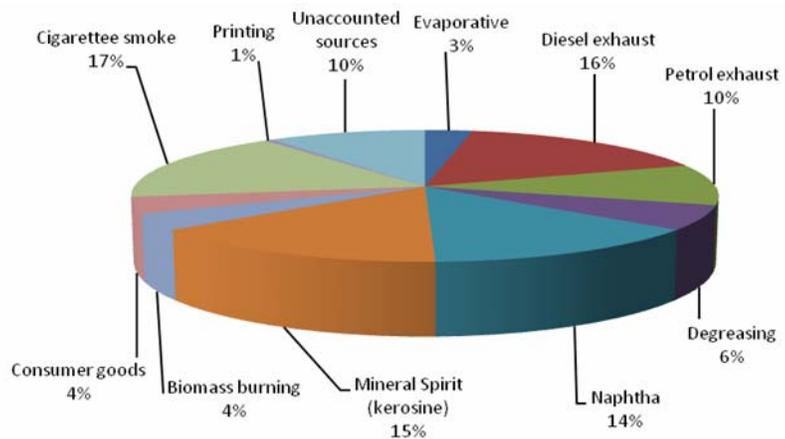
Figure 6.11: Source Contributions to Total VOCs at Kolkata Residential cum Commercial Locations During Monsoon



Alipore



Entally



Dunlop

Figure 6.12: Source Contributions to Total VOCs at Kolkata Residential cum Commercial Locations During Winter

It is observed that there is dominance of cigarette smoke, mineral oil and naphtha combustion emissions. The correlation coefficient r^2 values of the sources contribution ranges from 0.85 to 0.99. Ratio R/U which is a signed difference of measured and calculated concentration of species (residual), divided by the uncertainty of that residual lie well within the acceptable range. Acceptable values of R/U range from 0.5 to 2. Positive value of R/U indicates that one or more of the profiles are contributing too much to that species. Negative value of R/U is indicative of insufficient contribution to that species and a source may be missing.

However, R/U values for different species indicate improper representation of certain species concentration profiles. Chlorinated compounds, 1,3,5 trimethyl benzene are the major species which show improper representation.

Besides cigarette smoke, mineral oil and naphtha combustion emissions, consumer goods, biomass burning, degreasing, petrol exhaust and evaporative emissions also have significant contribution in residential cum commercial areas.

At industrial sites refueling (2%), biomass burning (3%), evaporative emissions, (4%) textile dyeing curing (4%), printing (4%), consumer goods (5%), degreasing (8%), petrol exhaust (9%), naphtha combustion (10%), cigarette smoke (11%), mineral oil combustion (12%) and diesel exhaust (13%) are the sources which contribute in increasing order.

At Petrol pumps sources which contribute significantly are refueling (16%), naphtha combustion (11%), petrol exhaust (10%), degreasing (10%), evaporative emissions (9%), mineral oil combustion (8%) diesel exhaust (8%), cigarette smoke (7%) and consumer goods (2%).

At traffic intersections evaporative emissions (1%), refueling (3%), degreasing (4%), cigarette smoke (10%), petrol exhaust (11%), diesel exhaust (13%), naphtha combustion (15%) and mineral oil combustion (15%) form major sources.

Chapter 7

Prediction of Ozone Concentrations

7.1 Need of Predicting Emissions

Prediction of effects is required for formulation of regulations to maintain clean air. Urban areas involve complex activities and therefore cover a wide variability and uncertainty in the spatial and temporal distributions of primary and secondary anthropogenic pollutants. This also makes it essential to use an authentic trend in the data for future prediction of the pollutant concentrations.

7.2 Basic Components

7.2.1 Parent Urban Chemical Transport Model

Regional scale models of atmospheric chemistry and physics can effectively simulate the processing of emissions on spatial and temporal time scales resembling those on the urban scale, allowing for both the time varying concentration within an area and export from a specific urban area to be computed. Comprehensive Air Quality Model with extensions (CAMx) (Environ, 2008), is an Eulerian model that solves the terrain following continuity equation, for the concentrations and fluxes of trace species. CAMx accounts for the emissions, vertical and horizontal transport and diffusion, gas and aerosol phase chemistry, and the wet and dry deposition of trace species. CAMx also considers the properties of the Earth's surface, the given atmospheric conditions, and the amount of incident solar radiation as a function of space and time, effect of the concentrations and distributions of trace species.

CAMx uses the continuity equation for a trace species in the atmosphere to account for these processes is by solving for each of the terms separately in the equation:

$$\begin{aligned} \frac{\partial c}{\partial t} = & - \nabla \cdot (c\mathbf{v}) + \frac{\partial(c\eta)}{\partial z} - c \frac{\partial}{\partial z} \left(\frac{\partial h}{\partial t} \right) + \nabla \cdot (\rho K \nabla (c/\rho)) + \frac{dc}{dt} \text{chemistry} \\ & + \frac{dc}{dt} \text{emissions} - \frac{dc}{dt} \text{deposition} - \frac{dc}{dt} \text{removal} \dots \dots \dots (1) \end{aligned}$$

Where, c is the concentration (moles or mass per unit volume) of a given species, v is the horizontal wind velocity, η is the vertical wind velocity, h is the vertical layer height, ρ is the atmospheric density, and K_v is the turbulent exchange diffusion coefficient.

According to this equation the net change in the concentration of a given species is the sum of: the convergence of the advective flux in the horizontal and vertical, and the diffusive flux; the chemical production and destruction, emissions, wet and dry deposition at the surface, and other physical removal processes (such as capture by cloud particles).

The assumptions are:

- all processes are uniformly distributed through each Eulerian grid box in which they occur;
- emissions are diluted through the grids adjacent to the surface, physical and meteorological variables are assumed to have a single average value over a grid box,
- tracers have a constant concentration throughout a grid box.

The advection routine is solved in mass-conserving flux form, driven by realistic assimilated meteorology from IMD during the sampling period. The amount of liquid water in the form of rain, the amount of cloud cover and the mass flux of air through the boundaries of the urban area. The vertical velocity is computed by integrating the density conservation equation. Wet removal occurs through Henry's Law processes, physical mixing, aqueous phase chemistry, and impaction by falling precipitation.

Dry removal occurs through first order surface resistance removal schemes for gases and aerosols, and gravitational settling for aerosols.

Gas phase chemistry is based on the Carbon Bond 4 approach (Gery *et al.*, 1989; Yarwood 2005), with a newer and more detailed representation of terpenes, low volatility organic species, and improved night time nitrogen chemistry.

Aerosol phase chemistry includes explicit inorganic aqueous phase chemistry, inorganic thermodynamics, and formation of secondary organic and inorganic aerosol.

Reduction in fluxes of incoming solar radiation as a function of overhead cloud thickness and reflection, and for surface reflection is accounted using photolysis scheme.

The precipitation processes include rain, and ice. All these are internally computed, based on the temperature and the strength of the vertical convection in the region.

7.2.2 Probabilistic Collocation Method

The probabilistic collocation method used by Tatang *et al.*, 1997 is one of several mathematical techniques which can be used for parameterization. Given a set of k input parameters x_j used to drive a model, $\{x_1, x_2, \dots, x_k\}$, there are M output responses y_j predicted by the model that are functions of the x_j values;

$$\{y_1, y_2, \dots, y_M\} = f(\{x_1, x_2, \dots, x_k\}) \quad \dots\dots\dots (2)$$

Where y_j are the physical concentrations, mass fluxes, and deposition fluxes of species that are approximated. Since there is a range of possible values which each input parameter can take, it is important to treat the input variables as being independent of each other with their statistics defined by their PDF over this range. All of the input variables are considered random, thus the output variables also are considered random variables.

The response surface is fitted specifically by a set of orthonormal polynomials (P_{ki})

Where i (= 1 or m below) is the order of the polynomial, g is the PDF of the random input variable

x_j , and δ_{lm} is the kronecker delta:

$$P_k^{-1} = 0 \quad \dots\dots\dots (3)$$

$$P_k^0 = 1 \quad \dots\dots\dots (4)$$

$$\int g(x_j) P_k^l(x_j) P_k^m(x_j) dx = \delta_{lm} \quad \dots\dots\dots (5)$$

Through these polynomials, the independent random variables can be written as

$$x_j = x_j^0 + x_j^1 * P_k^1, \quad \dots\dots\dots (6)$$

and the dependent variable y_j can be approximated by the polynomial chaos expansion:

$$y_j = y_j^0 + \sum_{i=1, N} y_j^i P_k^i \dots\dots\dots (7)$$

where y_j^i is a coefficient to be fit based on the parent model's predicted value for y_j at the given set of inputs $\{x_j\}$, and N is the order of the order of the polynomial fit.

In addition to forming the basis for the polynomial chaos expansion, the orthonormal polynomials are also used to help select the set of parameter values which are used to initialize the parent model. This set of input values, called collocation points, are solved for by finding the $N+1$ roots of the $N+1$ order polynomial corresponding to each input parameter x_j . These roots are from the high probability regions of each input parameter, and therefore the approximation of y_j is particularly good within the most probable range of values of the input parameters. In addition to this, a set of test points are generated from the solution of the $N+2$ roots of the $N+2$ order polynomial corresponding to each input parameter x_j . This second set of points take into account what the next higher order of estimation yields a better set of points for sampling the probability space spanned by the input parameters.

7.3 Methodology

7.3.1 Selected Inputs

The smallest possible set of input variables capturing the effects of urban chemical and physical processing must be derived in order to form a reduced form model which is as compact as possible. This set of inputs needs to be flexible enough to be applicable to the many variations of the properties of urban areas. The variables need to span the differences in geography, location, time of the year, atmospheric temperature, cloudiness, amount and type of precipitation, vertical motion, time tendency of emissions, spatial tendency of emissions, the amount of each type of emitted species, and the upwind concentrations of species of interest, as a function of space and time.

These input variable PDFs are defined and described in **Table 7.1** using the following formulas:

$$\text{Uniform } (a \leq x \leq b): f(x) = 1/(b-a) \dots\dots\dots (8a)$$

Beta ($a \leq x \leq b$; $p, q > 0$): $f(x) = [(x-a)^{p-1}(b-x)^{q-1}] / [(\int_0^1 t^{p-1}(1-t)^{q-1} dt)(b-a)^{p+q-1}] \dots$ (8b)

Lognormal ($x, m, \sigma > 0$): $f(x) = \exp(-(\ln(x/m))^2 / (2\sigma^2)) / (x\sigma\sqrt{2\pi}) \dots$ (8c)

Fixed: $f(x) = xS \dots$ (8d)

Where a, b, p, q, m, σ , and S are the parameters, and x is the input value, which in the case of the fixed equation, is the emissions of the appropriate parent species (either CO or BC).

Table 7.1: Descriptions of the Input Variable PDFs Used

Input Variable	Type of PDF#	Kolkata area	Urban
Day of the Year (Days)	Uniform (a,b)	1 365	
Geographic Latitude of Urban Area ($^{\circ}+90$)	Beta (p,q,a,b)	2.554 2.131 78.4 125.4	
Temporal Weight	Uniform (a,b)	0.00 1.00	
Spatial Distance (Km)	Uniform (a,b)	21.6 93.2	
Daily Average: Surface Temperature [$^{\circ}$ K]	Beta (p,q,a,b)	8.483 2.810 267.4 309.4	
Diurnal Temperature [$^{\circ}$ K]	Beta (p,q,a,b)	1.741 1.976 5.318 18.76	

Table 7.1 (contd.): Descriptions of the Input Variable PDFs Used

TVOC [ton/day]	Fixed (S)	0.2089
NOx [ton/day]	Fixed (S)	0.2511
<i>Boundary Values:</i>		
Ozone [ppb]	Lognormal (m, σ)	70.11 1.099
NOx [ppt]	Lognormal (m, σ)	19.22 1.595
TVOC [ppt]	Lognormal (m, σ)	472.98 2.534
Carbonyls [ppt]	Lognormal (m, σ)	502.65 3.015

See equations 8(a) - 8(d) for PDF formulas and parameters.

The first set of input variables in **Table 7.1** are for the time, location, emission spatial distribution, and temperatures as discussed later. The second set of input variables are fluxes for those species that are directly emitted in the urban area. The directly emitted species considered here are NOx (95% emitted as NO and 5% emitted as NO₂), and VOCs.

The other set of input variables in **Table 7.1** are the mole fractions of trace species along the boundaries (the four sides and the top) of the urban area that impact the chemical and physical processing inside the urban area. The trace species considered in this analysis are NOx, O₃, TVOCs (represented by toluene, xylene & chloroform) and Carbonyls. These concentration data were fitted by lognormal probability distribution functions, as given in **Figure 7.1** through **Figure 7.4**.

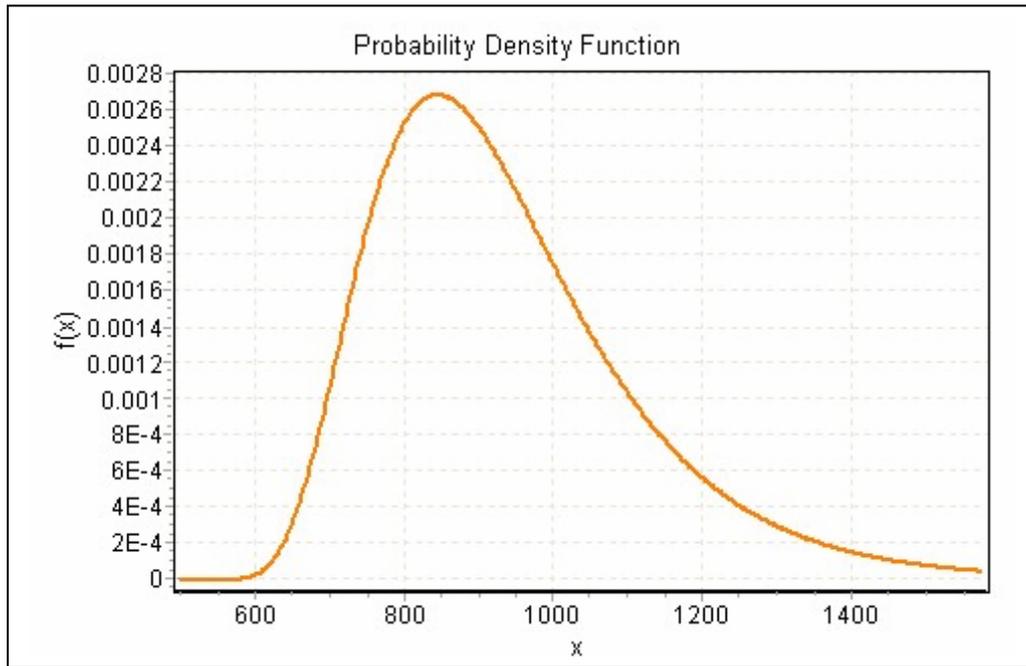


Figure 7.1: Lognormal Probability Distribution Function of Carbonyls

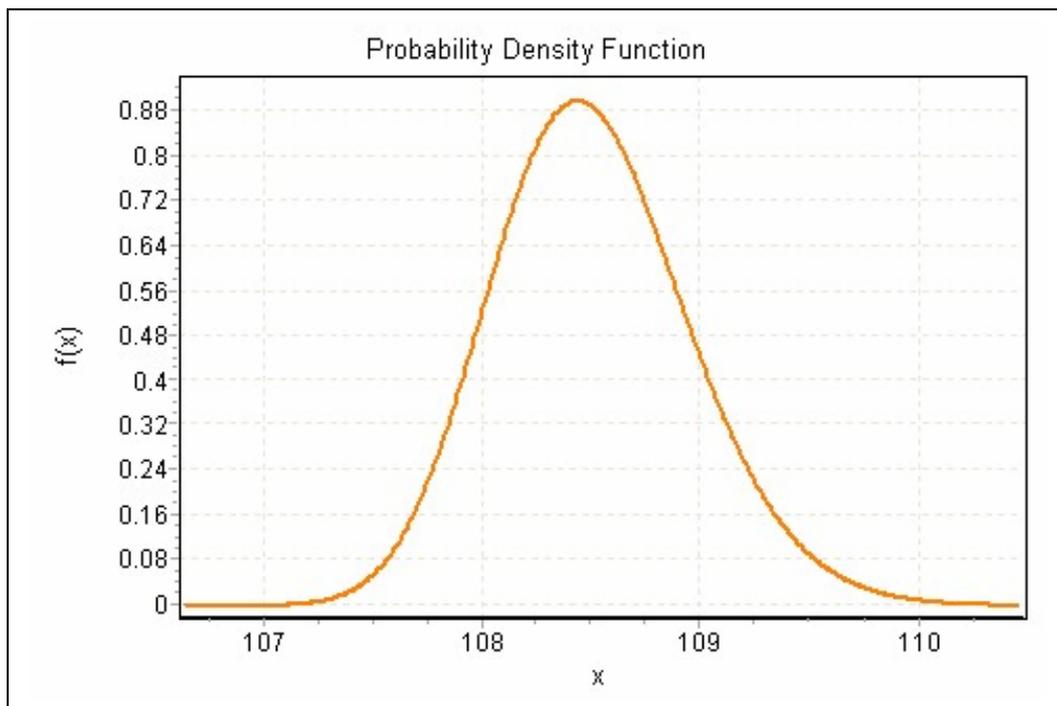


Figure 7.2: Lognormal Probability Distribution Function of NOx

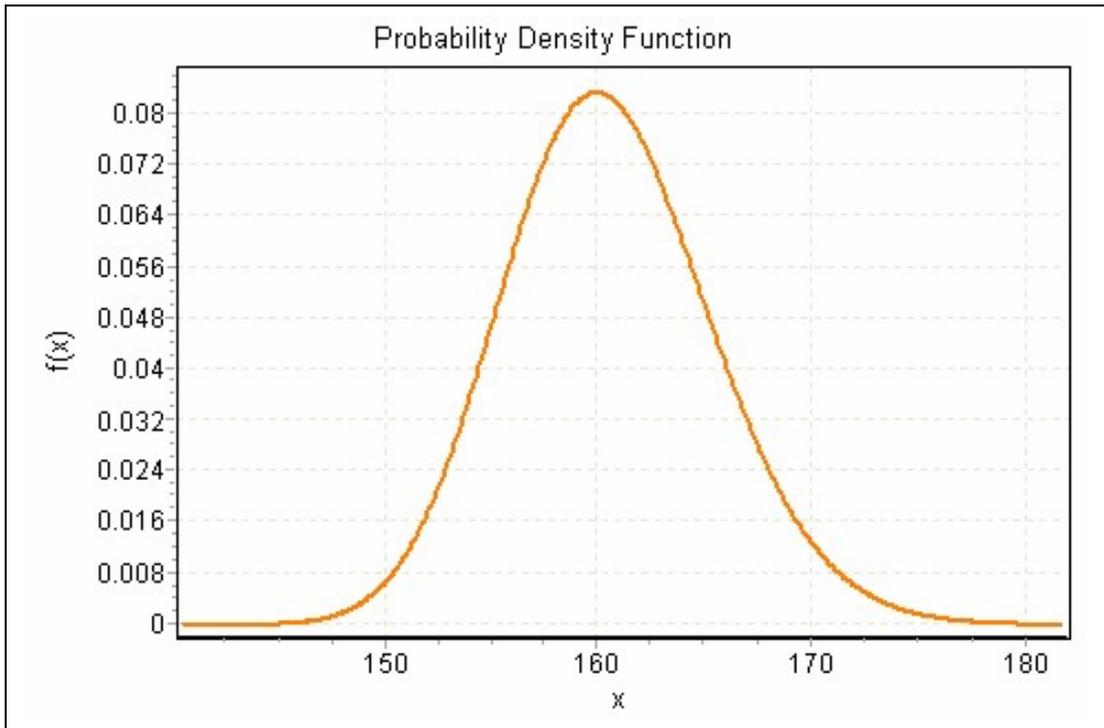


Figure 7.3: Lognormal Probability Distribution Function of Ozone

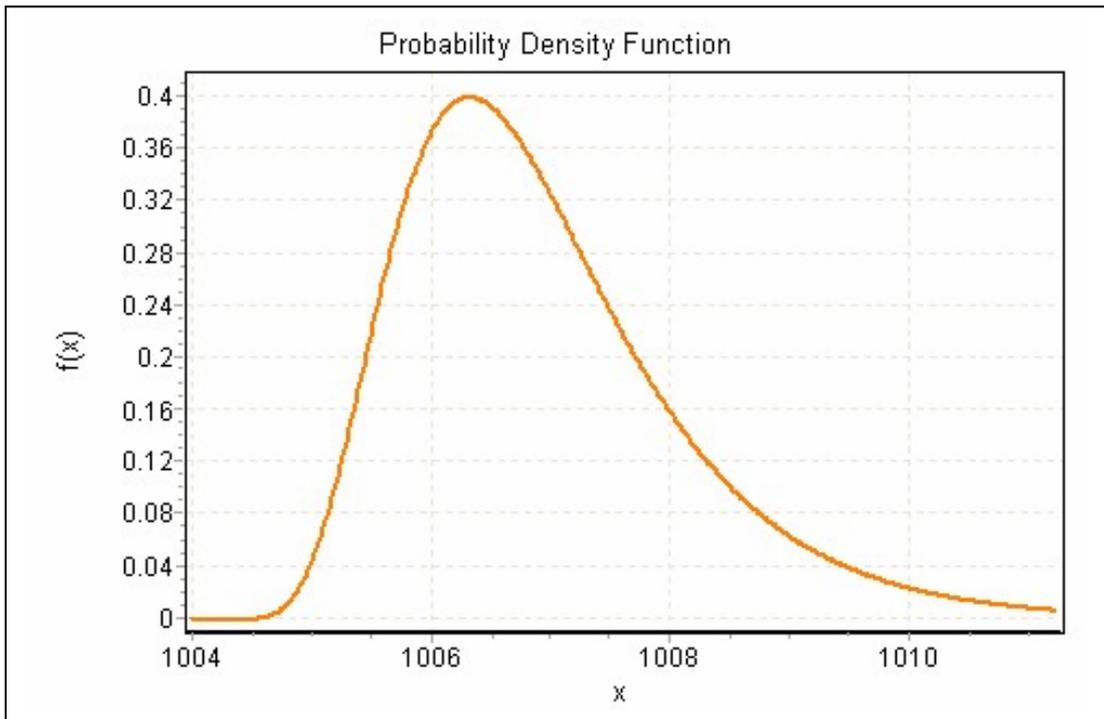


Figure 7.4: Lognormal Probability Distribution Function of Total Non Carbonyl VOC

The first two variables are the day of the year and the latitude of the urban region. These are both needed for computing the ultraviolet radiative flux. A uniform variable has been assigned, from 1 to 365 for the day of the year. A beta fit of the distribution of latitudes of urban area has been assumed, with an assumption that whole of urban area is of equal importance.

The daily average temperature and the daily diurnal temperature, at the surface of the urban area are the other inputs. The atmospheric temperature in the urban area and its range are important variables for determining the rates of many chemical reactions, Henry's Law partitioning, gas/aerosol phase partitioning, the state of water in the urban atmosphere, and the state and amount of precipitation. For the purposes of determining their global distribution, historical temperature data (Jones *et al.*, 1999) has been weighted by the beta PDF of latitude for the urban area, and the resulting data fitted by a beta function. The average 16 temperature of each vertical layer above the surface is computed assuming a linear decline with height with standard linear lapse rate of 6.5K/km. The spatial and temporal deviations from these layer averages in the temperature of each grid box of the urban domain are taken from the meteorology chosen for that particular urban region. The average daily surface temperature and average daily diurnal surface temperature are given in **Figures 7.5 & 7.6**.

The last physical input is rainfall (and the associated cloudiness), which impacts the radiative fluxes, the uptake of soluble gases, and the removal rate of aerosols. After extensive testing, it has been found that treating these inputs as separate variables using the PCM approach does not yield reasonable results, due to the extremely non-linear impact these variables have on the system. Therefore, separate metamodels were formed for each of the four meteorological conditions.

It is commonly found that emissions in urban areas have a time profile which is doubly peaked, with the peaks occurring around the times of the morning and evening rush hours. The first variable thus represents the temporal distribution of emissions, which mimicks transportation and habitation patterns of the people.

To account for this, an input variable (w_t) is defined that is uniformly distributed from 0 to 1, and is the weight given to this double peak temporal emissions spectrum when it is linearly added to a time invariant emissions profile. Therefore, for any given value of w_t the weights assigned to the double-peaked distribution is w_t and the weight assigned to the time invariant emissions distribution is $1-w_t$

(Yang *et al.*, 2005). A second input variable relates to the spatial distribution of emissions in the urban region. Such a distribution must consider that urban areas vary greatly in terms of their density of people, activity, and thus emissions. In general, different emitted species come from different sources, which themselves may be distributed independently from one another in many cases. However, since most emissions are related to the population in the urban centers, the emissions of both VOC and NO_x are considered to be spatially correlated. These spatial distributions are fitted by a 2-dimensional Gaussian function whose standard diameter has a uniform distribution.

Another input is required to simulate whether VOC emissions consist of a larger fraction of light hydrocarbons.

To address the issue of the impacts of the circulation, water content, and temperature on the processing in urban areas, three different realistic sets of meteorology have been used to drive the urban modeling system. The widely different cases are considered to represent different seasons and to numerically analyze the impact of adopting different types of realistic meteorology.

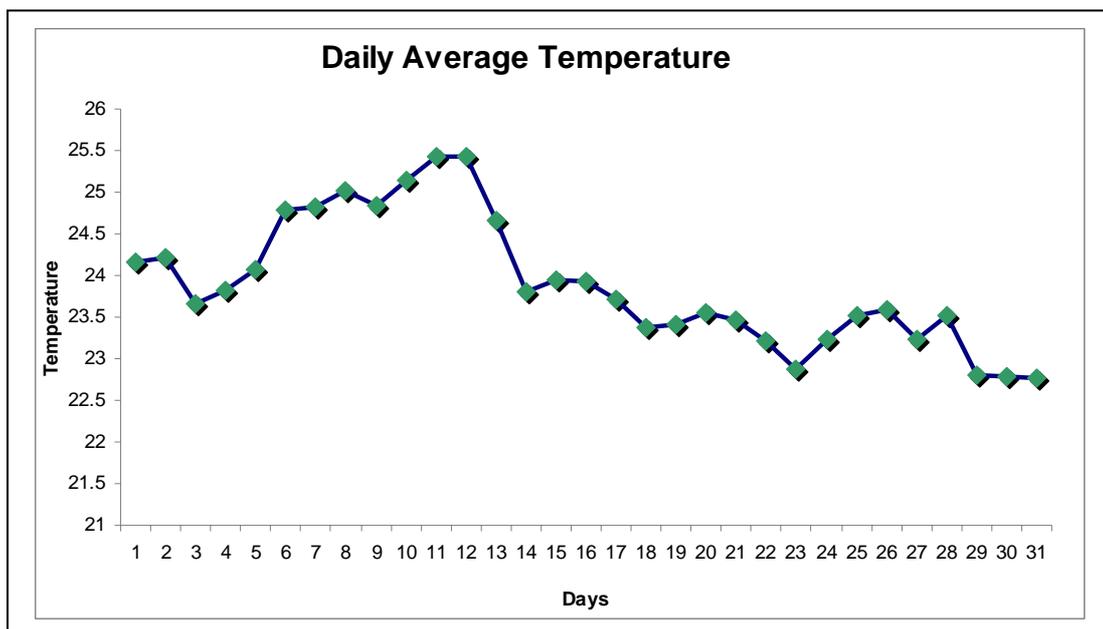


Figure 7.5: Average Daily Surface Temperature

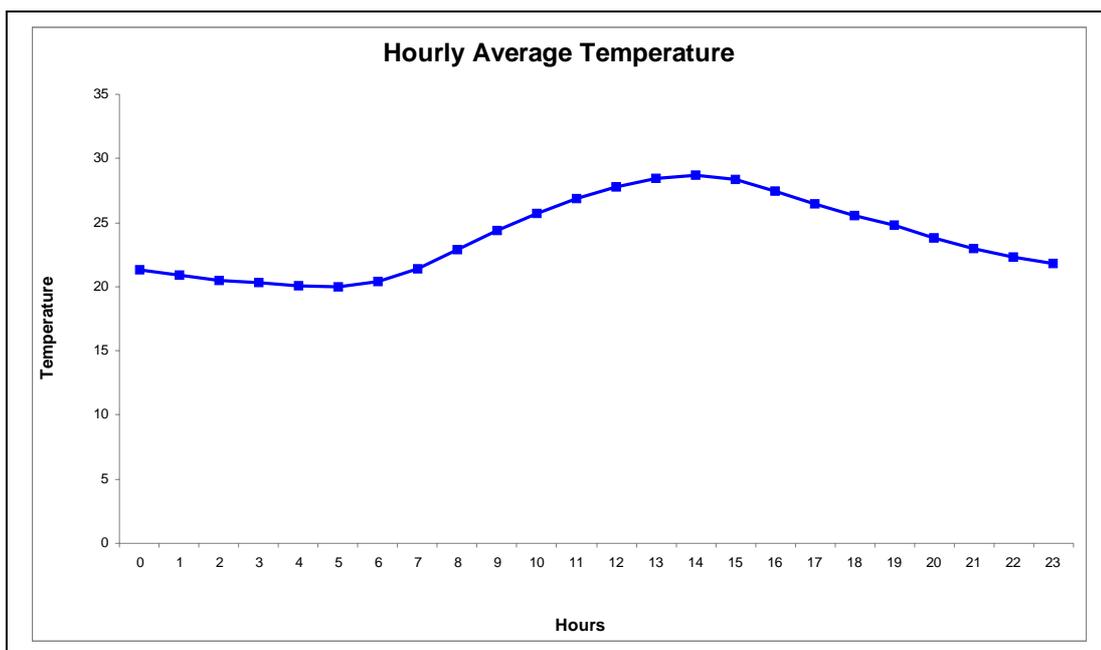


Figure 7.6: Average Daily Diurnal Surface Temperature

Concentrations, Mass Fluxes, and Deposition

The results for the urban concentrations for ozone, formaldehyde, acetaldehyde, toluene and xylene species are given in **Figure 7.7** through **Figure 7.11**.

The regions of higher mole fractions must have a larger net chemical production (production minus loss) of the species. Conversely, regions with lower mole fractions must have more a smaller or negative net chemical production of the species. Also, if the mole fraction remains constant across different regions, then this means that there is negligible net chemical production.

When looking at the metamodel results for the mass fluxes, emissions, chemical production or loss, and the deposition, it is straightforward to determine whether the urban area is a net importer or exporter of the species of interest. For a species to have a mass flux which is not equal to its emissions there must be a net amount of chemical processing, deposition, or convergence or divergence in the continuity equation. A convenient parameter is the ratio of the export flux to the emissions:

$$\text{Flux/Emiss} = (\text{Emiss} + \text{Chem} - \text{Dep})/\text{Emiss} = 1 + \text{Chem/Emiss} - \text{Dep/Emiss} \dots(9)$$

Here the Flux is the net mass flux [g/day] through the boundaries of the urban region, Emiss is the emissions [g/day] into the urban area, Chem is the net

chemical production [g/day] within the urban region, and Dep is the deposition [g/day] to the surface of the urban region.

Using this, if the mass flux is positive and larger than the emissions, then the in-situ chemical net production must be larger than the in-situ depositional losses. Conversely, if a species has a mass flux which is positive but smaller than its emissions, its losses due to deposition must be greater than its net chemical production. Furthermore, for a species to have a mass flux which is negative (a net flux into the region), the in-situ net chemical loss must be so large as to consume not only all of the emissions, but also some of the species mass transported through the boundaries into the urban area.

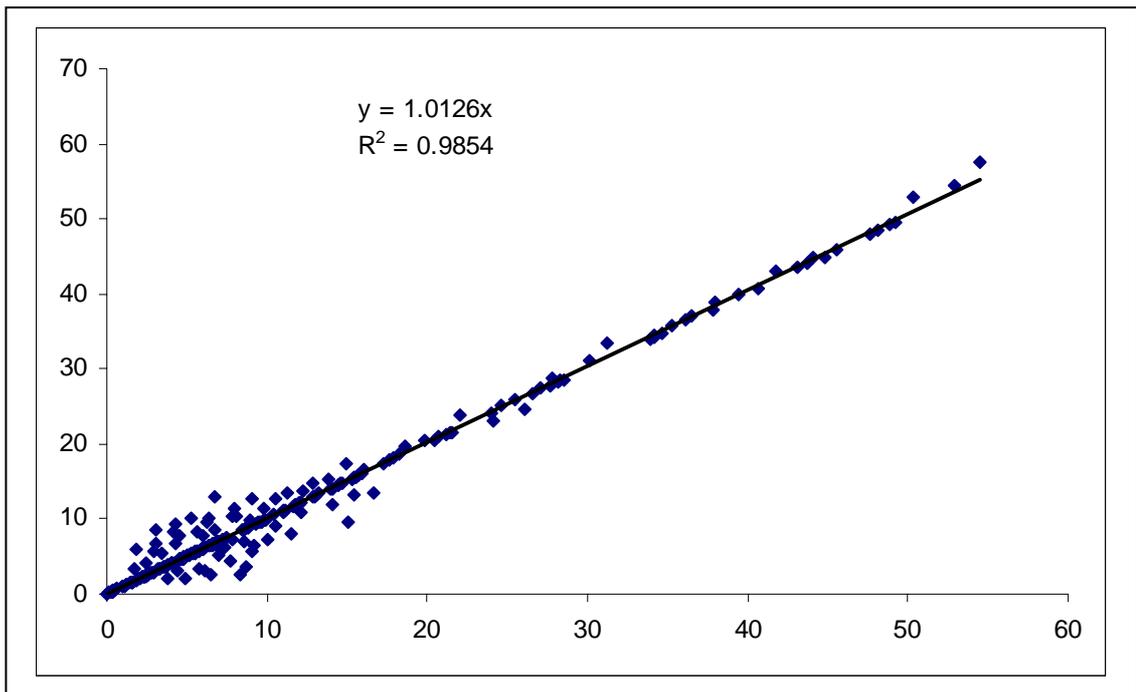
If X_i is the value computed by the metamodel, X_{ip} is the value computed by the CAMx model, and n is the number of points analyzed we have:

$$\text{normalized RMS} = \sqrt{(\sum_{i=1,n}(X_{ip}-X_i)^2/n)} / \sqrt{(\sum_{j=1,n}X_j^2/n)} \quad \dots\dots\dots(10)$$

The RMS error gives a measure of the absolute magnitude of the error.

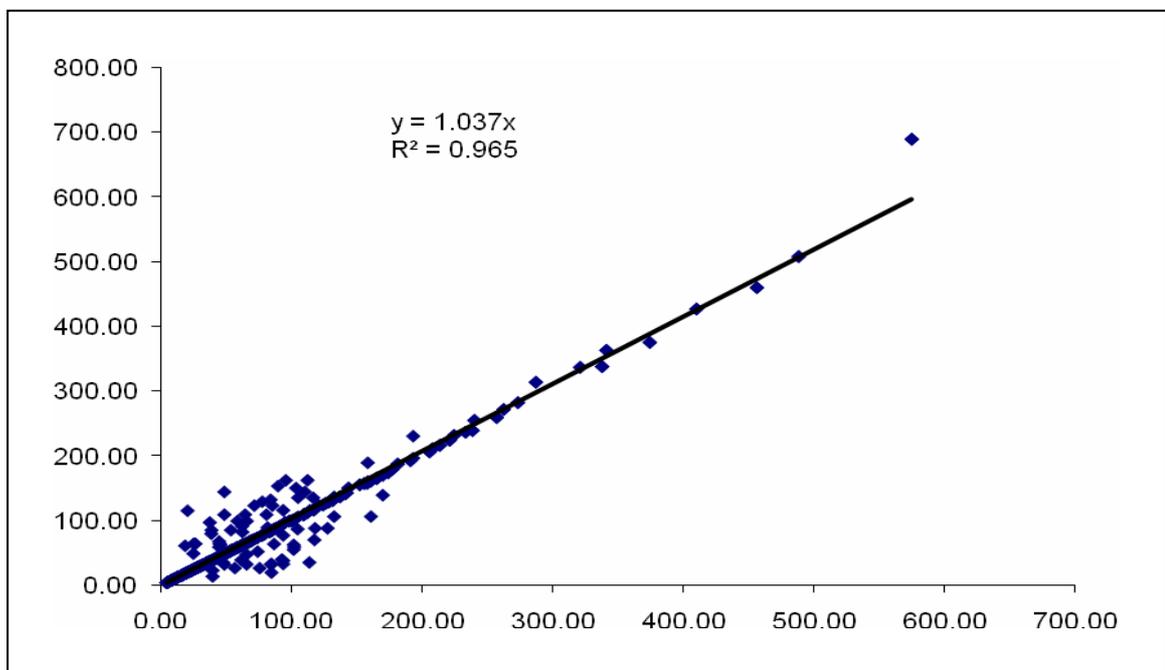
Normalized fractional RMS errors for species concentrations using CAMx model.

Species	Summer	Monsoon	Winter
Ozone	1.38E-01	2.68 E-01	1.46 E-01
Formaldehyde	2.98 E-01	3.75 E-01	3.01 E-01
Acetaldehyde	1.36 E-01	3.69 E-01	3.76 E-01
Toluene	7.94 E-01	0.89 E-01	8.15E-01
Xylene	3.57 E-01	9.67E-01	4.15 E-01



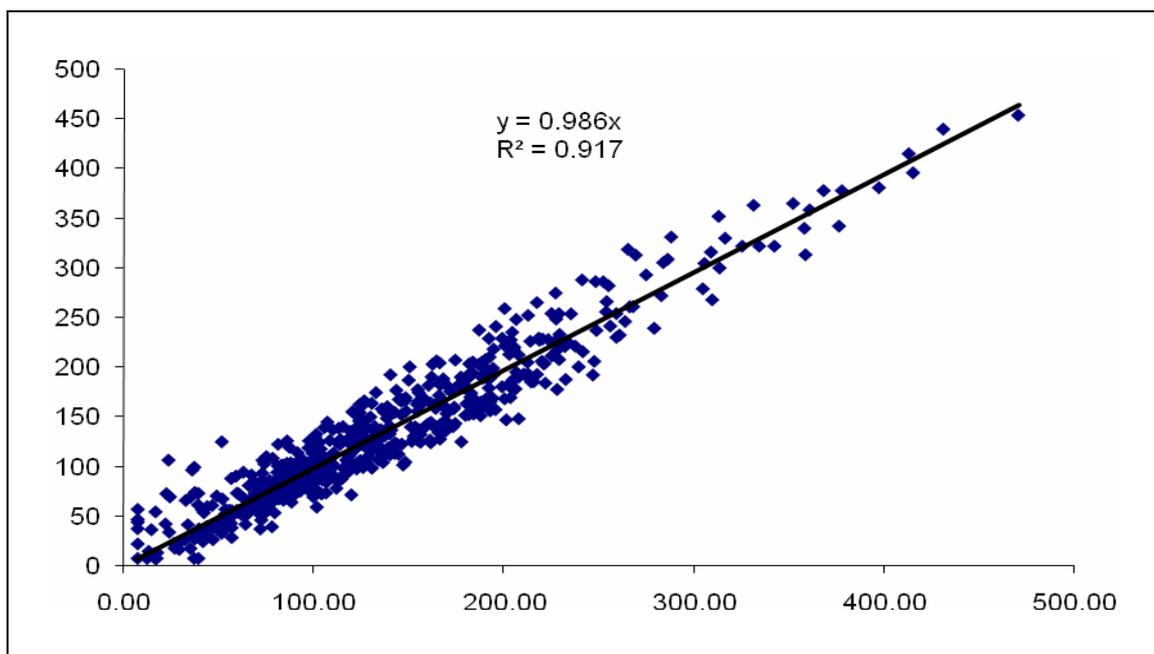
X Axis: Observed Concentration, Y Axis: Predicted concentration

Figure 7.7: Observed and Predicted Concentration of Ozone



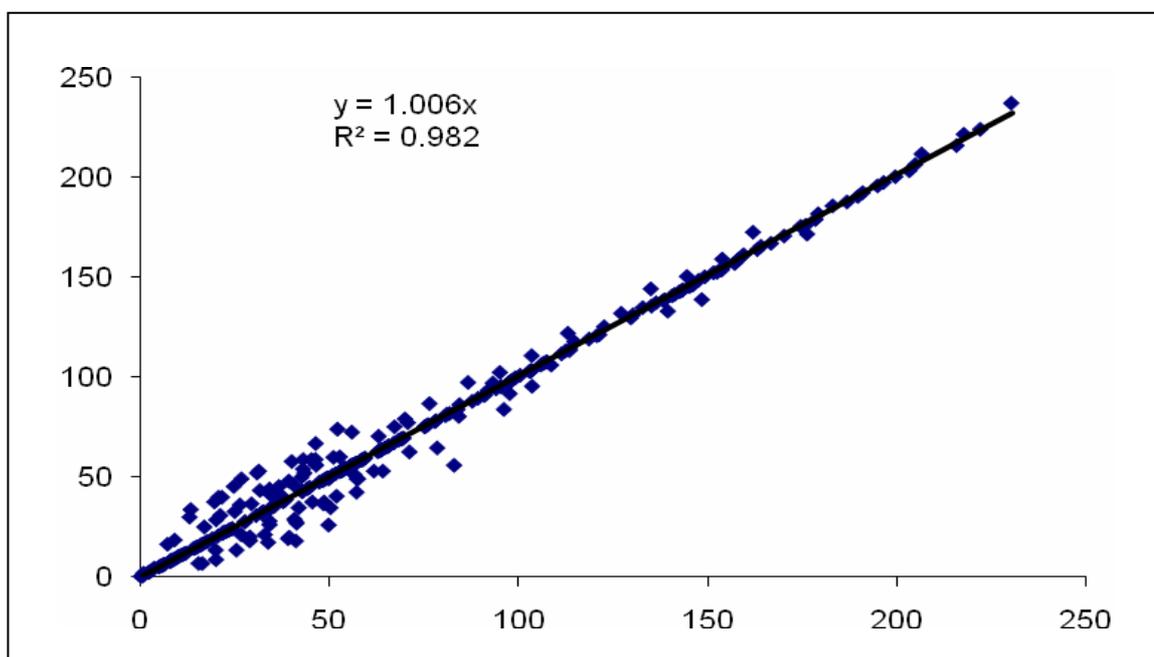
X Axis: Observed Concentration, Y Axis: Predicted concentration

Figure 7.8: Observed and Predicted Concentration of Formaldehyde



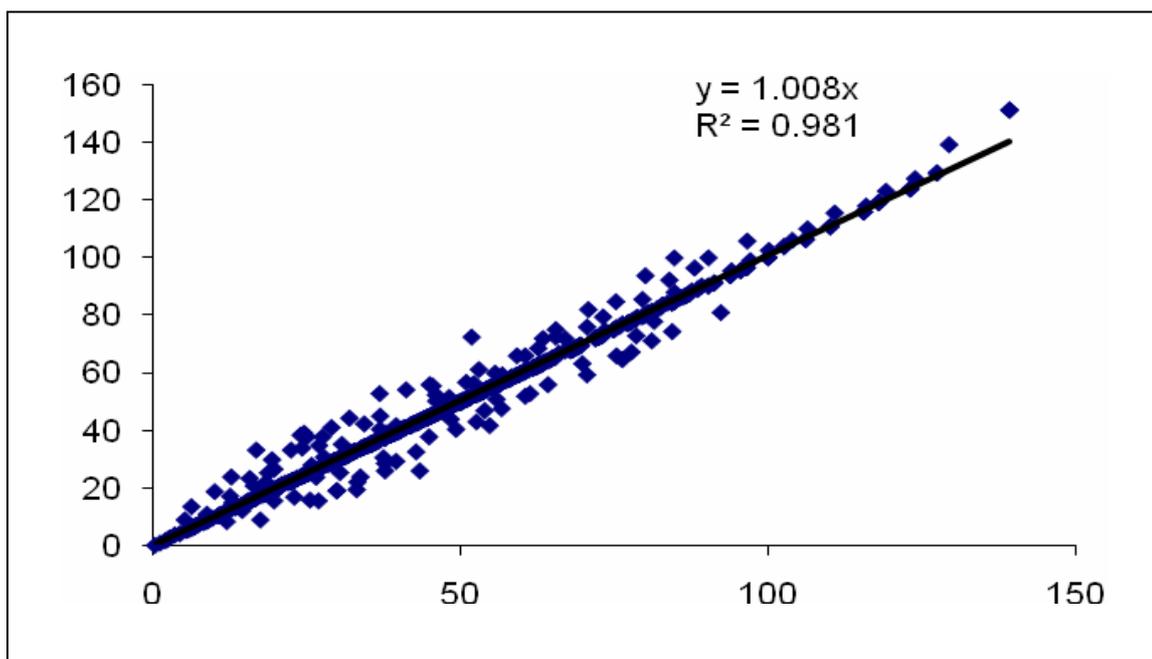
X Axis: Observed Concentration, Y Axis: Predicted concentration

Figure 7.9: Observed and Predicted Concentration of Acetaldehyde



X Axis: Observed Concentration, Y Axis: Predicted concentration

Figure 7.10: Observed and Predicted Concentration of Toluene



X Axis: Observed Concentration, Y Axis: Predicted concentration

Figure 7.11: Observed and Predicted Concentration of Xylene

Chapter 8

Health Risk Assessment

8.1 Assessment Steps

The human health risk assessment process includes consideration of risks to individuals and populations, including sensitive sub-populations, (e.g., children, pregnant women, the elderly and individuals with respiratory impairments). This includes four discrete steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization (USEPA 1997).

The hazard identification:

This step defines exposure conditions and catalogs environmental stressors (i.e., pollutants), receptors i.e. the human sub-population, and pathways by which receptors contact stressors i.e. the routes of exposure. Hazard identification is to recognize the conditions that may cause adverse effects, which may be acute (e.g., nausea or headaches), chronic (e.g., emphysema or central nervous system depression) or life-threatening (e.g., central nervous system disability or cancer). The nature of hazards caused by a single, repeated or lifelong exposure to pollutant(s) may be carcinogenic, non-carcinogenic or both. Carcinogenic hazards describe the development of any type of cancer in any part of the body. All health effects other than cancer are classified under this hazard category.

The dose-response assessment:

This step establishes a relationship between the extent of contact with a stressor via a specific route (e.g. oral, inhalation, dermal) and the nature and severity of adverse effects that result. Dose-response information of a pollutant can be obtained from epidemiology studies as well as animal studies.

Dose -response for non-carcinogens: For non-carcinogenic effect, toxicants have a “threshold dose” below which the body’s defensive mechanisms protect against adverse health effects. Exposure to the contaminant at sub-threshold doses is less likely to cause harm. The more an exposure exceeds the threshold, the more likely

and severe the health effect is likely to be. According to USEPA, a “reference dose” or Reference concentration (RfD or RfC) is a daily dose/concentration, which is expected to be without adverse effect to human populations, including sensitive individuals (USEPA 1997). The uncertainty surrounding the RfD/RfC is expected to be an order of magnitude or more. Discrete RfD/RfCs may be calculated for chronic (lifetime), sub-chronic (long term but less than lifetime), and acute (short term; hours or days) exposure periods.

Dose-response for carcinogens: Carcinogenic health effects do not have a simple dose-response relationship. Instead, they are considered to pose an incremental risk of causing cancer for each exposure increment above zero. Thus carcinogenic contaminants have no threshold limit for effects.

In assessing carcinogenic potential of a chemical, the USEPA classifies the chemical according to the credence of evidence from epidemiologic and animal studies, as follows:

Group A - Human Carcinogen (sufficient evidence of carcinogenicity in humans)

Group B - Probable Human Carcinogen (B1-limited evidence of carcinogenicity in humans; B2-sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans)

Group C - Possible Human Carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data)

Group D - Not Classifiable as to Human Carcinogenicity (inadequate or no evidence)

Group E - Evidence of Non-carcinogenicity for Humans (no evidence of carcinogenicity in adequate studies).

The USEPA follow a linear multi-stage model for carcinogenesis, which extrapolates relatively high doses used in animal studies to low environmental doses via a straight line. The slope of this line is the Carcinogenic Potency Slope (CPS), or Slope Factor (SF) which is the upper bound excess cancer risk per unit dose, $(\text{mg kg}^{-1} \text{ day}^{-1})^{-1}$.

The exposure assessment:

The third step of a human health risk assessment that is the exposure assessment determines i) which receptors are likely to be exposed to the contaminants of concern, ii) how the exposures may occur and iii) the magnitude and duration of the exposures. Human exposure can occur by inhalation (direct) and by indirect pathways such as dermal contact and ingestion of hazardous air pollutants deposited to soil and water. The duration of exposure is affected by the fraction of time that the sources of pollution are in operation as well as the fraction of time that individuals are present at a particular location. The extent to which an individual will be impacted by direct inhalation exposure can be expressed as a function of the duration of exposure, volume of air inhaled, and contaminant concentrations.

The risk characterization:

The final step of risk assessment integrates information from the three preliminary steps to estimate the likelihood of adverse effects. The risk characterization assumes that the carcinogenic effects as well as the non-carcinogenic hazard from different contaminants are additive. The calculated carcinogenic risk is the upper bound lifetime excess risk of contracting cancer from the exposure. The non-carcinogenic risk, calculated as Hazard Quotient (HQ) of individual pollutant, indicates the existence of some potential for adverse effects when the HQ value exceeds unity. The higher the HQ, the greater the possibility of effects.

8.2 Data Source

This study is on the last two steps of risk assessment process i.e., exposure assessment and risk characterization for human exposure towards VOCs. Information on hazard identification and dose-response assessment has been taken from previously reported studies and as documented in the online database of the Risk Assessment Information System (USEPA, RAIS). The toxicity values (RfC and unit risk) used in the risk calculation in this study associated with the target pollutants are also taken from the above database.

8.3 Assumptions:

Inhalation to be the primary exposure pathway of air pollutants to humans.

- The average person has a body weight of 70 kilograms and a breathing rate of $0.83 \text{ M}^3 \text{ hr}^{-1}$. This default assumption may underestimate risks to children and more highly sensitive individuals.
- Risk estimates assume that people spend their lifetime (70 years) exposed to the annual average ambient hazardous air pollutant concentrations estimated for their area. This assumption could lead to overestimation of potential health risks if pollution levels decline over time. It could lead to underestimation if people live in "hotspots" where pollutant concentrations are higher than area averages.
- Risk values do not incorporate chemical-specific uptake factors for each pollutant, but rather assume 100% of the inhaled dose is absorbed into the body. This could be a source of overestimation of risks.
- Exposures to hazardous air pollutants through other exposure routes, such as food and drinking water, are not taken into account. Omission of these exposures may underestimate potential human health risks.
- The lack of comprehensive cancer and non-cancer toxicity data for each hazardous air pollutant means that the cumulative risk estimates for cancer and non-cancer health effects may be underestimated
- A person may be exposed to a toxic air pollutant differently depending upon the activities (such as occupation, running, cooking, commuting) and microenvironment (indoor, in-vehicle). In this study we are not considering those factors and assuming a 24 hr average exposure derived from ambient concentration only. This may lead to an underestimation of risk.

8.4 Risk Assessment

8.4.1 Exposure calculation

The daily exposure (E in $\text{mg kg}^{-1}\text{day}^{-1}$) of an individual due to intake process (considering inhalation only) was calculated (US EPA 1997) from the equation (1)

$$E=C \cdot IR_a \cdot ED/BW_a \quad \dots\dots\dots (1)$$

Where, C is concentration (mg m^{-3}) of the target pollutant; IR_a is the adult Inhalation Rate ($0.83 \text{ m}^3 \text{ hr}^{-1}$, USEPA 1997); ED is Exposure Duration (in hour day^{-1} depending upon the nature of exposure); BW_a is adult Body Weight (70 kg).

8.4.2 Calculation of Chronic Non-Cancer Risk

Non-cancer risk, expressed as Hazard Quotient (HQ), is given as the ratio between the yearly average ambient concentration and the Chronic Inhalation Reference Concentration, RfC (a level below which adverse health effects are not likely to occur). This algorithm was used to calculate chronic non-cancer risk (i.e., risk associated with long-term exposures). Summation of HQs for individual contaminants gives Hazard Index (HI).

8.4.3 Calculation of Cancer Risk

Cancer risks was calculated from the equation (2)

$$\text{Risk} = C * \text{Unit risk} \dots\dots\dots (2)$$

Where, Unit risk is *Inhalation unit risk*, the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of or 1 mg/m^3 in air.

8.5 Estimated Daily Exposure and Risk Values

Risk assessment due to exposure towards toxic carbonyls and non-carbonyls were performed for different location category within Kolkata Metropolitan city. The exposures from individual pollutants are given in **Table 8.1**. General population will have maximum exposure of acetaldehyde (in industrial area and near petrol pumps) and acrolein (in residential area, near traffic crossing and also overall) owing to their high ambient concentration. Considering all the **toxic compounds studied** an average person with 70 kg of body weight is likely to receive an inhalation exposure of 20.2 mg per day in the city of Kolkata.

Table 8.1: Estimated Value of Daily Exposure in mg/kg/day from Individual Pollutant

Compounds	Industrial	Petrol Pump	Residential	Traffic crossing	Overall Average
Benzene	5.2E-03	1.1E-02	1.6E-03	7.4E-03	6.1E-03
Toluene	3.2E-02	2.4E-02	5.3E-03	1.5E-02	1.9E-02
Ethylbenzene	6.4E-03	7.5E-03	1.1E-03	4.9E-03	5.0E-03
Xylene	8.9E-03	1.4E-02	4.2E-03	7.1E-03	1.1E-02
Chloroform	1.6E-02	8.3E-03	2.6E-02	1.1E-02	1.5E-02
Tetrachloroethylene	9.3E-04	6.7E-04	5.7E-05	8.7E-05	4.8E-04
Methylenechloride	3.0E-04	2.2E-04	3.8E-04	2.0E-04	2.8E-04
Naphthalene	9.5E-04	1.2E-03	6.9E-04	4.6E-04	8.2E-04
Styrene	3.1E-03	4.0E-03	7.9E-04	4.7E-04	2.1E-03
Carbon Tetrachloride	5.9E-04	8.1E-04	3.0E-04	3.4E-04	6.4E-04
Formaldehyde.	2.1E-02	2.6E-02	1.8E-02	4.8E-02	2.8E-02
Acetaldehyde	4.4E-02	3.6E-02	4.0E-02	5.2E-02	4.3E-02
Acetone	1.3E-02	1.2E-02	1.6E-02	3.2E-02	1.8E-02
Acrolein	4.3E-02	3.6E-02	4.3E-02	5.5E-02	4.4E-02
Propionaldehyde	1.3E-02	9.1E-03	1.6E-02	1.0E-02	1.2E-02
Butanal	2.9E-03	4.5E-03	7.2E-03	3.9E-03	4.6E-03
Crotonaldehyde	9.2E-03	6.3E-03	6.3E-03	1.5E-02	9.3E-03
Benzaldehyde	5.7E-03	4.9E-03	5.5E-03	6.3E-03	5.6E-03
Isovalaraldehyde	7.6E-03	6.8E-03	7.1E-03	1.1E-02	8.1E-03
Valaraldehyde	9.9E-03	7.7E-03	9.0E-03	2.5E-02	1.3E-02
o-Tolualdehyde	5.2E-03	5.6E-03	4.0E-03	3.8E-03	4.6E-03
m,p-Tolualdehyde	2.1E-02	1.2E-02	1.7E-02	1.4E-02	1.6E-02
Hexanal	1.0E-02	1.0E-02	1.2E-02	3.7E-02	1.7E-02
2,5-Dimethylbenzaldehyde	7.8E-03	1.9E-03	3.4E-03	2.9E-03	4.0E-03

The estimate of non-cancer hazard quotient (HQ) for individual toxic compounds is given in **Table 8.2**. The hazard index (HI), i.e. the summation of all individual HQs, was found to be 7.82E+03 for overall Kolkata which is very high compared to the threshold value of 1. This indicates the possibility of serious non-cancer hazards or illness which can be faced by general population derived from the inhalation of toxic compounds in Kolkata air. The HI was found to be maximum for traffic crossing (9.72E+03) followed by industrial and residential area

(7.63E+03 for both the area) and least in petrol pumps 6.32E+03. Acrolein was found to have the highest HQ value due to its low RfC (reference concentration) value and high ambient concentration.

Table 8.2: Estimated Value of Non-Cancer Hazard Quotient in mg/kg/day from Individual Pollutant

Compounds	Industrial	Petrol Pump	Residential	Traffic crossing	Overall Average
Benzene	6.1E-01	1.3E+00	1.9E-01	8.6E-01	7.2E-01
Toluene	2.3E-02	1.7E-02	3.7E-03	1.1E-02	1.3E-02
Ethylbenzene	2.3E-02	2.6E-02	4.0E-03	1.7E-02	1.8E-02
Xylene	4.5E-02	7.1E-02	2.1E-02	3.5E-02	5.4E-02
Chloroform	5.6E-01	3.0E-01	9.3E-01	3.9E-01	5.4E-01
Tetrachloroethylene	1.2E-02	8.7E-03	7.4E-04	1.1E-03	6.2E-03
Methylenechloride	1.0E-03	7.4E-04	1.3E-03	6.8E-04	9.3E-04
Naphthalene	1.1E+00	1.4E+00	8.0E-01	5.4E-01	9.6E-01
Styrene	1.1E-02	1.4E-02	2.8E-03	1.6E-03	7.2E-03
Carbon Tetrachloride	3.2E-03	2.2E-02	3.9E-03	4.0E-03	7.1E-03
Formaldehyde.	7.4E+00	9.2E+00	6.4E+00	1.7E+01	1.0E+01
Acetaldehyde	5.0E-03	4.1E-03	4.5E-03	5.9E-03	4.9E-03
Acetone	1.5E-03	1.3E-03	1.8E-03	3.6E-03	2.1E-03
Acrolein	7.6E+03	6.3E+03	7.6E+03	9.7E+03	7.8E+03
Propionaldehyde	5.6E+00	4.0E+00	6.9E+00	4.4E+00	5.2E+00
Butanal	6.9E-01	1.1E+00	1.7E+00	9.2E-01	1.1E+00
Valaraldehyde	8.3E-02	6.4E-02	7.5E-02	2.1E-01	1.1E-01

Among the all the toxic compounds under consideration nine are carcinogenic. The probability of excess cancer risk for a person residing for 40 years in this city is described in **Table 8.3**. Considering all the carcinogens studied the cancer risk was found to be an alarming 3176 in every million population. According to Census 2001 the total population of Kolkata is 13,205,697 so the 41,935 persons are under threat to develop some kind of cancer only due to inhalation of these few carcinogens. Figure 1 describes the percentage contribution of different carcinogens towards the total cancer risk.

Table 8.3: Estimated Value of Cancer Risk* in Million Populations from Individual Pollutant

Compounds	Industrial	Petrol Pump	Residential	Traffic crossing	Overall Average
Benzene	1.4E+02	2.9E+02	4.5E+01	2.0E+02	1.7E+02
Ethylbenzene	5.6E+01	6.6E+01	1.0E+01	4.3E+01	4.4E+01
Chloroform	1.3E+03	6.7E+02	2.1E+03	8.8E+02	1.2E+03
Tetrachloroethylene	1.9E+01	1.4E+01	1.2E+00	1.8E+00	9.9E+00
Methylenechloride	4.9E-01	3.6E-01	6.3E-01	3.3E-01	4.6E-01
Naphthalene	1.1E+02	1.4E+02	8.2E+01	5.5E+01	9.8E+01
Carbon Tetrachloride	9.1E+00	6.2E+01	1.1E+01	1.1E+01	2.0E+01
Formaldehyde.	9.5E+02	1.2E+03	8.2E+02	2.2E+03	1.3E+03
Acetaldehyde	3.4E+02	2.8E+02	3.1E+02	4.0E+02	3.3E+02

*For 40 Years Residency Period in Kolkata City

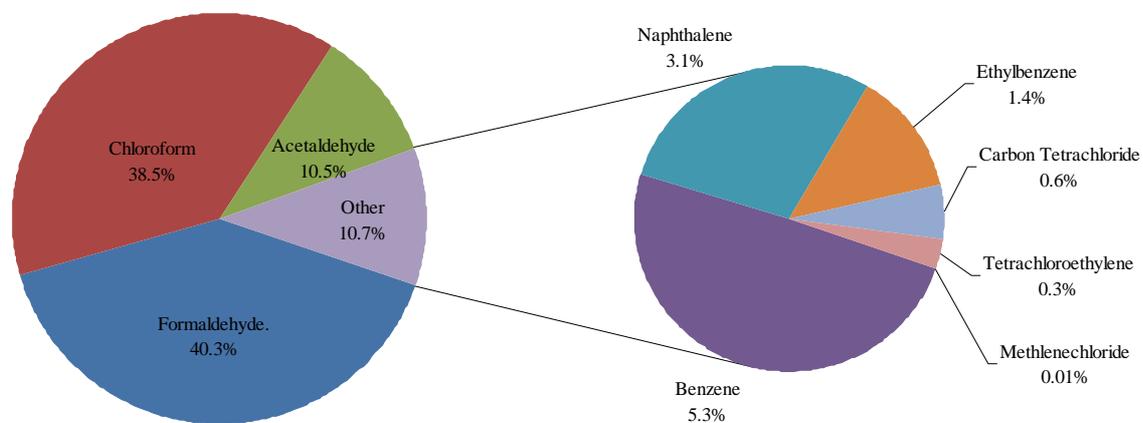


Figure 8.1: Percentage Contribution of Carcinogens Towards Total Cancer Risk

Chapter 9

Conclusions

9.1 Overall Conclusions

- (i) Source apportionment of VOCs shows that the major sources of VOCs in the Kolkata's ambient air are, petrol and diesel exhaust, combustion of naphtha and mineral spirit and cigarette smoke (**Figure 9.1**)

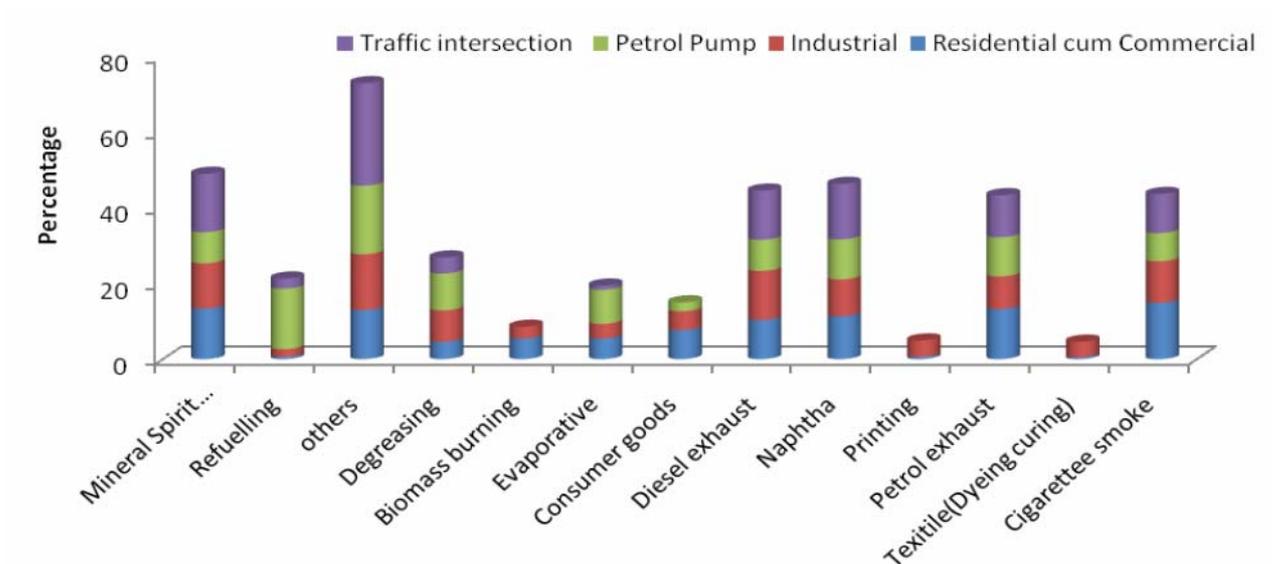
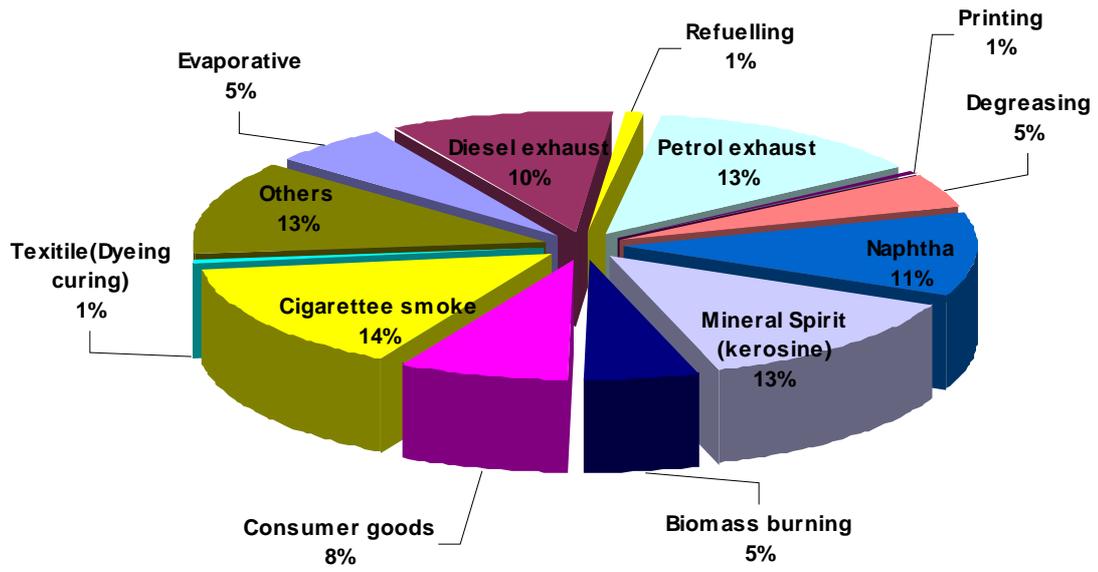
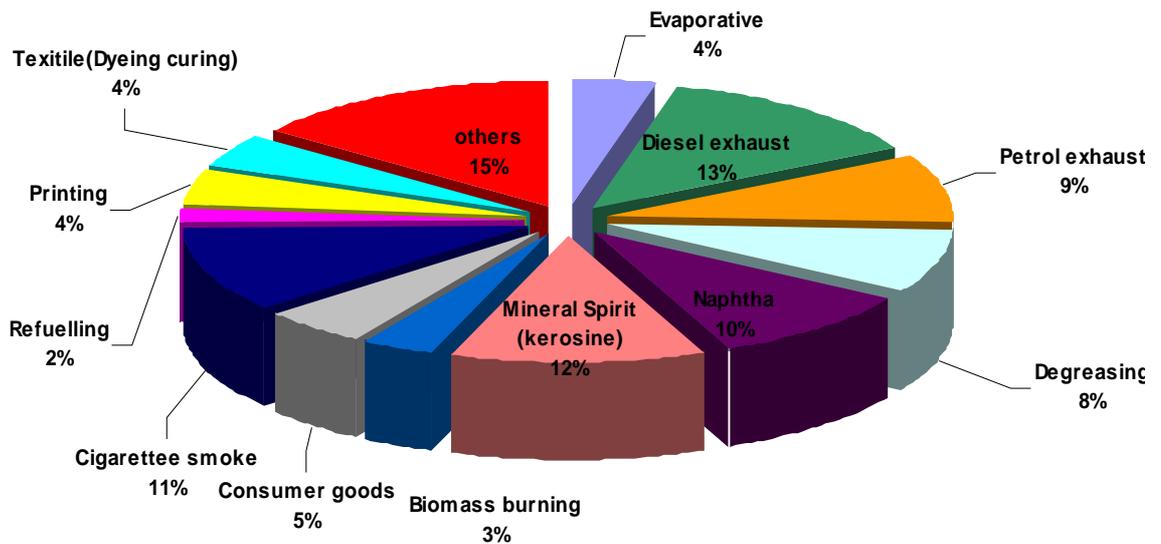


Figure 9.1: Contribution of Sources of VOCs at Different Category of Locations

- (ii) Contributions of different sources at each category of location are shown in **Figure 9.2**

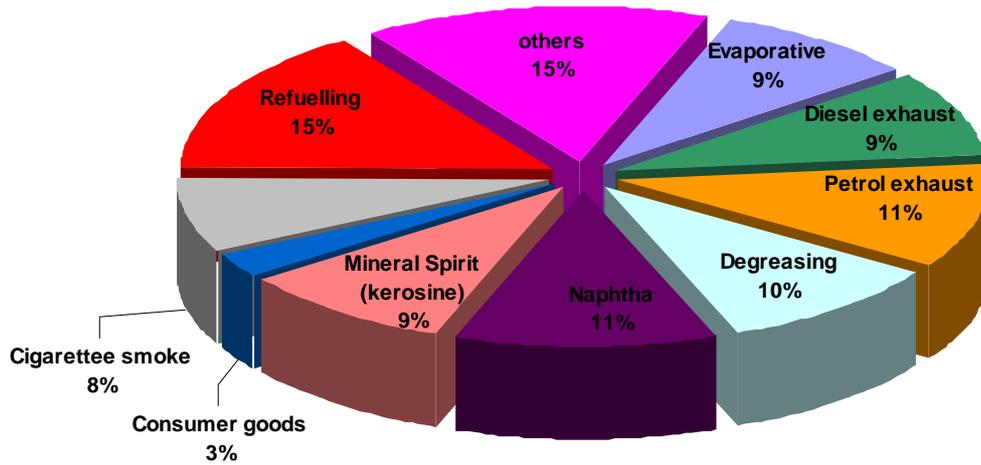


Residential cum Commercial

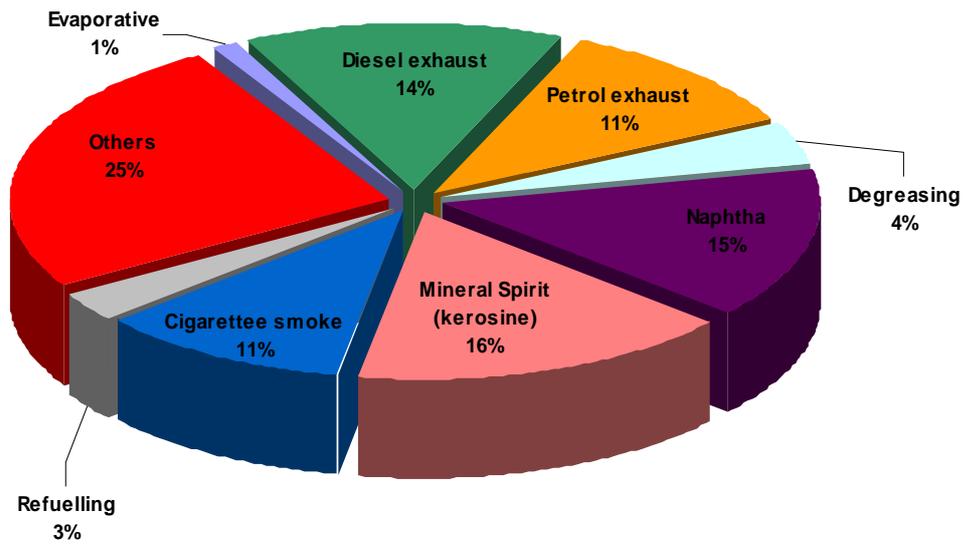


Industrial

Figure 9.2: Contribution of Various Sources towards Total VOC (Carbonyl & Non Carbonyl) Concentration in Ambient Air of Kolkata in Various Locations



Petrol Pump



Traffic Crossing

Figure 9.2(contd.): Contribution of Various Sources towards Total VOC (Carbonyl & Non Carbonyl) Concentration in Ambient Air of Kolkata in Various Locations

(iii) Directional contribution to TVOC is shown in **Figure 9.3a to 9.3d**. It is observed that during winter season TVOCs are transported into Kolkata air shed from the West to North quadrant. During pre-monsoon some TVOCs are also transported from North. During other seasons TVOCs are transported from the East to South quadrant.

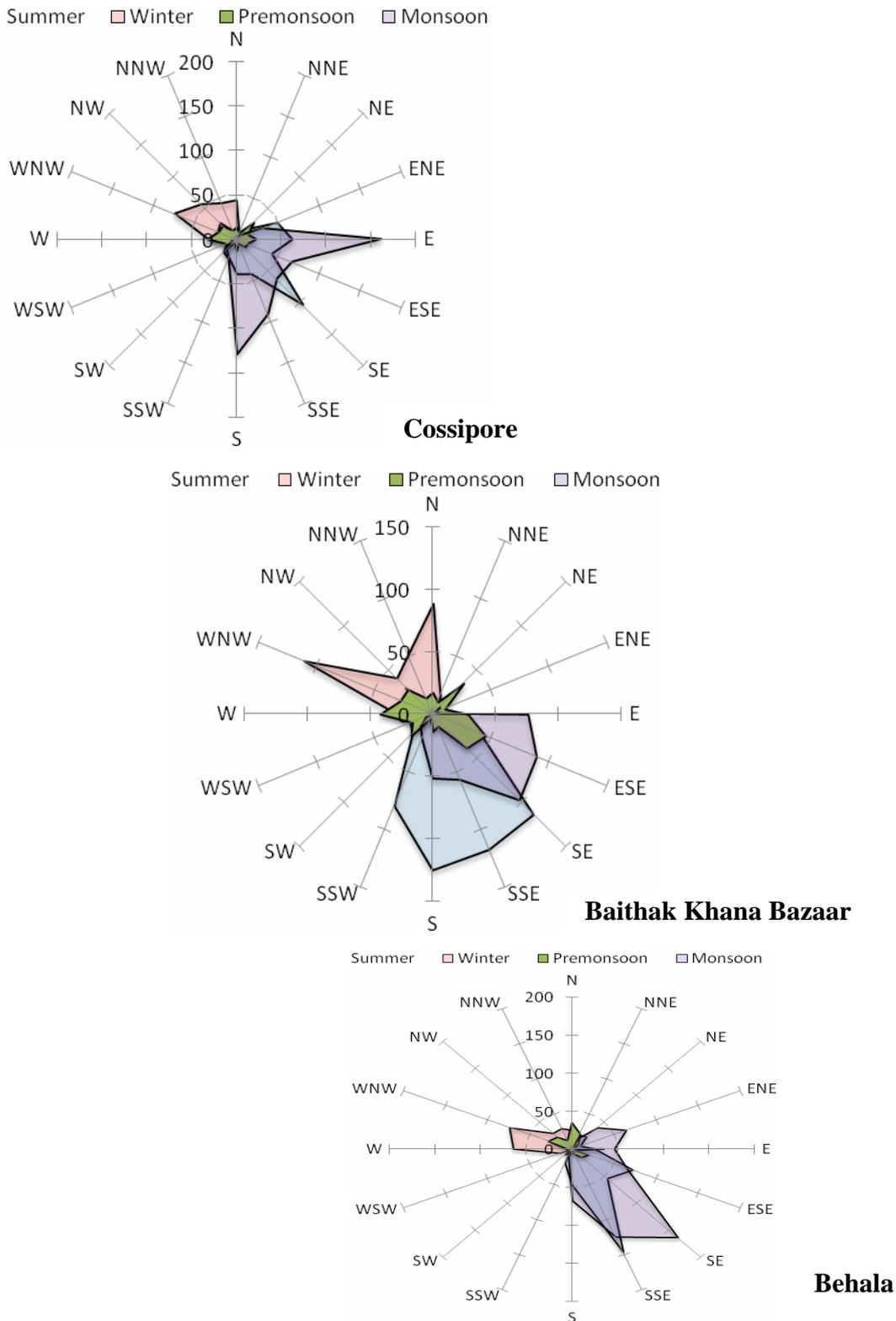


Figure 9.3a: Directional Contribution to TVOC at Industrial Locations

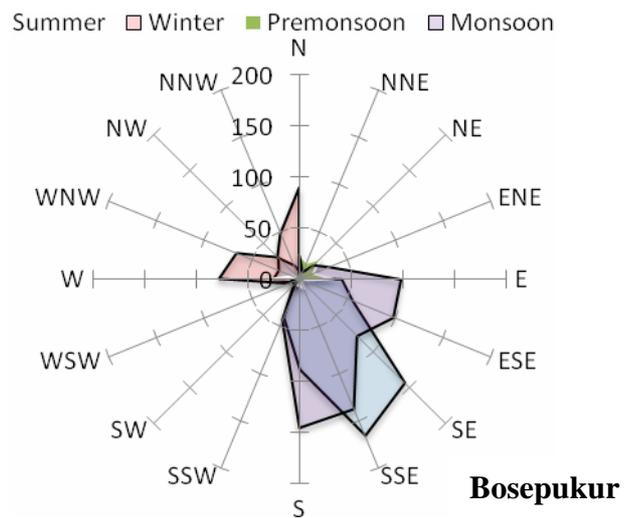
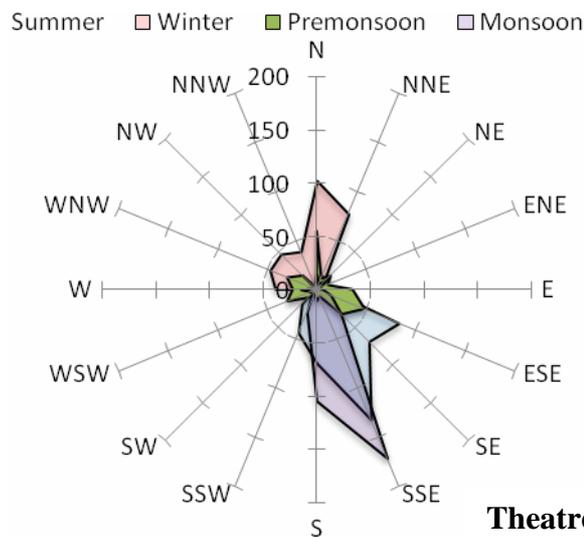
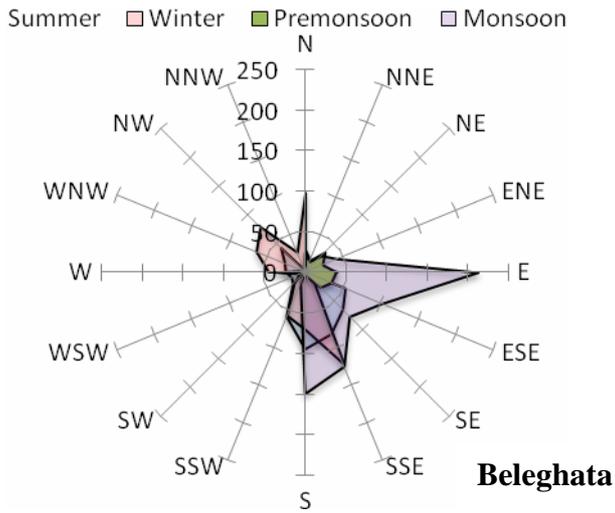


Figure 9.3b: Directional Contribution to TVOC at Petrol Pumps

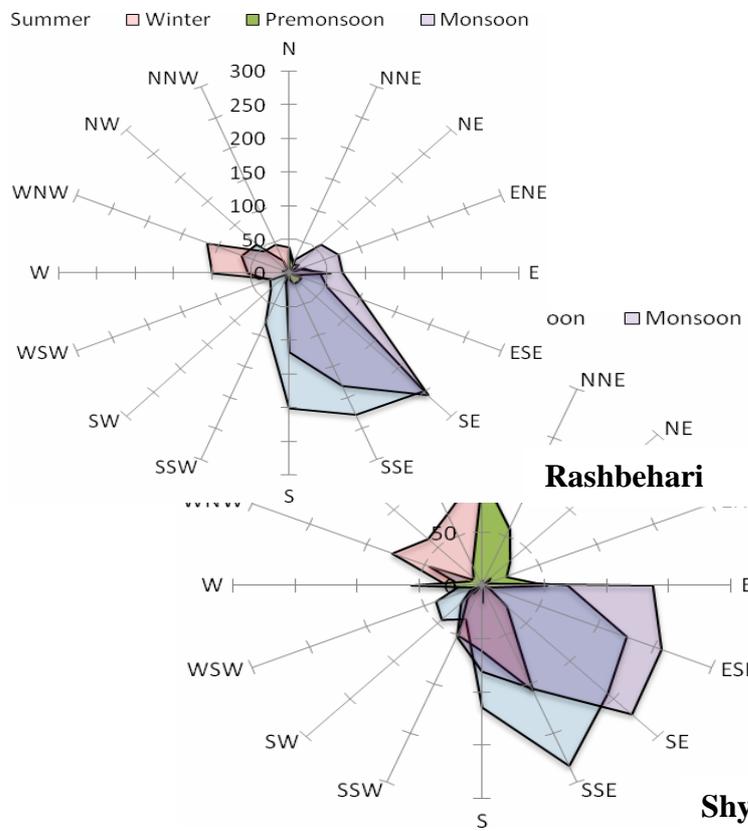
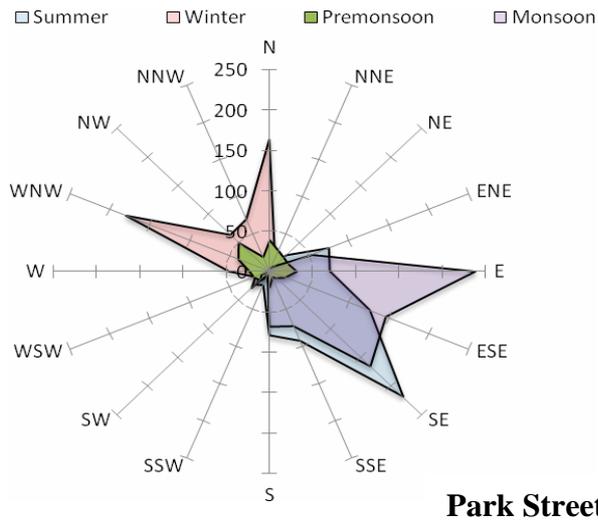


Figure 9.3c: Directional Contribution to TVOC at Traffic Intersections

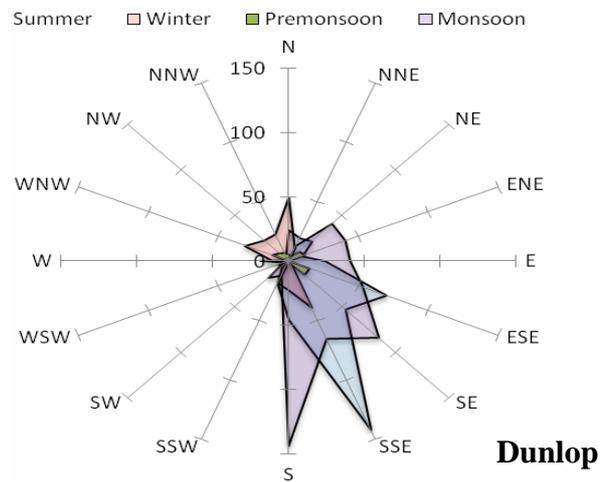
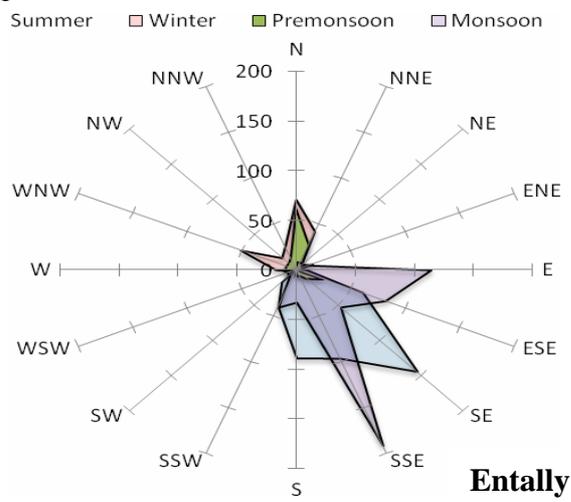
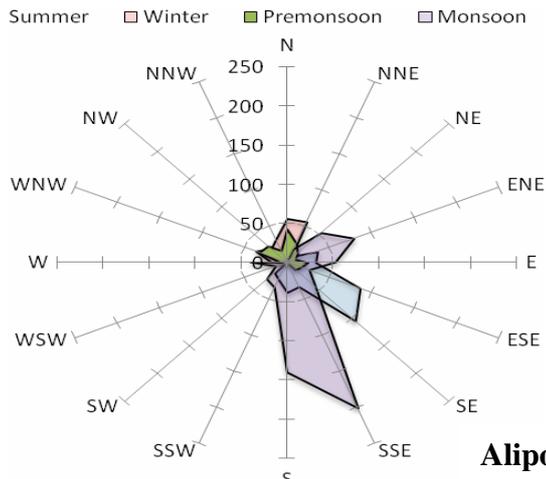


Figure 9.3d: Directional Contribution to TVOC at Residential Cum Commercial Locations

- (iv) The overall contributions to TVOC in the four different seasons studied at the 12 locations are shown in **Figure 9.4**. It is observed that local contribution to total TVOCs is considerable and higher than that transported from other areas.

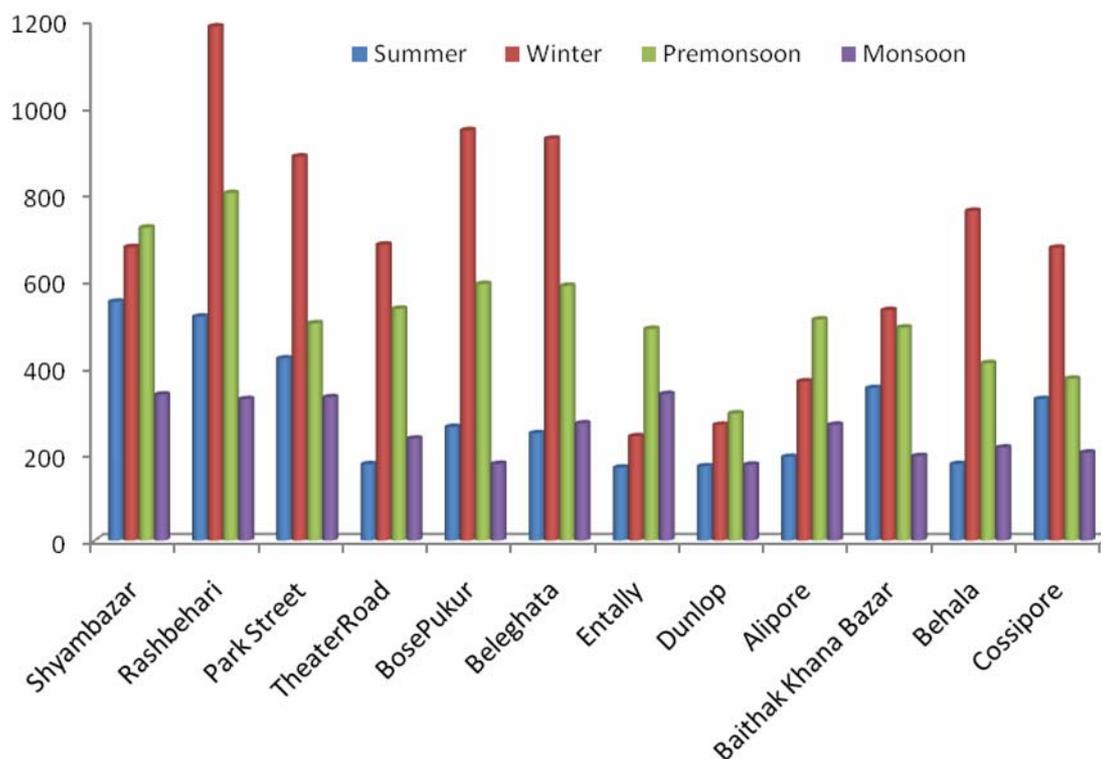


Figure 9.4: Local Contribution to TVOC at Different Locations

9.2 Specific Conclusions

- (i) VOCs in urban air shed of Kolkata are contributed mainly due to fuel burning
- (ii) Benzene levels are within the notified National Ambient Air Quality Standards
- (iii) Vehicle related sources typically contribute the largest to ambient VOCs
- (iv) Naphtha and mineral oil combustion as major sources indicate adulteration of fuel
- (v) High levels of chloroform may be due to use of bleaching powder in fish markets.

- (vi) High levels of Acrolein, Formaldehyde and Acetone may be due to cigarette smoke. This fact corroborates with fact that percentage of smoking population is highest in Kolkata in India.

Location	Percentage of Population Smoking(Age 15-49)		
	Men	Women	Total
India	33.3	1.6	34.9
Kolkata	50.0	0.1	50.1
Chennai	30.5	0.1	30.6
Mumbai	22.1	0.1	22.2
Hyderabad	21.9	0.1	22.0

Source: National Family Health Survey (NFHS-3), 2005-06
by International Institute of Population Sciences, Deonar, Mumbai

- (vii) High levels of observed formaldehyde and other carbonyls confirm cigarette smoke as a source besides the atmospheric chemistry.
- (viii) Kolkata urban airshed can be considered to be NO_x sensitive based on VOC/NO_x ratio

9.3 Recommendations

- (i) Studies for generating profiles of biogenic emissions of VOCs should be taken up.
- (ii) Source profiles of emissions due to garbage burning, tire burning and use of adulterated fuels in vehicles should be generated.
- (iii) VOCs identified should be quantified
- (iv) Chamber studies for evaluation of NO_x sensitive and VOC sensitive regimes and to addresses the issue of how ozone will respond are required. Environmental chamber studies carried out at low VOC/NO_x ratios close to rural ambient ratios would be extremely useful.
- (v) Reactions under low-NO_x conditions, such that reactions of organic peroxy radicals with HO₂ and other RO₂ radicals and of HO₂ with ozone dominate over the reactions of HO₂ and RO₂ radicals with NO should be studied.
- (vi) Source profiles relevant to Indian situations must be developed to enable obtaining of more realistic source apportionment.

- (vii) All Reactive Organic Gases (ROG) and TOG should be estimated
- (viii) PM_{10} / $PM_{2.5}$ should also be monitored at the same location to obtain more accurate source apportionments of a wider variety of chemical components and to produce aged source profiles which will allow direct attribution of reactive species to sources.
- (ix) The atmospheric chemistry of the carbonyl compounds requires more study. In particular, there is a need for absorption cross-sections, photo dissociation quantum yields, and photo dissociation product data (as a function of wavelength) for the carbonyl compounds.
- (x) Inventory of VOC and NO_x emission in Kolkata should be carried out
- (xi) Inorganic nitrates and carbon monoxide levels also need to be measured.
- (xii) In order to understand VOC-NO_x-O₃ chemistry in urban of Kolkata all species of nitrogen oxides should to be studied, and

9.4 VOC Mitigation Strategy

VOC emissions from stationary sources in Kolkata can be reduced by the of following approaches:

- (i) Resource management - Improving management and control processes to minimize emissions and wastage
- (ii) Product reformulation – reduction or elimination of organic solvents from products such as coatings used in a process. Options include high solids-low solvent coatings, water based and powder coatings. Elimination of VOC content from consumer goods by reducing solvent use.
- (iii) End of pipeline techniques strict control of emissions from major sources such as motor vehicles, power plants and other industries and commercial sectors – recycling of evaporated solvents e.g. adsorption/absorption of evaporative VOCs at petrol pumps and vehicles. and
- (iv) Regulatory approach - Strict regulations on VOCs emissions. Phasing out of polluting vehicles, high penalty on sale and use of adulterated fuel. Considering the health risks in terms of carcinogen and non carcinogen exposure the VOCs that need to be regulated are as follows:

Benzene,	Ethene, 1,1-dichloro-	Styrene
n-Propylbenzene	Isopropylbenzene	Ethylbenzene
Naphthalene	Toluene	p-Xylene
Isopropyltoluene	Benzene, 1,3-dimethyl-	Benzene, butyl-
o- xylene	Benzene, propyl-	Chloroform
1-Propene, 1,3-dichloro-	Benzene, 1,2,3,4-tetramethyl	Methylene Chloride
Benzene, 1,2,4-trimethyl-	1,3,5-Trimethylbenzene	Acetone
Carbon tetra chloride	Tetrachloroethylene	Butanal
Formaldehyde	Acetaldehyde	Styrene
Acrolein	Propionaldehyde	Valaraldehyde

- Implementing measures to control the use of VOC containing products such as organic solvents, vehicle finishing paints, adhesives and sealants.
- Minimising using aerosol consumer products such as hair sprays, air freshness and insecticides that uses VOCs as their propellants. Non aerosol consumer products should be promoted.
- Replace solvent based paints with water based paints.
- Store VOC containing products in air tight containers.

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Odour Thresholds of some VOCs and Carbonyls

	Odour Threshold (ppm)
Benzene	1.159
Ethyle benzene	2.3
Napthelene	0.84
Styrene	0.008
Toluene	2.9
Chloroform	85
1,2 dibromo 3 chloro propane	0.098
1,2- di chloro propane	0.25
1,3 dichloro propene	1
1,1,2,2- Tetrachloroethane	1.5
Tetrachloro ethylene	1
1,1,1 Trichloro ethane	100
Trichloro ethylene	100
p-Xylene	0.47
Acetaldehyde	0.21
Acrolein	0.16
Formaldehyde	0.51
Carbon tetrachloride	96
Hexane	130
Naphthalene	0.084
n-Valeraldehyde	0.028
Ethylbenzene	2.3
Tetrachloroethylene	1.5
Acetone	13
Crotonaldehyde	0.12
Ozone	0.045
Propane	16000