

1494

**ESTIMATION OF
VOLATILE ORGANIC COMPOUNDS (VOCS)
IN THE URBAN ENVIRONMENT OF DELHI**

*Dissertation Submitted to the Jawaharlal Nehru University
in partial fulfilment of the requirements
for the Award of Degree of*

MASTER OF PHILOSOPHY

PRATAP KUMAR PADHY

V, 152 p + plates + tables

SCHOOL OF ENVIRONMENTAL SCIENCES
JAWAHARLAL NEHRU UNIVERSITY
NEW DELHI-110067, INDIA

July, 1995

*...Dedicated to my
Bou & Nana...*



जवाहरलाल नेहरू विश्वविद्यालय
JAWAHARLAL NEHRU UNIVERSITY
NEW DELHI-110067

20th July 1995

CERTIFICATE

The research work embodied in the dissertation entitled "**Estimation of Volatile Organic Compounds (VOCs) in the Urban Environment of Delhi**", has been carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted in part or in full, for any other degree or diploma of the University.

Pratap Kumar Padhy
PRATAP KUMAR PADHY
(Candidate)

P. S. Ramakrishnan
PROF. P. S. RAMAKRISHNAN
(Dean)

C. K. Varshney 21.7.95
PROF. C. K. VARSHNEY
(Supervisor)

July, 1995
School of Environmental Sciences
Jawaharlal Nehru University
New Delhi-110067, India

ACKNOWLEDGEMENTS

I wish to take this opportunity to express my deep sense of gratitude to Prof. C.K. Varshney for his untiring supervision, constant help, suggestion and encouragement during the course of this study. I am also thankful to him to expose me into a new field.

I am grateful to Sri Gyan Batra, Chief, Nucon Engineers for helping me through out the study. I am grateful to Sri S. Venkataraman, Chief Manager (Safety and Environment Protection), IOCL, for allowing me to do some analysis at Faridabad. I am also grateful to Dr. Ghosh, Dr. Jain, Dr. Basu and Miss Vatsala of Research and Development Centre, Indian Oil Corporation Ltd., Faridabad for their help in using the Photovac Portable Photoionisation Gas Chromatography for analysing saturated and aromatic organic compounds.

I am thankful to Prof. P.S. Ramakrishnan, Dean, SES for extending necessary facilities.

I wish to thank Azeem, Paulraj and Chitrasen for their help in sampling. I thank my labmates, Maneesha, Indrani, Jyoti, Azeem, Deepa and Negi for providing a very cordial working atmosphere. I would also like to thank my friends, Paulraj, Chitrasen, Siba, Amulya, Moosa and Poonam for their untiring help. Thanking are also due to Mr. Baburam for his assistance in laboratory work.

It would be a sacrilege to record any formal gratitude to my father, mother, sisters, and brothers for their perennial encouragement and moral support without which it would have been impossible to accomplish this study.

Finally, the fellowship provided by the University Grant Commission is gratefully acknowledged.

Pratap Kumar Padhy

CONTENTS

	<i>Page</i>
<i>Certificate</i>	
<i>Acknowledgements</i>	
<i>List of Figures</i>	<i>i-ii</i>
<i>List of Tables</i>	<i>iii-iv</i>
<i>List of Plates</i>	<i>v</i>
<i>Chapter I</i> <i>Introduction and Review</i>	<i>1-44</i>
<i>Chapter II</i> <i>Materials and Methods</i>	<i>45-64</i>
<i>Chapter III</i> <i>Results</i>	<i>65-104</i>
<i>Chapter IV</i> <i>Estimation of VOC Emissions for India</i>	<i>105-110</i>
<i>Chapter V</i> <i>Discussion</i>	<i>111-128</i>
<i>Summary and Conclusions</i>	<i>129-134</i>
<i>References</i>	<i>135-152</i>

LIST OF FIGURES

- Figure 1. Principal directions of transformation of volatile organic components.
- Figure 2. Transformation of hydrogen containing intermediate in photochemical oxidation of methane in the troposphere.
- Figure 3. Trends of global CFCs production (in 000't).
- Figure 4. Trends of global petroleum, commercial energy and motor vehicle.
- Figure 5. Ombrothermic diagram of Delhi.
- Figure 6. Trends of point and non-point sources in Delhi (1960-1990).
- Figure 7. Delhi map showing sampling sites.
- Figure 8. Comparison in TVOC, methane and NMVOC levels among low, medium and heavy vehicular traffic sites.
- Figure 9. Relative Percentage of methane to NMVOC levels at different site categories (low, medium and high).
- Figure 10. Diurnal variation in the ambient concentrations of TVOC at AIIMS (November'94 - March'95;in ppm).
- Figure 11. Diurnal variation in the ambient concentrations of TVOC at JNU (November'94 - March'95;in ppm).
- Figure 12. Diurnal variation in the ambient concentrations of methane at AIIMS (November'94 - March'95;in ppm).
- Figure 13. Diurnal variation in the ambient concentrations of methane at JNU (November'94 - March'95;in ppm).

- Figure 14.** Diurnal variation in the ambient concentrations of NMVOC at AIIMS (November'94 - March'95;in ppm).
- Figure 15.** Diurnal variation in the ambient concentrations of NMVOC at JNU (November'94 - March'95;in ppm).
- Figure 16.** Comparison in the ambient levels of TVOC, methane and NMVOC among AIIMS, Bhikaji Cama and JNU during November to March (in ppm ; five months average).

LIST OF TABLES

Table 1.	Forest community models : Productivity and NMHC emission rate.
Table 2.	Total global methane emission from biogenic and geogenic sources.
Table 3.	Contribution to the VOC emission by different sectors of car.
Table 4.	Estimated atmospheric life time of selected NMHC.
Table 5.	List of selected VOCs and their potential health impacts.
Table 6.	Potential hazards of selected man made VOCs.
Table 7.	Green house effect associated with certain minor atmospheric VOCs.
Table 8.	Brief description of air sampling sites.
Table 9a,b.	Ambient levels of TVOC at different sites of Delhi (in ppm)
Table 10a,b.	Ambient levels of methane at different sites of Delhi (in ppm)
Table 11a,b.	Ambient levels of NMVOC at different sites of Delhi (in ppm)
Table 12a,b.	Monthly variation in the TVOC levels at different sites of Delhi during November'94 to June'95 (in ppm ; 24 hr average).
Table 13a,b.	Monthly variation in the methane levels at different sites of Delhi during November'94 to June'95 (in ppm ; 24 hr average).
Table 14a,b.	Monthly variation in the NMVOC levels at different sites of Delhi during November'94 to June'95 (in ppm ; 24 hr average).
Table 15.	Ratio of methane to NMVOC at different site category.

- Table 16.** Saturated (C₂ - C₉) and aromatic compounds at Delhi.
- Table 17.** Diurnal variation in the ambient concentrations of TVOC at AIIMS during November'94 to March'95 (in ppm).
- Table 18.** Diurnal variation in the ambient concentrations of TVOC at Bhikaji Cama during November'94 to March'95 (in ppm).
- Table 19.** Diurnal variation in the ambient concentrations of TVOC at JNU during November'94 to March'95 (in ppm).
- Table 20.** Diurnal variation in the ambient concentrations of methane at AIIMS during November'94 to March'95 (in ppm).
- Table 21.** Diurnal variation in the ambient concentrations of methane at Bhikaji Cama during November'94 to March'95 (in ppm).
- Table 22.** Diurnal variation in the ambient concentrations of methane at JNU during November'94 to March'95 (in ppm).
- Table 23.** Diurnal variation in the ambient concentrations of NMVOC at AIIMS during November'94 to March'95 (in ppm).
- Table 24.** Diurnal variation in the ambient concentrations of NMVOC at Bhikaji Cama during November'94 to March'95 (in ppm).
- Table 25.** Diurnal variation in the ambient concentrations of NMVOC at JNU during November'94 to March'95 (in ppm).
- Table 26.** An assessment of anthropogenic Vocs emission in India (1993-94)
- Table 27.** Comparative anthropogenic TVOC emission, emission percapita and emission per sq km of India with other countries.

LIST OF PLATES

Plate 1.	Site 1 : JNU Campus
Plate 2.	Site 2 : DLTA
Plate 3.	Site 3 : Chanakya Puri
Plate 4.	Site 4 : WWF
Plate 5.	Site 6 : Vijay Chowk
Plate 6.	Site 7 : S. J. Flyover
Plate 7.	Site 8 : Pahar Ganj
Plate 8.	Site 9 : Minto Bridge
Plate 9.	Site 10 : AIIMS
Plate 10.	Site 11 : South Extension
Plate 11.	Site 12 : Ashram
Plate 12.	Site 13 : Darya Ganj
Plate 13.	Site 14 : Bhikaji Cama Place
Plate 14.	Gas Sampling device
Plate 15a,b.	Nucon Gas Chromatograph
Plate 16.	A scene of Ring Road traffic
Plate 17.	Vehicle Showing Exhaust
Plate 18.	Indraprast Thermal Power Plant Showing Plumes
Plate 19.	Plume of Rajghat Thermal Power Plant
Plate 20.	Solid waste disposal site near Nizammudin
Plate 21.	Swamps besides Yamunna

CHAPTER I : REVIEW OF LITERATURE

Introduction

Our atmosphere consists of N_2 , O_2 , particulates, water vapour and a mixture of trace gases such as CO_2 , NO_x , O_3 , VOCs, inert gases, and H_2 . Trace gases like CO_2 and ozone play a critical role in shaping global climate and the living environment on the earth. Carbon dioxide build up due to the increasing combustion of fossil fuels is a major cause of green house effect. Depletion of stratospheric ozone is again of a major concern for life on earth. In addition to this, volatile organic compounds play a critical role in determining air quality. VOCs are a mixture of unidentified organic compounds present in atmosphere with individual vapour pressure greater than equal to 0.02 psi (pound per square inch, 1 psi = 0.0704547 kg/cm²). The composition varies with source and also over time because complex chemical reaction takes place in the ambient air.

Studies on VOCs were initiated in fifties but received a major impetus in late eighties, because some of them were found to be either toxic, mutagenic or carcinogenic (Lamb et al., 1980; Singh et al., 1981a, 1982; Duce et al., 1983) and also because of their involvement in tropospheric

ozone formation (Altshuller and Bufalini, 1971; Niki et al., 1972; Demerjian et al., 1974; Hanst et al., 1980; Aikin et al., 1982; Rudolph et al., 1989) and PAN (Crutzen, 1979; Singh and Hanst, 1981). At present ambient concentration some of the VOCs may not be directly deleterious to human health, but their potential indirect health effects on account of their implication in O₃ and PAN formation (Derwent and Jenkin, 1990) are quite significant.

Volatile organic compounds in the troposphere constitute over 80% of non-methane hydrocarbons (NMHC) between C₁-C₁₀ range (Lamb et al., 1980; Mayrsohn et al., 1977; Duce et al., 1983). NMVOC can be defined as compounds other than CH₄ which contain only carbon and hydrogen. The important NMHC are: ethane, ethene, acetylene, propane, propene, i-butane, n-butane, i-butene, 1-butene, 1,3-butadiene, benzene, toluene, cyclohexane, o-xylene, m+p -xylene, and ethyl benzene. Non-methane volatile organic compounds (NMVOC) include a large number of hydrocarbon species, a majority of which are photochemically reactive and many of them are toxic to man. As far as oxidants formation in the atmosphere is concerned, both NMVOC and CH₄ are important in photochemical ozone formation involving complex chemical reactions. VOCs particularly methane is well known green house gas posing radiative properties similar to carbon dioxide.

In view of the growing importance of VOCs, NMVOCs measurements have been undertaken in several urban areas since 1960 (Stephens and Burlsons, 1969; Lonnemann et al., 1974; Nelson and Quigley, 1982; Wathne, 1983; Grosjean and Fung, 1984; Sexton and Westberg, 1984; Colbeck and Harrison, 1985; Singh et al., 1985; EPA, 1986; Puxbaum and Lanzerstorfer, 1986; Jones, 1988; Robinson and Robbins, 1969; Zimmerman et al., 1978), however, from developing countries including India information on VOCs is altogether lacking.

1. Sources of VOCs (Emission)

VOCs are emitted into the atmosphere from many different sources which can be grouped into two major categories 1. Natural and 2. Anthropogenic.

1.1. Natural Sources:

Natural sources can be divided into : 1. Geogenic source and 2. Biogenic source. The quantity of VOCs emitted into the atmosphere from natural sources remain more or less the same. Emission of organic substances from geogenic sources can be traced to abiogenic synthesis or to the pool of hydrocarbons in the bowels of the Earth, formed in the geological past as a result of the activity of living organisms (Isidorov, 1990).

1.1. **Geogenic Sources** : Different earth processes such as volcanism, earth quake, faults result in VOC emission. These processes are stochastic and defy any prediction but the overall yearly emission of VOCs from geogenic sources remain more or less the same, hence, geogenic sources are also called stable sources.

Emission from the Earth's Crust : The Earth's crust contains gases in free state, sorbed by various rocks as well as dissolved in water. Large amounts of gaseous hydrocarbons are contained in stratal waters of gas bearing basins and oil pools (Zor'kin et al., 1980). The total amount of methane in sedimentary, granite and basalt layers is estimated to be 5.8×10^{19} g (Zor'kin et al., 1980). Gases from the sedimentary reservoirs diffuse through deep fractures and cracks and escape into the atmosphere.

Volcanism: It is shown that a number of organic compounds are released during volcanic eruptions into the atmosphere along with inorganic compounds (Beskrony et al., 1977; Bondarev et al., 1980; Markhinin, 1985; Menyailov et al., 1986). The first organic compound detected in the eruption gases and in the gases emitted from the cooling lava rivers was methane (Markhinin, 1985). Apart from methane, $C_2 - C_6$ homologous and light unsaturated hydrocarbons of the ethylene

series have also been identified (Markhinin, 1985). More than 150 compounds have been identified in volcanic eruptions. The main fraction consisting of normal C_{15} - C_{36} alkanes, C_{18} - C_{36} isoalkanes and some polynuclear aromatic hydrocarbon (Markhinin, 1985).

1.2. Biogenic Sources

The emission of organic compounds into the environment is a universal phenomenon. All living organism from single celled bacteria through higher plants and animals emit VOCs into the atmosphere. Secondary plant metabolites some of which being volatile in nature are important sources of VOCs. The volatile plant metabolites have been studied in detail because they play a significant role in ecological processes (Hutchinson, 1971, 1973; Hutchinson and Cowan, 1972). Volatile- oil- bearing plants emit hydrocarbon into the atmosphere through transpiration. VOCs emission occur through respiratory exchange or as a result of secretion. The emission of volatile organic compounds from plants increase upon injuries to plant tissues particularly to foliage (Isidorov, 1990). The active emission of organic compounds by plant foliage in the first few minutes after injury is considered to be a feature acquired through evolution to ensure nonspecific immunity to plants from microbial infection. These compounds

exhibit pronounced bacterial and fungicidal properties and hence preventing microbes to get into the damaged part (Isidorov, 1990).

The mechanism of NMHC emission has been studied in relation to emission of methanol by plants. Surface sterilized leaves of cottonwood, catalpa (*Catalpa speciosa*), and bean (*Phaseolus Vulgaris*) plants were found to emit methanol (MacDonald and Fall, 1993). To verify that methanol was not being supplied to the leaves either by other plant organs or by the soil solution, the cut ends of petioles from excised leaves were placed in distilled water and methanol emission was monitored. The methanol emission did not decrease, even after 2 hrs. Methanol emission was found to closely follow changes in stomatal conductance. Methanol produced in the leaf, seems to dissolve rapidly in the water, bathing the cell walls and then follows the water into the vapour phase and out through the stomata. A number of VOCs like isoprene, α -pinene, monoterpenes, β -pinene, ethylene, ethene, ethanol, aldehydes and ketones are released into the atmosphere. The major biogenic sources of VOCs are forests, grasslands, swamps and aquatic bodies.

Terrestrial Vegetation : Plants represent a major source of VOCs. Plants emit VOCs directly from their body into

the atmosphere or indirectly through exudation of organic compounds into the soil which ultimately diffuse into the atmosphere.

The rate of VOCs emission from leaves in different plant species varies considerably. VOCs emission from non-oak deciduous woodland differs by more than an order of magnitude (Guenther et al., 1994). The rate of emission also varies with biomass density.

Information on the rate of VOCs emission (Zimmerman, 1979; Lamb et al., 1985) and land cover data (Loveland et al., 1991; Hansen et al., 1992) is available only for U.S.A. woodlands. So far over 40,000 different kinds of VOCs emitted from plants have been identified. However the emission of VOCs, their number, relative composition and pattern of emission varies widely from one plant species to another (Harborne, 1991).

Investigations on VOCs emitted from the leaves of Oak and Pine in temperate forests have been mostly focused on the dominant hydrocarbons, namely isoprene, hemiterpene (C_5) and several monoterpenes (C_{10}).

Isoprene emission from plants was invented about 50

years ago (Sanadze, 1957). It has been shown that isoprene is the most abundant VOC emitted by over 78 different forest trees in USA (Rasmussen, 1972). BNMHC emissions consist of a mixture of different compounds of which isoprene and α -pinene are the major components (Zimmermann, 1979). Isoprene emissions represent a major transport of hydrocarbon from the biosphere to troposphere. The estimated magnitude of global isoprene emission, $350-400 \times 10^{12}$ g C/yr (Zimmerman et al., 1978; Rasmussen and Khallil, 1988), is large and of the same order of magnitude as global methane emission, $300-480 \times 10^{12}$ g C/yr (Cicerone and Oremland, 1988).

A study done in temperate climate on VOCs emission in a coniferous forest, consisting of arboreous trees with under canopy plants has identified 78 compounds of C atom one to ten (Churkin et al., 1976; Stepen et al., 1978; Isidorov et al., 1985; Isidorov et al., 1982; Khasanov et al., 1982). They could be paraffins, olefine and diene hydrocarbons, monoterpenes, saturated and unsaturated alcohols, aldehydes and ketones, esters, furan and their derivatives and chlorine containing compounds. Earlier these compounds were thought to be of anthropogenic origin except terpenes but subsequently they were also found to be emitted from natural sources in small quantities (Churkin et al., 1978; Stepen et al., 1978; Isidorov et al., 1985; Isidorov et al., 1982; Khasanov et al.,

1982).

Emission of NMHC has been also investigated in Tampa/ 2. Petersburg, fla, area (Zimmerman, 1979). The values obtained are given in Table 1.

TABLE:1 Forest Community Models: Productivity and NMHC Emission Rate.

Species	Biomass (g/m ²)	NMHC emission rate (µg/g/h)
Coniferous Forest type		
Overstory		
Loblolly pine	650	5.5
Understory	65	10.0
Mixed Forest Type		
Overstory		
Red maple	190	6.5
Sweet gum	176	60.9
Loblolly pine	165	5.5
Black gum	69	10.0
Understory	90	10.0
Deciduous Forest type		
Overstory		
Red maple	79.8	6.5
Black gum	160.2	10.0
Sweet gum	92.4	60.9
Oaks	122.4	25.3
Yellow poplar	42.6	6.5
Loblolly pine	3.0	5.5
American elm	1.2	3.9
Holly	42.6	2.7
Beech	18.6	6.5
Sweet bay	37.2	7.5
Understory	120.0	10.0

Data from: Zimmerman, (1979)

The composition of the volatile hydrocarbon emitted by plants has been studied by Churkin et al., 1976; Stepen et al., 1978; Isidorov et al., 1985; Isidorov et al., 1982 and

Khasanov et al., 1982. Emission inventories have been compiled (Lamb et al., 1987) which indicate that on a continental scale biogenic non methane hydrocarbon (BNMHC) emission represents a major fraction of the total hydrocarbons. The total emission of VOCs for U.S.A. is estimated to be 19 mt/yr from biogenic sources and 21 mt/y from anthropogenic sources (Lamb, 1989, personal communication). On local scale the contribution from BNMHC sources can also be large (Hov et al., 1983). For the southern part of British Isles, BNMHC emission have been estimated to contribute approximately 10% to the total O₃ loading in a stagnant air mass over the area for 4 days (Derwent and Hov, 1979).

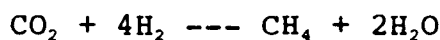
Plants suffering from physiological air pollution stress release high quantity of ethylene (Tingey et al., 1976; Tingey et al., 1978; Peiser and Shang, 1979; Bressan et al., 1979; Tingey, 1980; Bucher, 1981; Meyer et al., 1987; Chevrier et al., 1990; Mitra and Varshney, 1993).

The decompositing litter release hydrocarbons into the atmosphere. A precise characterization of biogenic VOCs sources is tedious because a large number of VOCs and plant species are involved.

Aquatic Vegetation : Marine and fresh water algae have been shown to emit alcohols, aldehydes, carboxylic acids, alkylphenols, S- containing compounds, terpenes and other hydrocarbons (Broddin et al., 1980).

Emission of Hydrocarbons from Microbial Sources :

Methane : Complex organic compounds are degraded by a group of anaerobic bacteria into simpler substances like CO₂, hydrogen, methyl alcohol and acetic acid which serve as substrate for enzymatic methane formation according to the following reaction sequence.



Anerobic methane formation is an universal phenomenon and cumulative global emission is highly significant. Total global methane emission from various ecosystems and other biotic bodies estimated by various workers is in the range of 157 to 1000 Tg/y (Table 2).

TABLE:2 Total global methane emission from biogenic and geogenic sources (Tg/y)

Source	Evaluation according to ref.			
	1	2	3	4
Swamps, Lakes, and Tundra, soil, seas	148-329	871	30-52	250-300
Rice fields	280	39	27-51	60-300
Animals	101-220	90	50-92	90-130
Termites	---	---	50-100	30-150
Total	529-829	1000	157-295	330-880

(1. Ehhalt, 1974 2. Sheppard et al., 1982 3. Seiler, 1982
4. Cicerone et al., 1983)

The total annual source strength of atmospheric CH₄ was estimated to be 500 Tg with anthropogenic source accounting for 340 Tg. With an estimated sink strength of 460 Tg/y the annual increase of atmospheric methane is 40 Tg (Sass, 1995).

Non-Methane Hydrocarbons : For a long time, the presence of methane homologous in soils was believed to be on account of their emission from sub surface reservoirs of oil and gas. Recently it has been shown that in natural soils gaseous hydrocarbons, comprising of methane, ethane, ethylene and propane of which the latter two are in relatively high proportion (Min'ko, 1988). The ethane and propane are formed as by products of the reactions leading to methane formation (Orlov et al., 1987).

Factors Affecting VOCs Emission from Natural Sources :

Light and Temperature : Yokouchi et al., (1983) studied the relationship between α -pinene emissions from pine trees and various physical and chemical parameters. The rate of terpene emission appear to be independent of light but increase exponentially with temperature (Tingey et al., 1979, 1980; Lamb et al., 1985). Thus there is both a diurnal and seasonal variation. Emissions decrease at night and during the winter months. Yokouchi and Ambe (1984) found that light influences terpene emission. A two-fold reduction in emission at night could not be completely explained on account of difference between leaf and ambient temperature. The rate of emission from any one leaf calculated in this way is strongly dependent on temperature and the amount of incident solar radiation (Tingey, 1981; Tingey et al., 1981).

For terpenes the main removal processes include both chemical such as ozonolysis and the reaction with hydroxyl radicals, and physical processes such as wind dilution. Study has shown that the concentration of monoterpenes is maximum at noon (1300 h) and in afternoon (1600 h), in a diurnal cycle (Bufler and Wegmann, 1991). Concentration decrease was observrd after 1900h. During the night and in the early morning (2200-0800) very low concentrations could be found (Bufler and Wegmann, 1991).

Isoprene emission is strongly dependent on photosynthetically active radiation (PAR) at low light levels but become saturated at less than one-half of full sunlight (Guenther et al., 1993). Isoprene emission increase exponentially with the increase in leaf temperatures upto approximately 30°C but declines at 40°C (Guenther et al., 1993). Isoprene emissions is both light and temperature dependent and occur predominantly in sunlight (Tingey et al., 1979; Lamb et al., 1987). Temperature directly affect the emission rate by altering the vapour pressure of isoprene in the leaf. Isoprene emission from broad-leaved trees occurs only from around April to September and during day light hours (Anastasi et al., 1991).

Methanol emission is regulated over short term by temperature and stomatal conductance. Methanol emission rate from limber pine (*Pinus flexilis*) needles has been shown to be temperature dependent (Robert et al., 1993).

Age of the leaves : Isoprene emission from young leaves is less as compared to mature leaves (Kuzma and Fall, 1993). Variation of relative humidity between 30 and 100% had only a minor effect on isoprene emission rates (Guenther et al., 1991).

Moisture : Drought reduces methanol emission substantially. When water is withheld from bean plants for 5 days, the emission was reduced to $19 \pm 2\%$ (MacDonald and Fall, 1993).

1.2. Anthropogenic Sources of VOCs

Anthropogenic sources of VOCs are very wide and not easy to quantify because new sources are being added almost every day. The main anthropogenic sources of VOCs include emission due to fossil fuel production and combustion, evaporation of liquid fuels and solvents, fugitive emission from industrial processes and natural gas leakage (Isaken and Hov, 1987).

1.2.1. Stationary Sources of VOCs :

Coal Mining : Coal is a hard black mineral formed from living organism buried under earth for millions of years. The dead organisms under high pressure and heat get decomposed and degraded under anerobic environment resulting in the formation of a complex mixture of volatile organic compounds which occupy coal seams (Bertard et al., 1970; Dhar et al., 1991). During mining, these volatile substances are released into the atmosphere. Beside the emission of volatile

hydrocarbons during the mining operation, coal itself contains some remnant gaseous hydrocarbons which are slowly released with the passage of time during processing, storage and utilization.

Coal mining is a major source of CH₄. It has been estimated that CH₄ emission from coal mining (Banerjee et al., 1994) has increased from 0.06 million tonnes to 0.4 MT between the year 1951 and 1991 and may rise further to 0.6 MT by the turn of the century. It may be pointed out that the Indian coal seams are inherently much less gassy as compared to their European and American counterparts (Banerjee, 1980).

Thermal Power Plants : The emission of NMVOCs are dependent upon the type of fuel used. Information on VOCs emission from power stations are limited. Thermal power plants use coal and/or petroleum fuel for generating electricity. The organic compounds emitted from power plants include paraffins, aldehydes (formaldehyde and acetaldehyde), aliphatic hydrocarbons, aromatic hydrocarbons (toluene, benzene, ethylbenzene and xylene) and chlorinated hydrocarbons (tetrachloroethane) (Corine, 1986; Shih and Takata, 1981; Zelinski et al., 1980; Veldt et al., 1983). In certain studies attention has been paid to specific hydrocarbons such as

toluene, ethylbenzene, xylenes, n-nonane, n-propylbenzene, tetrachloroethene and 1,2,3-trimethylbenzene (Cuffe et al., 1964; Ahlberg et al., 1983; Alfheim et al., 1983; Littman et al., 1977; Garcia et al., 1992).

Petroleum Industry (Prospecting and Refining)

Emission of VOCs at each stage of fossil fuel cycle is unavoidable. Whilst emission occurs from a variety of industries, but the petroleum industry is one of the main industrial sources of volatile hydrocarbons (Lubkert and De Tilley, 1989). Petroleum refineries are a prominent source of VOCs emission. Petroleum refineries in general are odorous and hydrocarbons are emitted at almost every stage of processing. Apart from emissions during petroleum refining, evaporation occurs during storage, transportation and distribution to individual user. Fugitive emissions are unavoidable (Brice and Derwent, 1978).

Industries : The sources of VOCs emission next to automobile transport are industrial enterprises. The greatest contribution is made by oil refining and chemical industries (44.2%) (Benkovitz, 1982). Several thousands organic compounds are emitted from the industries (Isidorov, 1990). In developed countries industrial emissions amount to 20 to 25% of the

total hydrocarbon emission for that country (Benkovitz, 1982). The coke used in industrial processes mostly emits paraffins, aromatics, aldehydes and olefins. The emission from the chemical industry is mainly on account of production of synthetic materials and from solvent evaporation. These synthetics (ethylene, polypropylene) are made from natural gas and petrol. At the end of the 1970s in the USA approximately 26.7 Tg of hydrocarbons were emitted annually of which about 5.2 Tg was emitted from the industry (Benkovitz, 1982).

The VOCs emissions from solvent evaporation are relatively much higher as compared to their emission from manufacturing which happens to be the largest anthropogenic sources of VOCs emission. It is estimated that 85% of solvent used finally enters the atmosphere (Concawe, 1986). Paper, plastic and allied products, rubber, tyre, food, drink industries (Baking, production of vegetable oils, animal rendering, production of solid fats and margarine, fish processing, coffee processing, beer and spirits) are also important industrial sources of VOCs emission.

Other important VOCs related to industrialization are represented by a family of chlorofluorocarbons compounds particularly CFC₁₁ CFC₁₂ and halons responsible for stratospheric O₃ depletion and also contributing to green

house effect because of their radiative properties similar to CO₂.

Domestic Cooking : Due to socio-economic constraint a large population in the developing countries use biomass such as cow dung, crop residues and wood as fuels. All the biological renewable source of energy emit high quantity of VOCs during combustion. It is thought that the world's worst air pollution problem could be the wood smoke inhaled by poor rural women while cooking (The State of India's Environment, 1984-85). The major part of the emission consists of paraffins while aromatics, olefins represent only 10%.

Natural gas supplied to industry or used for cooking is a relatively clean source of energy but its combustion products contain at least 22 different organic compounds (Gotz, 1979) formaldehyde being the major component (Gotz, 1979).

Residential Heating Units : Most of these heaters are of the same design and construction as the smoky stoves in use 100 years ago (Sheeton, 1981) and permit high quantity of hydrocarbons.

Wood Stoves : CO, gaseous HCs, and PAHs are the main

component of incomplete combustion.

Incineration : Incineration of liquid and solid wastes creates the problems of noxious emission and odour.

1.2.2. Mobile Sources :

Automobile : Automobile exhaust is the main sources of VOCs emission in urban areas. Presently we are witnessing an explosive growth of automobiles both in developed and developing countries. A large number of organic compounds are emitted and a total of more than 500 organic compounds have been identified in exhaust gas mixture. Hampton et al., (1982) published one of the most complete lists of volatile organic substances comprising about 450 compounds.

The C_1 - C_2 hydrocarbons are present in greatest amounts, with many highly branched alkanes, alkyl naphthenes, polyalkyl substituted benzenes and naphthalenes have also been detected. The most part is contributed by methane, ethylene and acetylene. Unburnt hydrocarbons are represented by benzene and its homologues (20%) and the C_4 - C_8 alkanes (about 13%). Vehicle exhaust hence is enriched with more reactive and toxic compounds than those present in the initial fuel. According to various estimates in USA the emission of hydrocarbon from

automobile is 53 to 63% (Zinger, 1985). In Hungary and Czechoslovakia the amount of hydrocarbons emitted from automobile exhaust has increased by a factor of 1.7 to 2.4 during 1975 to 1990. In Hungary, 30 to 35% of pollutants arise from automobile exhaust gases. According to CONCAWE, 1986, 0.49% of the products (petrol and distillate oil) enter the air during the distribution.

The emission of organic compounds for various assemblies of motor cars with spark ignition is given in Table 3.

Table:3 Contribution to the VOCs emission by different sectors of car

Type of sector	% emission
1. Exhaust	50
2. Evaporation from tanks and carburetors	20
3. Leakage from crank case	25

Data from (Kashmiura et al., 1983).

TH-731

Measurements have been made to determine emission from four- and two- stroke engines which showed that the emissions from 2-stroke engines are considerably higher than those from 4-stroke motors and the emission factor was higher by four times (Berces et al., 1988). It has been shown that most of the traffic related emissions come from the exhaust of



petrol driven vehicle (Molnar, 1990). Automobile exhaust represents a significant source of ethylene and aldehydes.

Other Mobile Sources : Other mobile sources which include railways, aircrafts and steamers, also emit large quantities of hydrocarbons. Tankers which transport crude oil release high quantities of VOCs due to accident during transportation.

1.2.3. Miscellaneous Sources of VOC :

Municipal Sources : In sewage treatment plants at all stages malodorous volatile organic substances are emitted. Some of the most harmful volatile components are organo-mercury compounds (CH_3HgCH_3 and CH_3HgCl) formed as a result of microbiological methylation of inorganic salts of this metal.

Almost all major cities of the world are plagued with problem of solid waste disposal. Sanitary landfills are most popular for the final disposal of solid waste. The sanitary landfill sites remain under anerobic condition leading to the formation and emission of methane and a large number of other VOCs (Hofler et al., 1986; Angrick, 1987;

Bingemer and Crutzen, 1987). At many places sanitary landfills are even viewed as a commercially viable source of methane. One ton of waste in the landfills emits approximately 25-30 m³ of methane for 25 y, and 70% of this quantity is emitted in the first 10 y (Vanni and Esposito, 1982).

Forest Fire and Biomass Burning : Among miscellaneous sources this is the most important source of organic compounds. According to Robinson at the end of the 1960s forest area of about 7 X 10⁶ ha was burnt annually. The combustion efficiency of damp vegetation is low, only about 20% of the material destroyed by fire is oxidized completely. The remaining amount of biomass is emitted either in the form of volatile organic compounds or in the form of solid particulates (ash and condensation aerosol).

Biomass burning or forest fires may emit a large number of organic compounds, but the composition of VOCs emitted from such sources had not been studied in detail. In smoke gases over 50 volatile C₁-C₈ compounds have been identified (Curtzen et al., 1979; Westberg et al., 1981; Greenberg et al., 1984). They contained methane and other C₂-C₇ paraffins, C₂-C₇ alkene hydrocarbons, benzene and its homologues, C₁-C₃ alcohols, C₁-C₇ carbonyl compounds including some unsaturated aldehydes and ketones (Curtzen et al., 1979;

Westberg et al., 1981; Greenberg et al., 1984).

In addition to the above two factors, some episodic events may lead to the emission of high amount of VOCs as happened in gulf war fire (January'91), gas well fire (Andhra Pradesh Godavari delta, January'95), accidental fire in Jwalapuri PVC market on 6th June'95, fire in high rise building (Kailash building, Connaught Place, 13th June'95, Ashoka Eatate, Barakhamba Road, 28th June'95) and methane build up in chocked sewers which was responsible for a powerful blast in the Connaught Place area in New Delhi in April'95.

1.2.4. Factors Affecting Anthropogenic Emission : The composition and quantity of motor vehicle emission depends on the type of engine, age, maintenance, size of the vehicle, type of fuel used, and among other things, operating condition of the vehicle e.g., speed, altitude, and ambient temperature.

Vehicle speed : According to MOBILE 4 (1986) prediction fleet average emission rates (NMHC) continuously decrease as average speed is increased. The 1985 fleet average NMHC rate at 88 km/h was 32% of the values at 8 km/h. The ratio of NMHC/NOx varied from 2.2 g/km at 8 km/h to 0.7 g/km

at 88 km/h with an ambient temperature of 24°C and at a altitude of 152 m.

Ambient Temperature : According to MOBILE 4 (1986) data, the 1985 fleet average NMHC emission rate was lowest at 24°C and elevated at higher and lower temperature. The NMHC/NO_x ratio is minimum at 24°C and maximum at 38°C, 1.3 and 4.6 g/km, respectively at a vehicle speed of 32 km/h and altitude 152 m. The elevation of the NMHC/NO_x ratio at 38°C occurs primarily because of increased evaporative HC emissions predicted by MOBILE - 4 (1986).

Altitude : The rate of emission of NMHC is increased when the altitude of vehicle is increased. The emission is approximately 2.6 g/km at a height of 152 m to 3.2 g/km at a height of 1676 m at an ambient temperature of 24°C and vehicle speed 32 km/h (MOBILE 4, 1986).

3. Role of VOCs in Atmospheric Chemistry

The tropospheric lifetime of volatile hydrocarbons ranges from several months to hours. Most of the compounds are oxidized in the lowest 2 km of the troposphere (Rudolph et al., 1989; Kasting and Singh, 1986; Brewer et al., 1983). Estimated atmospheric lifetime of some selected NMHC are given

in Table 4.

TABLE:4 Estimated Atmospheric Lifetime of Selected NMHC¹.

Hydrocarbon	Lifetime ^a (days)	
	Global	Tropics
Ethane	92.0	20.0
Propane	22.0	5.3
n-Butane	80.0	2.1
n-Pentane	52.0	1.5
Acetylene	24.0	6.7
Ethylene	1.9	0.7
Propene	0.5	0.2
Benzene	16.0	4.8
Toluene	3.0	0.9
o-Xylene	0.4	0.4
Isoprene	0.2	0.07
α -Pinene	0.1	0.07
β -Pinene	0.2	0.08
C ₂₀ H ₄₂	21.3	5.1

¹Singh and Zimmerman (1992).

^aTropics: T = 298 K; OH = 2×10^6 mols/cm³, O₃ = 7.4×10^{11} mols/cm³. Global: T = 275°K; OH = 6×10^5 mol/cm³, O₃ = 7.4×10^{11} mols/cm³.

The primary hydrocarbons are relatively insoluble and not likely to be removed by dry and wet deposition. But the concentration of NMHC is dependent upon OH⁻radical and ozone concentration. As the concentration of above compounds are relatively more in tropics, the life span of NMHC in tropics is less as compared to global average.

The concentration of VOCs are in the troposphere may increase due to emission, or decrease due to deposition,

dilution or rapid or slow increased atmospheric reactions (Yokouchi and Ambe, 1988; Tille et al., 1985; Carter and Atkinson, 1987 (FIGURE 1)).

The above figure shows that electronically excited molecules of organic compounds participate in multi-stage (only two stages are shown) gas phase photochemical reactions. They serve on the one hand as sinks and on the other as sources of new organic compounds. Another pathway is the sorption of gaseous impurities by the particles of solid and liquid aerosols and subsequent chemical transformations in the condensed phase. These reaction can proceed both in visible light and in the dark. In the each of these stages , final inorganic oxidation products (CO_2 and H_2O) are formed. For a single volatile hydrocarbon in the presence of tropospheric concentrations of NO_x , CO , H_2O and other trace components, several hundred chemical reactions may take place (Greenberg and Zimmerman, 1984; Atkinson et al., 1988; Atkinson and Lloyed, 1984). Scavenging of volatile hydrocarbons from the atmosphere is mainly due to their reaction with OH , O_3 , O , HO_2 and NO_3 species (Darnall et al., 1976; Brice and Derwent, 1978), forming secondary pollutants (Lamb et al., 1980).

Alkanes : Oxidative decomposition of saturated hydrocarbons starts with the abstraction of a H_2 atom in the

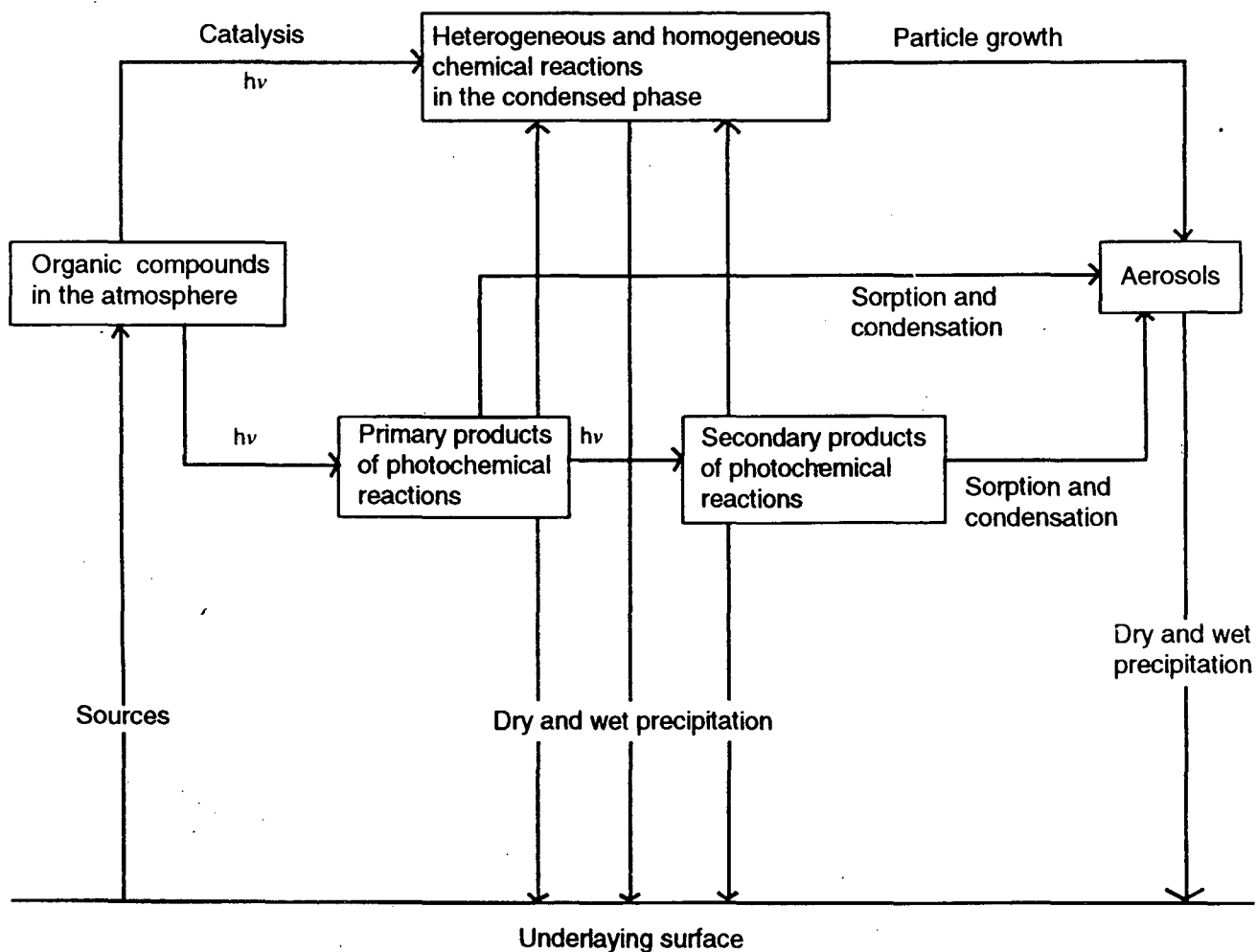
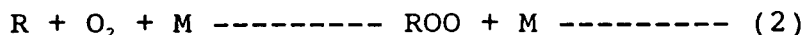
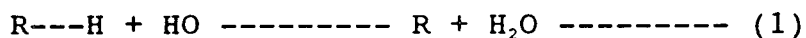
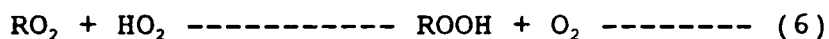
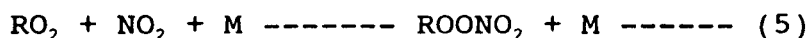
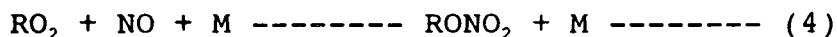
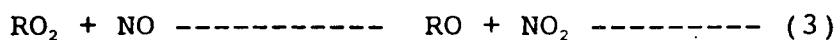


Fig.1 Principal directions of transformation of volatile organic components in the atmosphere.

interaction with a hydroxyl radical. The alkyl radical formed in the first phase attaches an O₂ molecule to give a new unstable particle, an alkylperoxide radical:



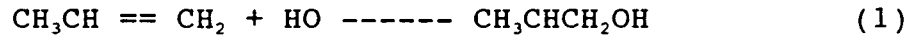
Further transformations may occur in several alternative directions with the participation of NO and NO₂ molecules or radical particles (Atkinson et al., 1987).



Alkenes : Hydrocarbon containing a double carbon-carbon bond are highly reactive. In this case under the conditions of troposphere, the processes of attachment on the double bond play a major role (Atkinson and Llyod, 1984).

The study of the behavior of various alkenes show that the rate of hydroxyl addition increases with the degree of substitution of hydrogen atoms at the double bond by alkyl groups.

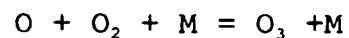
The addition of a hydroxyl radical initiates a chain of transformations.



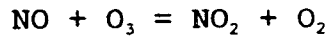
According to Atkinson and Lloyd (1984) the reaction takes place mainly according to Eq (1). Further oxidation of the above compound occurs and Formic acid is formed in the presence of NO. The complete oxidation of propylene leads to ozone formation and with incomplete oxidation NOx is found.

Chemistry of Ozone Formation : Secondary pollutants arise from photochemical reactions involving hydrocarbons and NOx, O₃ is the most commonly studied secondary pollutant. Nitrogen dioxide (NO₂) and photochemically reactive organic compounds (ROC) are the major reactants of ozone in the troposphere and in the planetary boundary layer (Fishman and Crutzen, 1978).

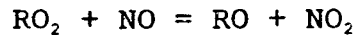
The only feasible route for the production of ozone in the polluted troposphere is the photolysis of NO₂ :



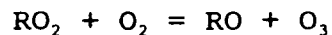
however the rapid formation of NO by O₃ maintains an overall balance between oxidizing and reducing agents:



The presence of peroxy radicals (RO_2) produced by the degradation of hydrocarbons leads to new ozone formation as follows:

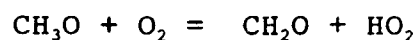
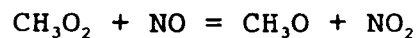
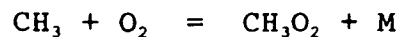
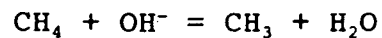


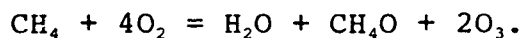
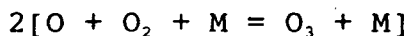
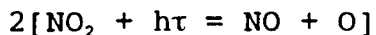
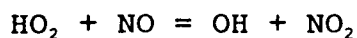
thus the reaction can be summarized as



Ozone formation and destruction are dependent upon the oxides of nitrogen, it is for this reason ozone concentration varies from time to time. But in a atmosphere containing VOCs, ozone destruction by NO_x doesn't occur because most of the peroxy radicals have more oxidation potential than ozone. NO_x instead of reacting with ozone, reacts with peroxy radical. So ozone doesn't get destroyed by NO_x and accumulated in the atmosphere.

Formation of ozone by methane in the atmosphere follows a different route (Peake and Fong, 1990) and the reaction sequences are as follows.





Transformation of hydrogen containing intermediate in the photochemical oxidation of methane in the troposphere is given in Figure 2.

Photochemical ozone creation potential (POCP) has not been calculated for methane. But a careful study to calculate POCP have been studied (Skold et al., 1992). The result they got reveals the following :

1. The most effective ozone producers; ethene and acrolein.
2. The medium effective ozone producers with POCP values, in most cases 40-60 % of the value for ethene; alkanes, alkenes and aromatics.
3. Compounds with low POCP values, in most cases 10-35 % of the POCP value ethene; alcohols, ketones, aldehydes (except acrolein) and esters, i.e., all oxygenated organics.
4. Compounds with a POCP value about zero: chlorinated organics except allyl chloride which should be placed in group 2.

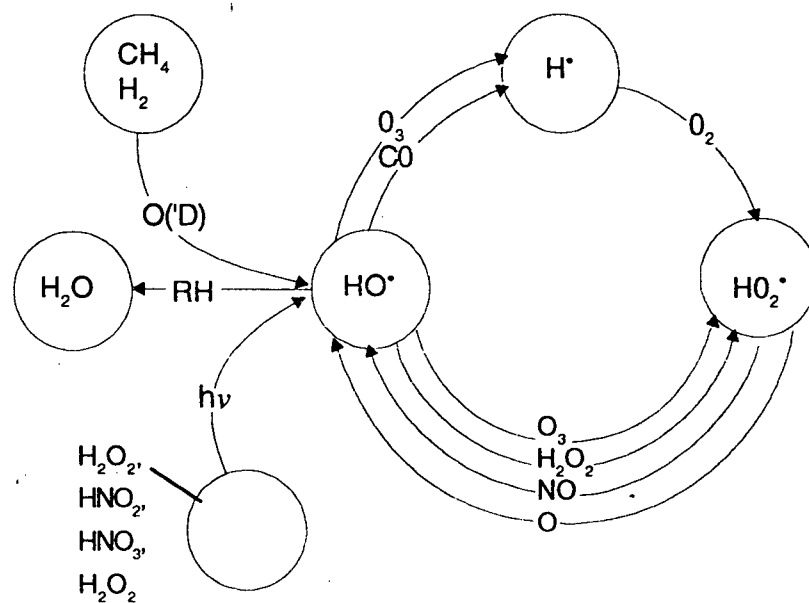


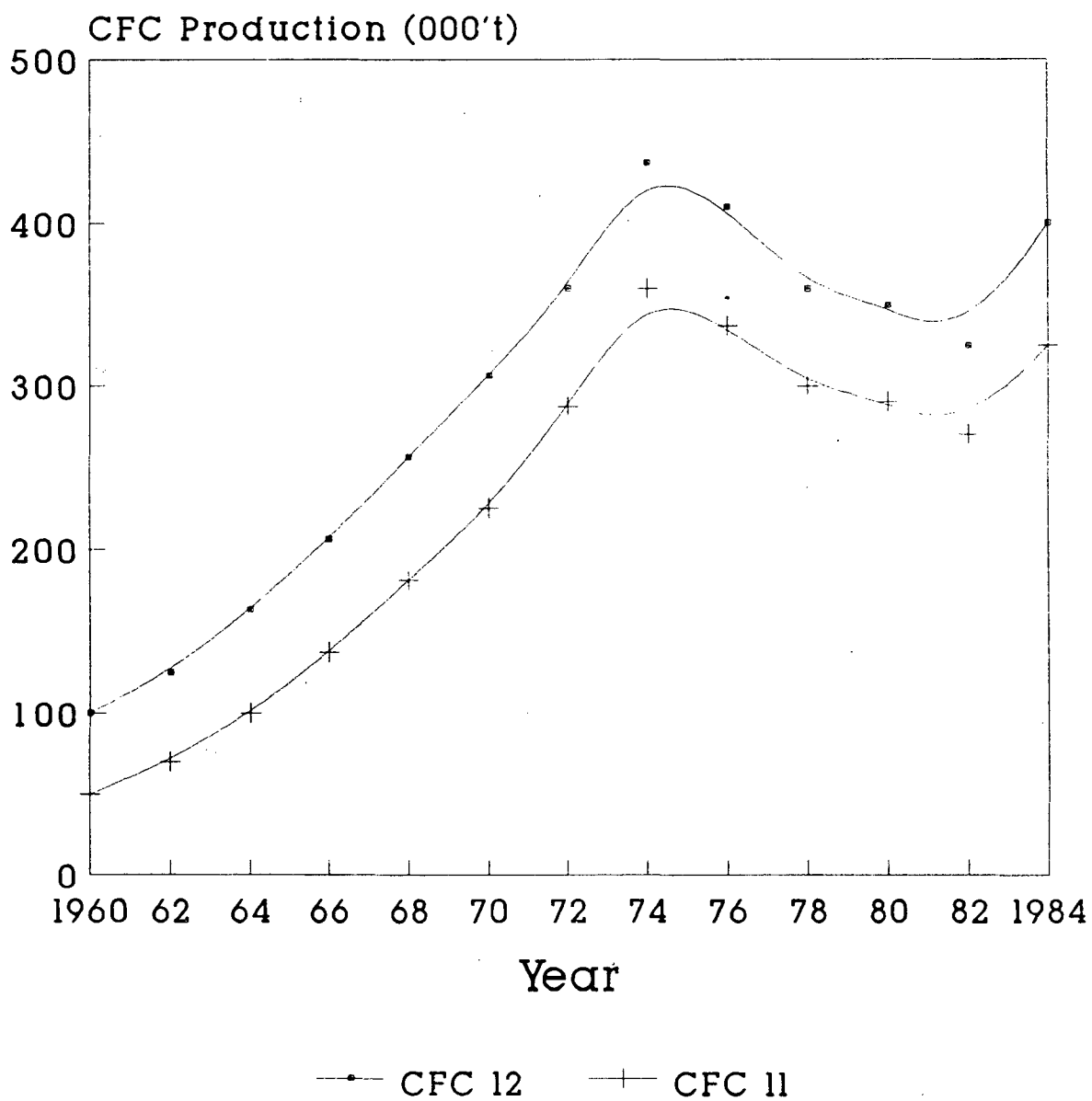
Fig.2. Transformation of hydrogen-containing intermediates in the photochemical oxidation of methane in the troposphere

4. VOCs Emission Trends :

So far no attempt has been made to assess total emission of hydrocarbons from natural and anthropogenic sources including methane and NMVOC. However good estimates are now available with regard to man made hydrocarbons viz., CFCs (Gwynne, 1987, Figure 3), Halons etc., as a result of the worldwide concern resulting in the Montreal Protocol. The present annual average concentrations of CFC-11 and CFC-12 are 280 ppt and 484 ppt respectively with an annual growth rate of 4% (Engelman 1994), 5-8% (Brasseur and Hitchman, 1988). In view of the implication of the methane in green house effect, there has been a great deal of activity in the recent years regarding methane emission from anthropogenic sources such as rice paddies and natural sources. The latest estimates of natural and anthropogenic global emission of methane is about 400-600 Tg/y (Cicerone and Oremland, 1988). The annual average concentration of methane for the year 1994 was 1.737 ppm (Khalil and Rasmussen, 1994) which represents 115% increase over its pre-industrial levels (0.808ppm) and an annual growth rate of 0.5-1% (Engelman, 1994).

The trend of anthropogenic emission of VOCs has not been studied except in USA. Estimate of the anthropogenic emission of volatile organic compounds in US for the period

Trends of Global CFCs Production (in 000't).



(From 1960-84)

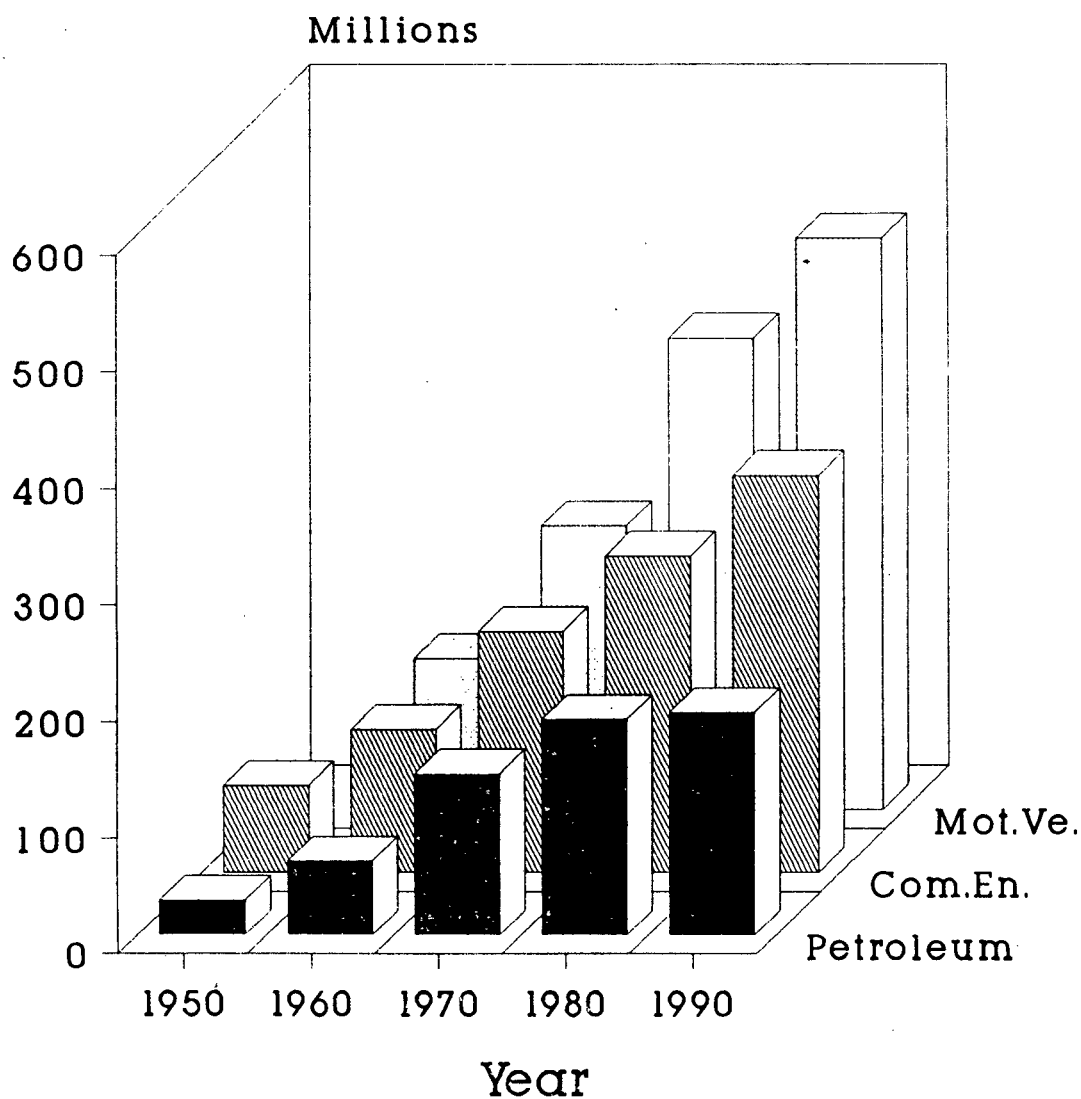
Figure.3

from 1985-2004 reveal that total yearly emission of VOCs into the ambient environment in US has been 25.1, 23.6, 23.9 and 25.4 mt/y for the year 1985, 1994, 1999 and 2004 (Jack Faucett Associates, 1986, Federal Register, 1987) respectively. It may be observed that the total anthropogenic VOC emission has reduced from 25.1 mt/y in the year 1985 to 23.6 mt/y in the year 1994. This reduction has been on account of various measures taken by the US administration to reduce the VOC emission. The reduction in VOC emission has been achieved mostly on account of improved fuel efficiency, better engine performance, proper vehicle maintenance and all round improvement of efficiency.

However projections of VOC emission for the year 1999 and 2004 show that in spite of the VOC emission control technology and overall efficiency in fuel use and other related operations the VOC emission are likely to increase in the coming years (USEPA, 1986; Federal Registrar, 1987).

In developing countries awareness about VOCs is lacking. Data for different VOCs source categories, like transportation; petroleum consumption, energy use for the period from 1950-90 are given in Figure 4.

Trends of Global Petroleum, Commercial Energy and Motor Vehicle



1st & 2nd(Tj,consumption),3rd (no.)

Figure.4

In view of the rapid growth in the automobile sector during the last two decades and the predicted growth in future suggest that the fossil fuels consumption is going to increase in the coming years (Derwent and Hov, 1979; Hough and Derwent, 1987; Rutten et al., 1988; Molnar, 1990).

Rapid industrial development and urban expansion particularly in the third world countries, also point out that VOC emission in the coming years is bound to increase at a rapid pace world wide.

The importance of VOC in atmospheric chemistry and global climate is most vital. Hence it is important that the proper inventory of VOC from anthropogenic sources need to be taken up or a high priority to keep a track of VOC emission from anthropogenic sources.

5. Effect of VOCs on Living System

Volatile organic compounds are suspected to be cancer inducing compounds.

5.1. Direct Effects

Toxic Effects : Among the aldehydes of importance are

formaldehyde and acrolein, both are potent irritants. Methyl bromide is considered to be more toxic than CH_3Cl (NAS, 1978). Six haloethanes, $\text{CH}_2\text{ClCH}_2\text{Cl}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, CH_3CCl_3 , $\text{CH}_2\text{ClCHCl}_2$, $\text{CH}_2\text{ClCCl}_3$, and $\text{CHCl}_2\text{CHCl}_2$, are measured by the author, Singh et al., (1981) because of their potential toxicity particularly the first three. Monochlorobenzene is moderately reactive. The secondary products like benzaldehyde and phenols are also toxic (Singh et al., 1981).

Carcinogenic Effects : Benzene which is a potent carcinogen and also occurs in the ambient environment has been the focus of investigation in main laboratories to understand its health implication (Hester and Meyer, 1979; Bruckmann et al., 1988; Fishbein, 1984; Albert, 1978). Emission of benzene through motor exhaust arises due to incomplete combustion of fuel, dealkylation of benzene homologs and by direct evaporation of fuel (Brief et al., 1980; Clark et al., 1984; Tsani-Bazaca et al., 1981). On the basis of the limited studies carried out so far toluene and xylene (Federal Register, 1977), Chloroethylenes like, CH_2Cl_2 , CHClCl_2 and CCl_2Cl_2 (Albert, 1978; Greenberg and Parker, 1979; Altshuller, 1980), Chloroform and CCl_4 (NAS, 1978; Padgett, 1980; Altshuller, 1980) are suspected to be potent carcinogens.

Estimated lifetime risk of benzene is two times greater than that of vinyl chloride for equal exposure (Padgett, 1980). The lifetime risk associated with CH_2CCl_2 , and CCl_2CCl_2 are six and two times greater over the risk of vinyl chloride (Padgett, 1980). Estimated carcinogenic potential of 1,2 dibromoethane is 50 times more than that of 1,2 dichloroethane (Padgett, 1980). List of some of the chemicals and their potential hazards are given in Table 5 and 6.

Health Implication of Indoor Pollution by VOCs :

The pollution of the ambient atmosphere has been the focus of attention, but the problems of indoor pollutions are no less serious.

VOCs in Work Environment : A report by Molhave et al., (1986) suggests that the volatile organic substance in indoor air provoke the discomfort described by WHO as the sick building syndrome (WHO, 1982). Different types of sick building syndromes have been studied like, irritated eyes, nose and throat, dry mucous membranes, red skin, tiredness and headache, dizziness and cough. There is also effect to sensory system. The study also shows the change in mid expiratory flow, eye irritation, nasal discharge, decreased physiological functions and tiredness (Kjaergaard et al., 1991)

TABLE:5 List of selected VOCs and their potential health impacts.

pollutants	mutagenic or carcinogenic potential	Reference
Vinyl chloride	Animal and Human carcinogen	(1)
Vinylidene chloride	--do--	(2)
Carbon tetrachloride	--do--	(1)
Benzene	--do--	(1)
Chloroform	Animal carcinogen	(1)
Ethylene dichloride	--do--	(2)
Methylene chloride	--do--	(3)
Trichloroethylene	--do--	(2)
Tetrachloroethylene	--do--	(4)
1,1,2-trichloroethane	--do--	(4)
1,1,2,2-tetrachloroethane	--do--	(4)
Chlorobenzene	--do--	(2)
Ethylene dibromide	--do--	(1)
1,4 dioxane	--do--	(5)
O-dichlorobenzene	suspected carcinogen	(2)
O-dichlorobenzene	--do--	(2)
O-chlorobenzene	--do--	(2)
P-chlorobenzene	--do--	(2)
Styrene	--do--	(5)

1. IARC (1982) 2. Fishbein (1979a,b) 3. NTP (1985)
 4. Singh et al. (1981) 5. Haseman et al. (1984).

TABLE:6 Potential hazard of selected man made VOCs¹.

VOCs	Potential hazard
Chlorofluorocarbons (F ₁₁ , F ₁₂ , F ₁₁₃ , F ₁₁₄)	Man made chemicals implicated in stratospheric ozone depletion and green house warming.
Halomethanes	Bacterial mutagens and suspect carcinogen.
Haloethanes and Halopropane	--do--
Chloroalkenes	--do--
Aromatic HCs	mostly suspected carcinogens.

¹Singh et al., 1992.

Work places like printing industry, plastic and PVC wire houses, work environment in refineries, petrochemical industries the level is high. Apart from industrial living and working environment in rural areas in developing countries fire wood or organic waste are used for cooking result in serious air pollution problems. Study showed that a tonne of particulates from household woodstoves may actually lead to more than 500 times the human exposure than a tonne of particulates from a coal fired power station. The study of Kirk Smith, A.L. Aggarwal from the National Institute of Occupational Health (NIOH), Ahmedabad and R.M. Dave of the Jyoti Solar Energy Institute at Vallabh Vidyalaya in Gujarat (1981) show that women while cooking inhale 40 times above the volume of suspended particles considered safe by WHO. In barely 3 hours they inhale an amount of carcinogenic benzo(a)pyrene that is more than any industrial worker working for 8 hours.

7.2. Indirect Effects

In some locations ozone levels in the troposphere are high enough to affect plant and animal life. Ozone was first identified as a significant, phytotoxic, gaseous air pollutant in southern California half a century ago (Lefohn et al., 1990). The primary and secondary ozone standards have

been shown to violated in many parts of Europe, N. America and Asia (Grennfelt et al., 1988).

The model calculations show that even a slight increase in the content of methane and its homologues, chlorofluoro-methane and other halogen-containing compounds in the atmosphere can lead to additional heating of earth (Wang et al., 1980) (Table 7).

TABLE:7 Greenhouse effect associated with certain minor atmospheric VOCs.

Component	Centre of absorption band (μm)	Increase in conc: as compared with current values by n times	Increase in the average temp. of the Earth ($^{\circ}\text{K}$)
CH_4	7.66	2	0.20 - 0.28
C_2H_4	10.5	2	0.001
CF_2CL_2	9.13, 8.68, 10.93	20	0.36 - 0.54
CFCL_3	9.22, 11.82	20	0.36 - 0.54
CCL_4	12.99	2	0.01 - 0.02
CH_3CL	13.66, 9.85, 7.14	2	0.01 - 0.02

7. Control of VOCs Emission :

In view of the serious problems of air quality associated with VOCs, efforts are being made to reduce VOCs

emission specially in non-attainment areas (areas where ambient ozone concentration chronically violates the prescribed ozone standard). In many European and North American areas control of VOCs emission should be taken up as a part of integrated air pollution control measures to prevent build up of oxidants. Because of the likely growth in the consumption of the fossil fuels, control of VOCs emission should be taken up even in areas which at present are free from problems.

VOC studies are mainly from industrialized countries but our knowledge about VOC level in the ambient environment particularly in developing countries including India is lacking. Recent studies have shown considerable ozone build up in Delhi where ozone levels frequently exceeds the ozone standard prescribed by WHO and ISI (Varshney and Aggarwal, 1992). High ozone level in the ambient air is a positive indication of the presence of large amounts of ozone precursors namely VOCs and NO_x. It is therefore important to determine the status of VOCs in the atmospheric environment. The present study was under taken to determine VOCs level in the urban environment of Delhi. An attempt has been also made to estimate VOC emission in India using emission factors for various activities given in literature.

Chapter II : Materials and Methods

A. The Study Area

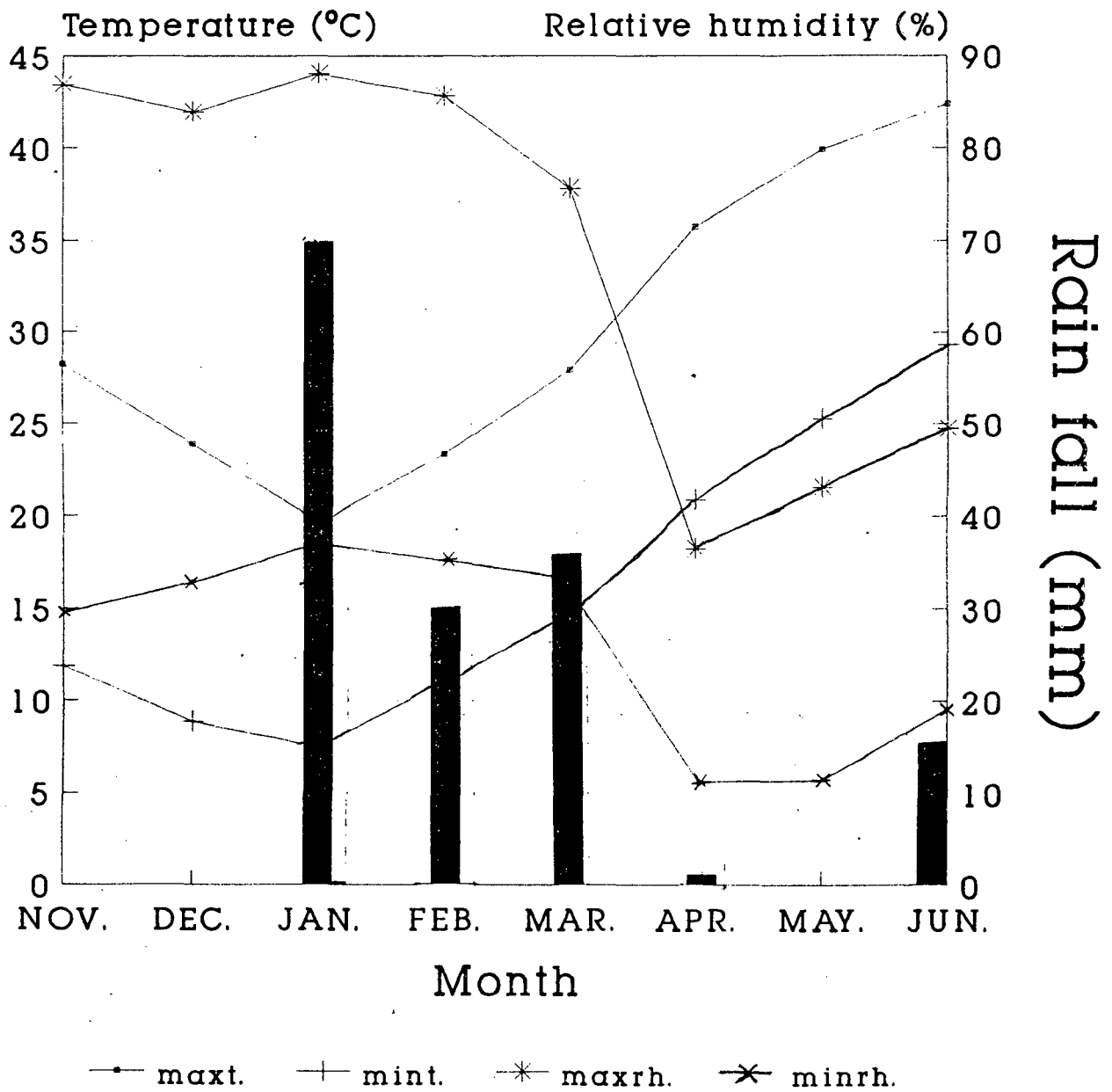
Delhi, the capital city of India is located between 76°50'E - 77°23'E and 28°12'N - 28°53'N on the west bank of river Yamuna. It lies in subtropical belt and experiences a maximum temperature of 46°C in summer and minimum of 1°C in winter. It has a monsoon climate with an yearly average rainfall of 72.7 mm (1994), 90.9 % of which is received during June-August (July-60.8%) (Figure 5).

Delhi, the third populous city of India, is spread over an area of 1483 sq km, has a population 94.2 lakhs. The total number of motor vehicles and industries have increased from 204078 and 26000 in 1971 to 1923787 and 85000 in 1991 (DSH, 1992). A rapid increase (Figure 6) in point sources (industries) and non-point sources (vehicular traffic) affect the air quality significantly.

B. Site Description

In Delhi 14 different sites were selected for the estimation of VOCs in the ambient air. The following

Ombrothermic Diagram of Delhi



(All the terms in monthly average)

Figure.5

Trends of Point & Non Point Source in Delhi (1960-90)

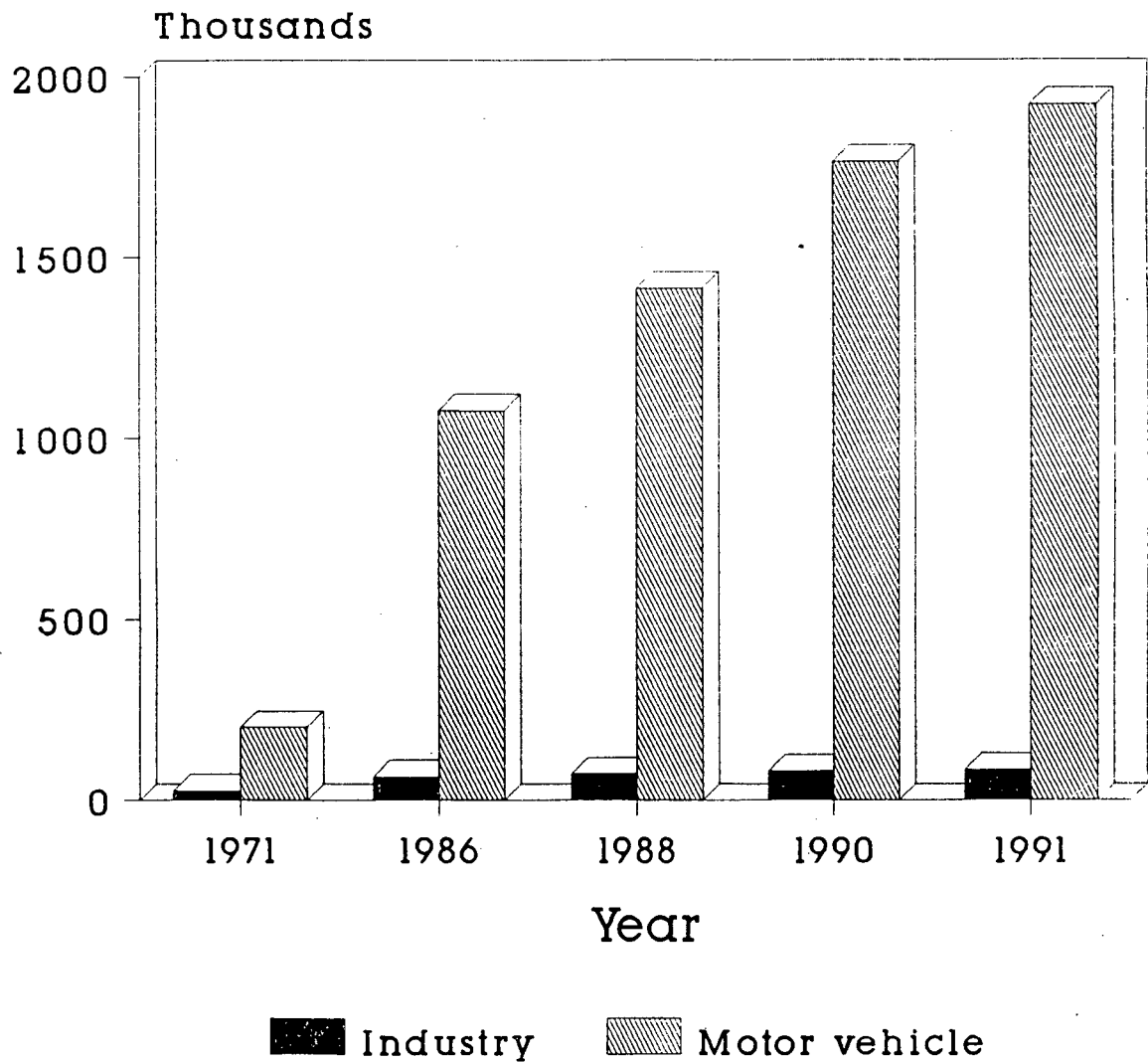


Figure.6

considerations were kept in mind while selecting the sites.

1. Sites should include regions with different activities.
2. Sites should cover different parts of Delhi as far as possible.

The sites are:

- 1) JNU (behind Central Library)
- 2) Delhi Lawn Tennis Association Court (inside)
- 3) Chanakya Puri (road side in front of British High commission)
- 4) World Wide Fund for Nature New Delhi (road side)
- 5) Vijay Chowk (road side towards parliament)
- 6) Kamal Ataturk Marg (road side near to PM's House)
- 7) Safdarjang Fly Over (from highest position)
- 8) Pahar Ganj (in front of New Delhi railway station)
- 9) Minto Bridge (after over bridge towards station)
- 10) All India Institute of Medical Sciences (crossing)
- 11) South Extension (in between ring road)
- 12) Ashram (crossing)
- 13) Darya Ganj (Delhi gate crossing)
- 14) Bhikaji Cama Place, crossing (selected only for 24hr sampling).

Figures showing different sites are given in Plate 1-Plate 13.

A brief description about the sites are given below.

Plate 1. Site 1 : JNU Campus



- Plate 2.** Site 2 : DLTA
- Plate 3.** Site 3 : Chanakya Puri
- Plate 4.** Site 4 : WWF
- Plate 5.** Site 6 : Vijay Chowk
- Plate 6.** Site 7 : S. J. Flyover
- Plate 7.** Site 8 : Pahar Ganj



- Plate 8. Site 9 : Minto Bridge
- Plate 9. Site 10 : AIIMS
- Plate 10. Site 11 : South Extension
- Plate 11. Site 12 : Ashram
- Plate 12. Site 13 : Darya Ganj
- Plate 13. Site 14 : Bhikaji Cama Place



- Site 1 :** JNU lies in extreme south of Delhi, relatively pollution free locality selected to serve as a control site for comparison.
- Site 2 :** DLTA is situated in between two different habitats, one side being Africa Avenue and the other side deer park. Air samples were drawn from inside the court towards park.
- Site 3 :** Chanakya Puri is relatively low and fast traffic area in the south west of Delhi where most of the embassies are situated.
- Site 4 :** WWF is situated in the institutional area of Lodhi Road in the central part of Delhi.
- Site 5 :** Vijay Chowk is situated near Central Secretariat from where Raj Path starts. It is not a main traffic corridor, wide enough and the traffic density is low except during morning, evening and working days.
- Site 6 :** Kamal Ataturk Marg (K.A. Marg) is near Ashoka Hotel close to Prime Minister's House in central Delhi. At this site traffic density is not high, fast moving and free from any traffic jam.
- Site 7 :** Safdarjang Fly Over represent a major traffic corridor and joins South to Central Delhi and remains busy during most of the day.

- Site 8 :** Pahar Ganj a densely populated and major commercial and residential area near to Connaught Place and New Delhi Railway Station.
- Site 9 :** Minto Bridge lies towards the North of Connaught Place which is the biggest office cum-commercial center in the city.
- Site 10:** AIIMS crossing on Ring Road, carries the maximum traffic in Delhi. It is estimated that during peak hour 16,000 passenger car units (PCU) remain in traffic.
- Site 11:** South Extension located on the Ring Road is a busy modern shopping complex having high traffic density with a distinct peak in the morning and evening.
- Site 12:** Ashram is on the eastern section of the Ring Road and carries the maximum traffic going out from Delhi to other states and vice versa.
- Site 13:** Darya Ganj is a busy commercial area and is supposed to be one of the most polluted areas of Delhi.
- Site 14:** Bhikaji Cama Place is an office cum-modern commercial complex in South Delhi on the Ring Road which has a heavy traffic for most of the day.

These selected sites may be grouped into following three categories:

- a) JNU (Low vehicular traffic)
- b) From 2nd to 7th (Medium vehicular traffic) and
- c) From 8th to 14th (Heavy vehicular traffic).

A brief sites characteristics are given in Figure 7 & Table 8.

C. Sampling Procedure

Air samples were drawn from a height of 2 meters from the ground drawn by a 30 ml air tight disposable syringe. The gas sampling device is shown in Plate 14. The gas sample bottles of 10 ml were purged with the ambient air by repeatedly blowing the air into the bottle by keeping the tip of the needles at the bottom of the bottle. After repeated purging for 4-5 times the gas sample bottles were closed by a rubber stopper and immediately sealed by an aluminum cap using a sealing machine. The bottles containing air samples were kept in a black polythene bag and brought to the laboratory for analysis. The time lag between drawing of air sample and the analysis was from 30 minutes to 3 hr.

However for few specific studies (C_2 - C_9 , saturated and aromatics) the sampling procedure was different. For this

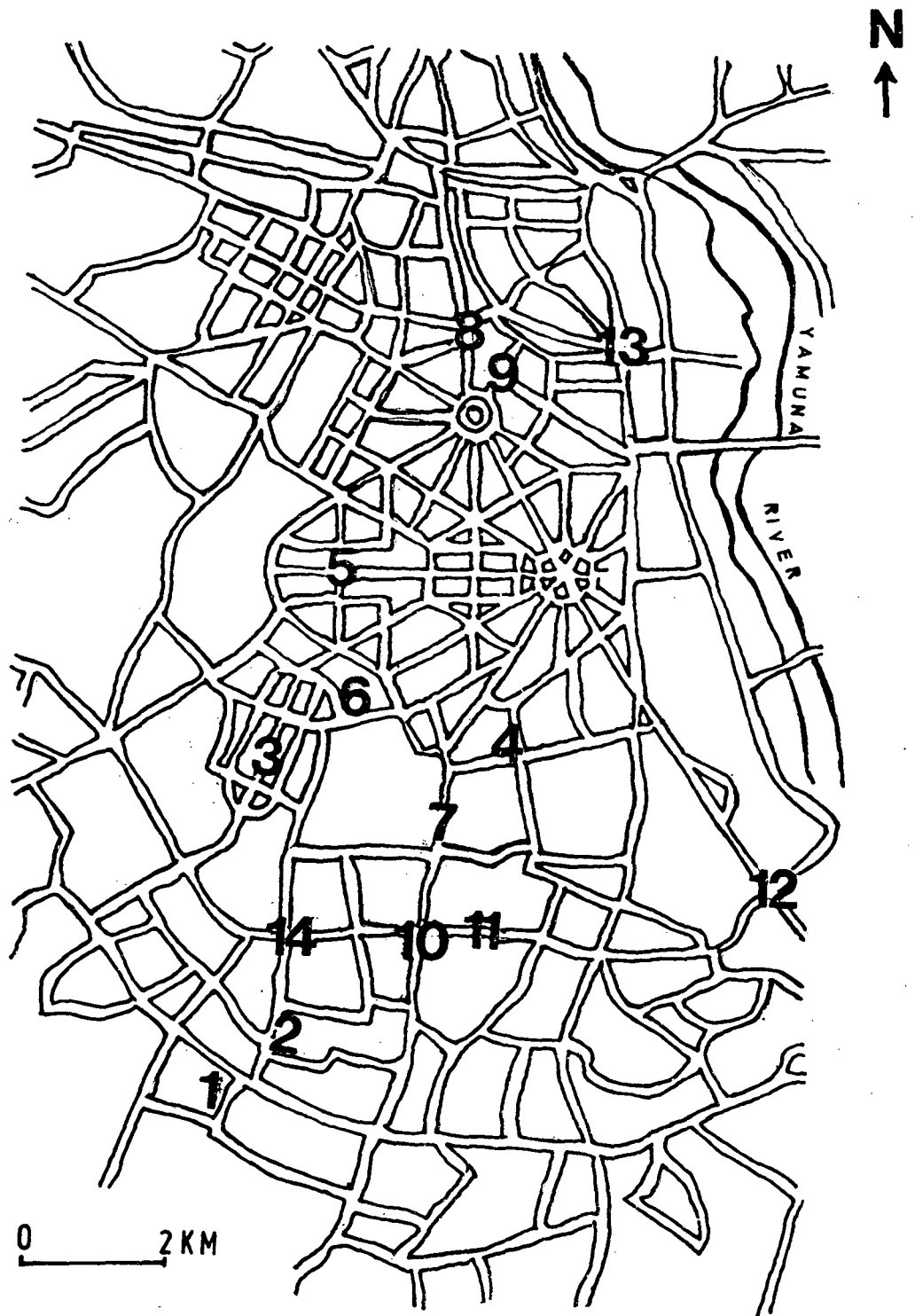
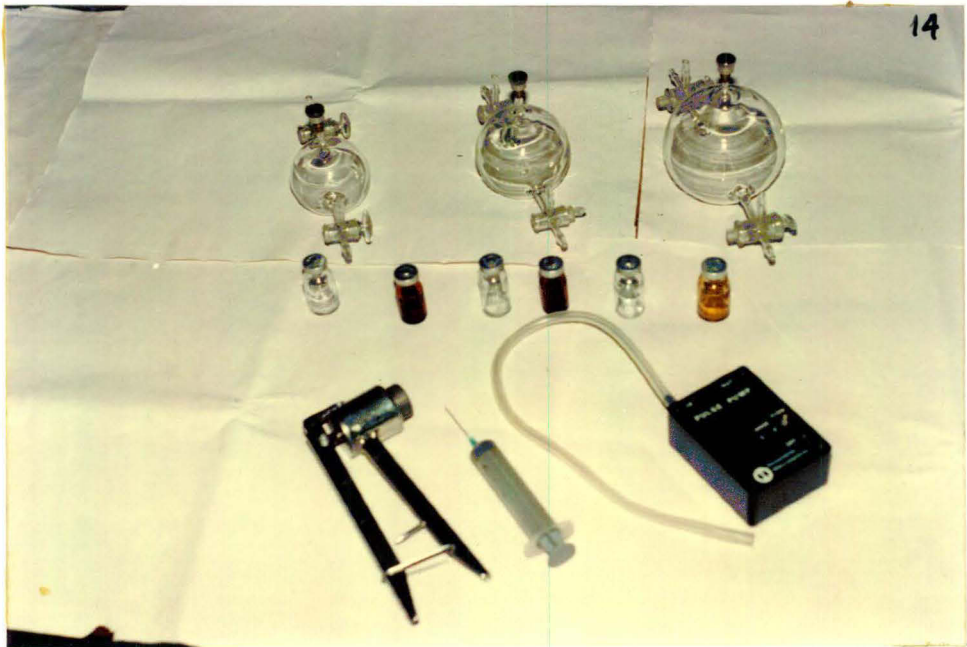


FIG.7. MAP OF DELHI SHOWING SAMPLING SITES

Table:8 Brief description of air sampling sites

Site	Location	Activity Area	Relative Traffic Density
Darya Ganj	North East	Urban	+++++
Ashram	South East	Urban	+++++
South Extention	South	Mar. complex	+++++
AIIMS	South	Urban	+++++
Pahar Ganj	Central	Urban	+++++
Minto Bridge	Central	Urban	+++++
S. J. Flyover	South	Sub urban	+++++
Vijay Chowk	Central	Semi urban	+++++
K.A. Marg	Central	Semi urban	+++++
WWF	Central	Residential	+++++
Chanakya Puri	South West	Residential	+++++
DLTA	Souyh west	Sub urban	+++++
JNU	South West	U. Campus	+

Plate 14. Gas Sampling device



purpose the gas sampling was done by using glass sampling valve (bottles of 500 ml and 250 ml) with vacuum pump connected to one end of the bottle. The other end was kept free in ambient air. The air was sucked through the stopper and then through the bottle. The sampling was done for 5 minutes and after that the bottles were sealed from both sides and were taken to laboratory for analysis. In this case large size valves were selected because the samples had to be transported from a long distance and one should have sufficient quantity of sample for analysis at a place which is far away (around 40 kms) from sampling sites.

D. Sampling Schedule

Schedule 1 : In one case all the 13 sites of Delhi were taken except Bhikaji Cama Place. The sampling were done in the afternoon time in between 3.30 PM to 6 PM. For this purpose sampling were done consecutively for two days to cover up all the 13 sites by keeping the duration of sampling same in both the cases to avoid any error in concentration. The sampling started from the month of November and continued upto June with an interval of 15 days.

Schedule 2 : Samples of 3 hr duration were collected for 24 hr sampling, where samples were taken monthly in 3 hr duration in 3 sites, viz. AIIMS, Bhikaji Cama and JNU. So except 3 o'clock morning samples, all other 7 samples were collected. This was done once in every month. For all the above studies 2 sets of samples were collected to detect total volatile organic compounds (TVOC) and methane separately.

E. Gas Analysis Technique

Principle of GLC :

Basically, chromatography consists of 2 phases. One phase is a fixed or stationary phase. This phase may be either a solid, as in adsorption chromatography, or a liquid held by a solid, as in partition chromatography. The other phase is mobile and is generally referred to as the moving phase. This phase may be a gas, liquid or volatile solid. When phase equilibria occurs between the sample components, the moving phase and the fixed phase, the sample components are distributed or partitioned between the phases.

In gas chromatography, the sample is vaporized (if not already in this form) and the mixture is passed by a stream of inert gas (carrier) through a rigid container (column) containing a packing material. The packing has

different affinities for each particular component in the mixture and lets each component pass through at a different rate. As each component emerges from the column, it is observed by a sensitive detecting device like Flame Ionization Detector (FID). The column effluent is mixed with hydrogen and passes through a jet into a chamber through which air is passed. The hydrogen is ignited to produce a continuous flame, they under go combustion. A very small proportion of the carbon atoms undergoes ionization during this combustion process. An electrode, which is polarized with respect to the jet, collects these ions and the resulting electrical current is amplified to provide the chromatographic signal.

Hydrocarbons containing N_2 , O_2 , or halo-atoms give reduced response. Thus FID HC analyzer are almost universally calibrated in terms of a gas as CH_4 or Hexane and the output is read in ppm or Carbon measured as Methane or Hexane.

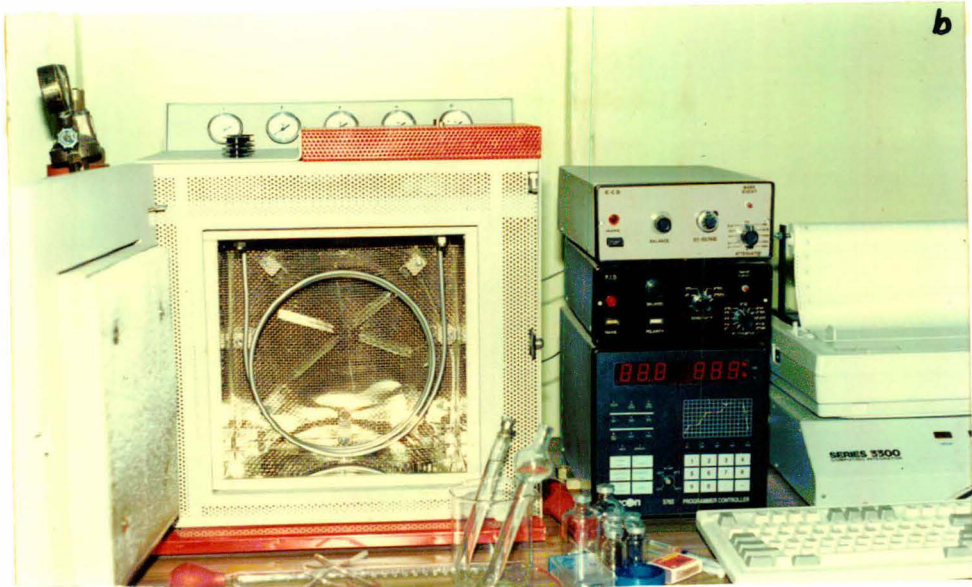
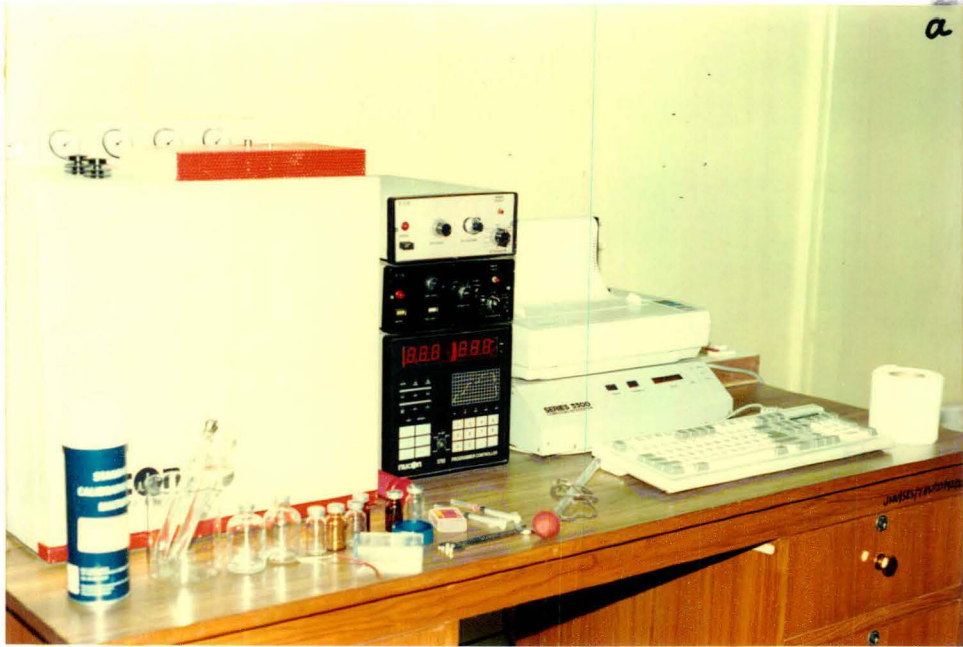
Preparation of standard curve : A standard calibration gas mixture of 108 vpm methane in air, was obtained and the standard curve was prepared by diluting known concentrations of methane with air. Vials of same volume (68 ml) were used to dilute the standard to get a series of low concentrations. At first the vials were closed with tight film rubber stoppers and sealed with special aluminum cap. Few glass beads were

introduced prior to sealing for mixing the standard gas introduced with the air present inside the vial properly. A set of five vials were taken and standard gas of 1 ml - 5 ml were injected respectively after removing a small amount of air from each vial to maintain the air pressure with the outside. Then the vials were shaken to get a proper mixture of standard gas and air. After mixing 1 ml of gas was withdrawn from each vial and injected into the column for analysis.

The concentrations of individual vial obtained after calculation and the respective peak areas obtained after analysis were plotted to get standard curve which was subsequently used to get the concentration of samples.

Estimation of TVOC : It is estimated with the help of Nucon Gas Chromatograph, Series no 6900 containing blank column (Length- 2m, External diameter 1/4 inch, Internal diameter 1/5 inch, made up of stainless steel) equipped with a Flame Ionization Detector (FID) (Plate 15a,b). The column was maintained with isothermal temperature of 40°C by the help of a heater and a fan which is placed behind to mix the hot air inside to maintain isothermal temperature. The carrier, fuel and air used were zero air, hydrogen and zero air with gas pressures < 0.1 Kg/cm² (flow rate 30 ml/min), 0.8 Kg/cm² (flow rate 30 ml/min) and 0.8 Kg/cm² (flow rate 300 ml/min)

Plate 15a,b. Nucon Gas Chromatograph.



respectively. Both the injection and detection temperatures were 100°C. The gas chromatograph was standardized using a standard calibration mixture of methane in the air (108 vpm, EDT Research, London). One ml of gas sample was withdrawn from the vial headspace with a 2 ml hypodermic syringe and injected into the column slowly and the peak area obtained was matched with the standard curve prepared in advance to obtain the concentration of TVOC in ppm in text sample.

Estimation of Methane: It is also done by the help of same instruments and detector. The temperatures of oven, injection and detection were kept same and also the fuel and air except for the carrier gas which was replaced by Nitrogen with a pressure of 1.5 Kg/cm² (flow rate 30 ml/min) and the column used here is made up of stainless steel with 80 Porapak-R packing material (column used-2 m, Internal diameter 1/12 inch). The pressure and flow rate of both fuel (Hydrogen) and zero air were same. In the same way one ml of sample was injected into the column suddenly and the peak area was matched in similar way to obtain the concentration in ppm.

The value of Non-Methane Volatile organic compounds was obtained by deducting the values of CH₄ from TVOC.

Estimation of Aromatic and C₂ - C₉ Hydrocarbons : Air samples were fed to Photovac Portable Photoionization Gas Chromatography model- 10S70 by using the column Tris- 2- Cyano Ethoxy Propane (TCEP, 7%), coated on solid support Chromosorb at Indian Oil Corporation Limited, Research and Development Division. Description about the column is given below.

Physical characteristics

Length 4 feet, Diameter 1/8".

Chemical characteristics

It separates aromatics from saturates

The experiment is done at room temperature by using Nitrogen as carrier gas (flow rate = 10 ml/min.).

F. Statistical Analysis

The data have been subjected to the following statistical treatments.

Standard deviation : The standard deviation was calculated according to the following formula (Snedecor and Cochran, 1978):

$$S. D. = \sqrt{d^2/n-1}$$

where n = no. of samples, d = deviation from mean.

Chapter III : Results

TVOC in the ambient environment of Delhi

Total Volatile Organic Compounds (TVOC) levels at the 13 sites in Delhi during November'94 to June'95 varied between 3.889 - 42.579 ppm (Table 9a,b). The average concentration was found to be between 19.620 ± 6.339 ppm (Table 9b). The maximum TVOC was measured at South Extension where the concentration was 42.579 ppm (Table 9b). The minimum concentration of 3.889 ppm was at JNU (Table 9a).

The concentration of TVOC in low vehicular traffic area (JNU) varied between 3.889 - 5.438 ppm (Table 9a). On medium vehicular traffic areas (Site two - Site seven) the values obtained were 10.008 - 25.4 (Table 9a). Whereas, for heavy vehicular traffic areas (Site eight - Site thirteen) the concentration was between 16.432 - 42.579 ppm (Table 9b).

Methane in the ambient environment of Delhi

Methane levels at the 14 sites in Delhi during November'94 to June'95 varied between 0.998 - 8.974 ppm (Table 10a,b). The average concentration was found to be between

TABLE:9.a Ambient Levels of TVOC at Different Sites of Delhi (in ppm)

DATE	JNU	DLTA	C.PURI	WWF	KAMARG	VCHOWK	SJFLY.
17/11/94	4.967	12.881	10.816	16.244	15.865	17.426	25.400
05/12/94	4.846	12.650	11.777	15.680	15.938	15.661	23.434
28/12/94	4.945	10.977	11.274	13.604	13.080	18.615	13.931
17/01/95	5.438	14.761	14.340	15.372	18.680	13.144	14.253
15/02/95	4.912	12.986	12.787	13.516	17.564	12.245	12.559
09/03/95	3.889	10.278	11.634	11.884	15.895	11.185	10.721
25/03/95	4.475	11.082	11.676	11.655	14.604	11.267	10.008
10/04/95	4.692	11.302	12.502	12.009	14.802	12.003	10.210
02/06/95	4.782	10.953	10.234	10.572	12.394	10.901	10.023
AVERAGE	4.771 ± 0.395	11.985 ± 1.342	11.893 ± 1.134	13.392 ± 1.900	15.424 ± 1.873	13.605 ± 2.732	14.504 ± 5.534

TABLE:9.b Ambient Levels of TVOC at Different Sites of Delhi (in ppm)

DATE	M.BDGE	P.GANG	AIIMS	S.EXT.	ASHRAM	DGANJ	AVG.
17/11/94	27.816	32.606	39.287	42.579	41.437	42.336	25.4± 12.7
05/12/94	31.981	31.438	35.105	32.539	36.412	39.627	23.6± 10.9
28/12/94	26.383	27.616	22.067	34.053	32.421	40.700	20.7± 10.3
17/01/95	22.953	31.552	23.013	22.407	33.670	34.717	20.3± 8.4
15/02/95	30.307	30.020	21.338	20.595	31.301	32.060	19.4± 8.6
09/03/95	27.984	27.413	19.396	19.435	30.154	29.689	17.6± 8.3
25/03/95	26.479	25.644	17.102	17.494	28.555	27.199	16.7± 7.5
10/04/95	25.923	25.021	19.952	17.329	30.021	27.235	17.2± 7.5
02/06/95	22.923	22.897	17.873	16.432	27.834	25.039	15.6± 6.8
AVERAGE	26.972 ± 2.832	28.245 ± 3.164	23.903 ± 7.389	24.762 ± 8.774	32.422 ± 4.040	33.178 ± 6.102	19.62 ± 6.33

TABLE:10.a Ambient Levels of Methane at Different Sites of Delhi (in ppm)

DATE	JNU	DLTA	C.PURI	WWF	KAMARG	VCHOWK	SJFLY
17/11/94	1.171	2.272	2.375	3.720	3.398	3.720	4.261
05/12/94	1.248	2.107	2.019	2.672	2.821	2.451	3.987
25/12/94	1.297	2.221	2.408	2.835	2.512	4.468	2.732
17/01/95	1.422	3.698	3.324	3.686	4.066	2.830	2.966
15/02/95	1.179	2.534	2.375	2.657	3.460	2.360	2.523
09/03/95	0.998	2.150	1.620	1.854	2.568	1.568	1.786
25/03/95	1.005	1.635	1.630	1.901	2.359	1.763	1.570
10/04/95	1.024	1.212	1.612	1.998	2.500	1.503	1.420
02/06/95	1.024	1.223	1.383	1.503	2.310	1.321	1.302
AVERAGE	1.152 ± 0.142	2.116 ± 0.711	2.082 ± 0.572	2.536 ± 0.750	2.888 ± 0.576	2.442 ± 0.014	2.505 ± 1.030

TABLE:10.b Ambient Levels of Methane at Different Sites of Delhi (in ppm)

DATE	M.BDGE	P.GANJ	AIIMS	S.EXT	ASHRAM	D.GANJ	AVG.
17/11/94	5.825	6.740	6.703	7.267	7.148	7.433	4.77± 2.093
05/12/94	5.624	5.539	6.230	5.785	6.483	7.433	4.18± 1.986
25/12/94	4.957	5.861	4.491	6.418	5.636	8.974	4.21± 2.069
17/01/95	5.028	7.253	5.078	4.733	7.120	7.476	4.51± 1.785
15/02/95	5.177	5.080	3.960	3.873	5.637	5.662	3.57± 1.397
09/03/95	4.601	4.590	3.546	3.369	5.326	5.044	3.00± 1.435
25/03/95	4.602	4.449	2.961	2.965	5.042	4.631	2.80± 1.356
10/04/95	4.801	4.672	3.702	2.871	5.203	4.523	2.84± 1.479
02/06/95	3.980	3.972	3.342	2.803	4.923	4.021	2.54± 1.307
AVERAGE	4.955 ± 0.525	5.350 ± 1.036	4.445 ± 1.233	4.453 ± 1.584	5.835 ± 0.816	6.133 ± 1.632	3.607 ± 1.275

3.607 ± 1.275 ppm (Table 10b). The maximum CH₄ level was recorded at Darya Ganj and the concentration was 8.974 ppm (Table 10b). The minimum concentration of 0.998 ppm was at JNU (Table 10a).

The concentration of methane in low vehicular traffic area (JNU) varied between 0.998 - 1.422 ppm (Table 10a). On medium vehicular traffic areas (Site two - Site seven) the values ranged between 1.212 - 4.468 (Table 10a). In areas with heavy vehicular traffic (Site eight - Site thirteen) obtained concentration varied between 2.803 - 8.974 ppm (Table 10b).

NMVOC in the ambient environment of Delhi

The ambient level of Non-methane volatile organic compound in Delhi at 14 sites varied between 2.891 - 35.312 ppm (Table 11a,b). The average concentration was 16.025 ± 5.262 ppm (Table 11b). The maximum NMVOC was measured at South Extension, the concentration was 35.312 ppm (Table 11b). The minimum concentration of 2.891 ppm was at JNU (Table 11a).

The concentration of NMVOC at JNU varied between 2.891 - 4.016 ppm (Table 11a). For medium vehicular traffic areas (Site two - Site seven) the values were 8.128 - 21.138 (Table 11a). In heavy traffic areas (Site eight - Site

TABLE:11.a Ambient Levels of NMVOC at Different Sites of Delhi
(in ppm)

DATE	JNU	DLTA	C.PURI	WWF	KAMARG	VCHOWK	SJFLY
17/11/94	03.746	10.654	08.486	12.524	12.467	13.706	21.139
05/12/94	03.598	10.543	09.758	13.008	13.117	13.171	19.447
28/12/94	03.648	08.756	08.866	10.769	10.568	14.147	11.199
17/01/95	04.016	11.063	11.016	11.686	14.614	10.314	11.287
05/02/95	03.732	10.452	10.412	10.859	14.104	09.885	10.036
09/03/95	02.891	08.128	10.014	10.030	13.327	09.617	08.935
25/03/95	03.470	09.447	10.046	09.754	12.245	09.504	08.438
10/04/95	03.668	10.090	18.890	10.011	12.302	10.500	08.790
02/06/95	03.758	09.930	08.851	09.069	10.084	09.580	08.721
AVERAGE	03.614 ± 0.290	09.895 ± 0.902	10.704 ± 2.994	10.856 ± 1.243	12.536 ± 1.405	11.158 ± 1.821	11.999 ± 4.554

TABLE:11.b Ambient Levels of NMVOC at Different Sites of Delhi
(in ppm)

DATE	M.BDGE	P.GANJ	AIIMS	S.EXT.	ASHRAM	D.GANJ	AVG.
17/11/94	21.991	25.866	32.584	35.312	34.289	34.903	20.58± 10.708
05/12/94	26.357	25.899	28.875	26.754	29.929	32.190	19.43± 8.983
28/12/94	21.426	21.755	17.576	27.635	26.785	31.716	16.52± 8.317
17/01/95	17.925	24.299	17.935	17.674	26.550	27.241	15.81± 6.703
05/02/95	25.130	24.940	17.378	10.036	25.672	26.398	15.31± 7.399
09/03/95	23.383	22.823	15.850	16.066	24.828	24.645	14.65± 6.980
25/03/95	21.877	21.195	14.141	14.529	23.513	22.568	13.90± 6.185
10/04/95	21.122	20.349	16.250	14.458	24.818	22.712	14.92± 6.091
02/06/95	18.943	18.925	14.531	13.629	22.911	21.018	13.07± 5.558
AVERAGE	22.017 ± 2.533	22.894 ± 2.367	19.457 ± 6.209	19.565 ± 7.874	26.588 ± 3.342	27.043 ± 4.611	16.025 ± 5.262

thirteen) the NMVOC concentration varied between 10.036 - 35.312 ppm (Table 11b).

A seven month comparative TVOC, methane and NMVOC levels at different vehicular traffic sites (low, medium and high) is given in Figure 8.

Seasonal Variation :

TVOC : The monthly variation in TVOC concentration at different site in Delhi is given in Table 12a,b. The monthly average during November-February varied between 19.39 ± 8.636 ppm to 25.35 ± 12.75 ppm. The maximum concentration was observed in the month of November. The monthly average during March-June varied between 15.60 ± 6.83 ppm to 17.18 ± 7.95 ppm. The concentration of TVOC was relatively higher in winter as compared to spring and summer periods.

Methane : The monthly variation in Methane concentration at different sites in Delhi is given in Table 13a,b. The monthly average during November-February varied between 3.575 ± 1.393 ppm to 4.771 ± 2.093 ppm. The maximum concentration was observed in the month of November. The monthly average during March-June varied between 2.546 ± 1.307 ppm to 2.905 ± 1.391 ppm. The concentration of methane is

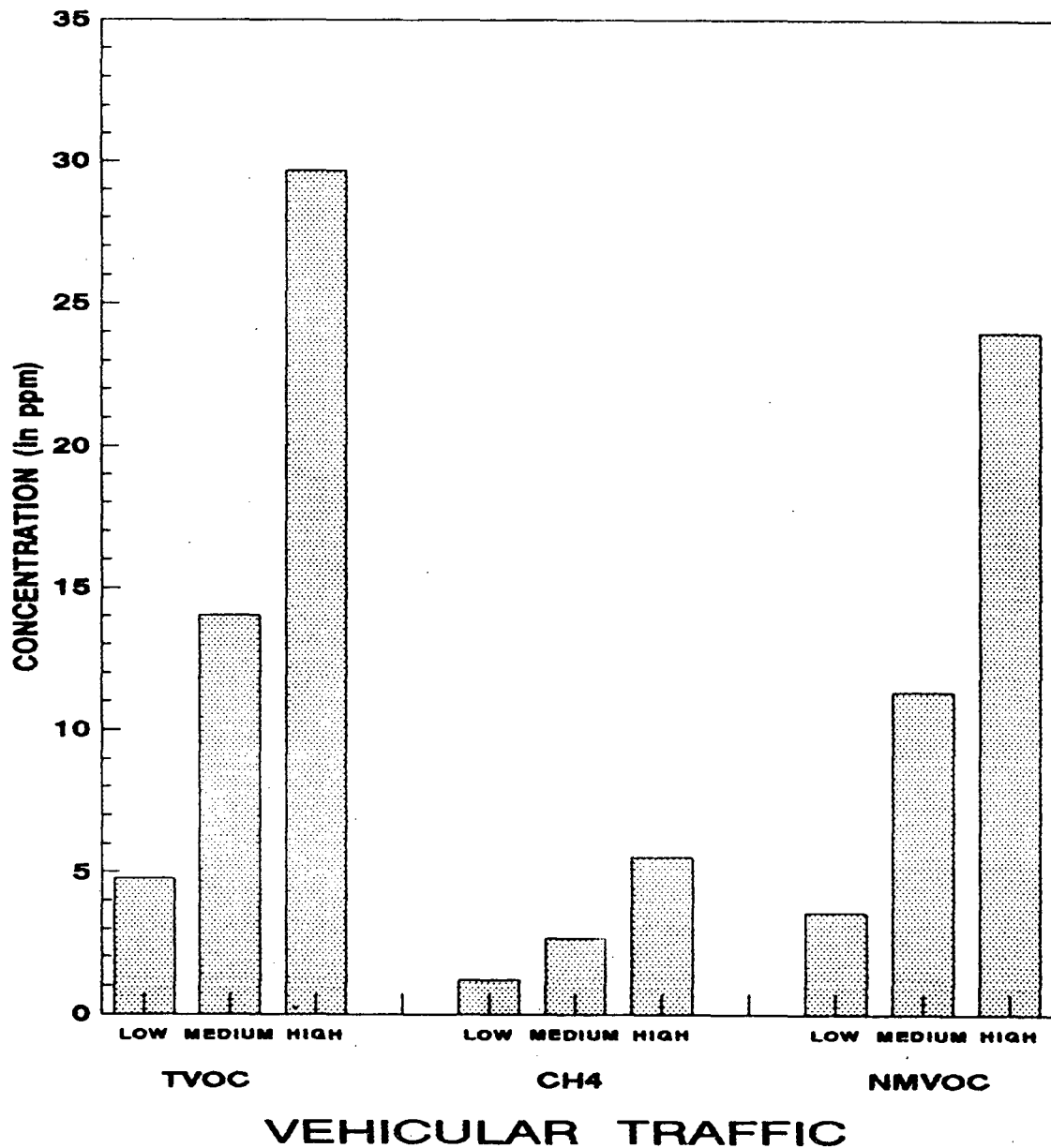


Figure 8. Comparison in TVOC, methane and NMVOC levels among low, medium and heavy vehicular traffic sites.

TABLE:12.a Monthly Variation in TVOC Levels at Different Sites of Delhi during Nov'94-Jun'95 (in ppm;24hrs average)

MONTH	JNU	DLTA	C.PURI	WWF	KAMARG	VCHOWK	SJFLY
NOV'94	4.967	12.881	10.816	16.244	15.865	17.426	25.40
DEC'94	4.8955	11.813	11.525	14.642	14.509	17.138	18.68
JAN'95	5.438	14.761	14.340	15.372	18.680	13.144	14.25
FEB'95	4.912	12.986	12.787	13.516	17.564	12.245	12.55
MAR'95	4.182	10.680	11.655	11.769	15.249	11.226	10.36
APR'95	4.692	11.302	12.502	12.009	14.802	12.003	10.21
JUN'95	4.782	10.953	10.234	10.572	12.394	10.901	10.02
AVERAGE	4.771 ± 0.346	11.985 ± 1.334	11.893 ± 1.265	13.392 ± 1.931	15.424 ± 1.913	13.605 ± 2.521	14.50 ± 5.287

TABLE:12.b Monthly Variation in TVOC Levels at Different Sites of Delhi during Nov'94-Jun'95 (in ppm;24hrs average)

MONTH	M.BDGE	P.GANG	AIIMS	S.EXT.	ASHRAM	D.GANJ	AVG.
NOV'94	27.816	32.606	39.287	42.579	41.437	42.336	25.3± 12.75
DEC'94	29.182	29.527	28.586	33.296	34.416	40.163	22.1± 10.42
JAN'95	22.953	31.552	23.013	22.407	33.67	34.717	20.3± 8.47
FEB'95	30.307	30.02	21.338	20.595	31.301	32.06	19.3± 8.63
MAR'95	27.231	26.528	18.249	18.464	29.354	28.444	17.1± 7.95
APR'95	25.923	25.021	19.952	17.329	30.021	27.235	17.1± 7.50
JUN'95	22.923	22.897	17.873	16.432	27.834	25.039	15.6± 6.83
AVERAGE	23.291 ± 2.660	24.768 ± 3.309	21.037 ± 7.068	21.387 ± 9.077	28.504 ± 4.210	28.749 ± 6.889	17.15 ± 6.279

TABLE:13.a Monthly Variation in CH₄ Levels at Different Sites of Delhi during Nov'94-Jun'95 (in ppm;24hrs average)

MONTH	JNU	DTA	C.PURI	WWF	KAMARG	VCHOWK	SJFLY
NOV'94	1.171	2.272	2.375	3.720	3.398	3.720	4.261
DEC'94	1.272	2.164	2.213	2.753	2.666	3.459	3.359
JAN'95	1.422	3.698	3.324	3.686	4.066	2.830	2.966
FEB'95	1.179	2.534	2.375	2.657	3.460	2.360	2.523
MAR'95	1.001	1.892	1.625	1.877	2.463	1.665	1.678
APR'95	1.024	1.212	1.612	1.998	2.500	1.503	1.420
JUN'95	1.024	1.223	1.383	1.503	2.310	1.321	1.302
AVERAGE	1.152 ± 0.143	2.116 ± 0.789	2.082 ± 0.613	2.536 ± 0.806	2.888 ± 0.612	2.442 ± 0.891	2.505 ± 1.023

TABLE:13.b Monthly Variation in CH₄ Levels at Different Sites of Delhi during Nov'94-Jun'95 (in ppm;24hrs average)

MONTH	M.BDGE	P.GANJ	AIIMS	S.EXT	ASHRAM	D.GANJ	AVG.
NOV'94	5.825	6.740	6.703	7.267	7.148	7.433	4.771± 2.093
DEC'94	5.2905	5.700	5.360	6.101	6.059	8.203	4.200± 1.966
JAN'95	5.028	7.253	5.078	4.733	7.120	7.476	4.513± 1.785
FEB'95	5.177	5.080	3.960	3.873	5.637	5.662	3.575± 1.397
MAR'95	4.6015	4.519	3.253	3.167	5.184	4.837	2.905± 1.391
APR'95	4.801	4.672	3.702	2.871	5.203	4.523	2.849± 1.474
JUN'95	3.98	3.972	3.342	2.803	4.923	4.021	2.546± 1.307
AVERAGE	4.955 ± 0.537	5.350 ± 1.118	4.445 ± 1.180	4.453 ± 1.599	5.835 ± 0.853	6.133 ± 1.542	3.607 ± 1.266

relatively higher in winter as compared to spring and summer months.

NMVOC : The monthly variation in NMVOC concentration at different sites in Delhi is given in Table 14a,b. The monthly average during November-February varied between 15.31 ± 7.39 ppm to 20.58 ± 10.70 ppm. The maximum concentration was in the month of November. The monthly average during March-June varied between 13.07 ± 5.55 ppm to 14.92 ± 6.091 ppm. The NMVOC levels are relatively higher during winter as compared to spring and summer periods.

The ratio between methane to non-methane volatile organic compounds for different sites (low, medium and heavy vehicular traffic) are given in Table 15.

TABLE 15: Ratio of Methane to NMVOC at different site category

Site Category	TVOC (ppm)	Methane (ppm)	NMVOC (ppm)	Ratio (M/N)
Low traffic	4.781	1.188	3.585	0.331
Medium traffic	14.032	2.663	11.369	0.234
Heavy traffic	29.687	5.517	24.010	0.229

TABLE:14.a Monthly Variation in NMVOC Levels at Different Sites of Delhi during Nov'94-Jun'95 (in ppm;24hrs average)

MONTH	JNU	DTA	C.PURI	WWF	KAMARG	VCHOWK	SJFLY
NOV'94	03.746	10.654	08.486	12.524	12.467	13.706	21.13
DEC'94	03.623	09.649	09.312	11.888	11.842	13.659	15.32
JAN'95	04.016	11.063	11.016	11.686	14.614	10.314	11.28
FEB'95	03.732	10.452	10.412	10.859	14.104	09.885	10.03
MAR'95	03.180	08.787	10.030	09.892	12.786	09.560	08.68
APR'95	03.668	10.090	18.890	10.011	12.302	10.500	08.79
JUN'95	03.758	09.930	08.851	09.069	10.084	09.580	08.72
AVERAGE	03.674 ± 2.232	10.089 ± 0.687	10.999 ± 3.326	10.847 ± 1.157	12.599 ± 1.381	11.029 ± 1.708	11.99 ± 4.32

TABLE:14.b Monthly Variation in NMVOC Levels at Different Sites of Delhi during Nov'94-Jun'95 (in ppm;24hrs average)

MONTH	M.BDGE	P.GANJ	AIIMS	S.EXT.	AHSRAM	D.GANJ	AVG.
NOV'94	21.991	25.866	32.584	35.312	34.289	34.903	20.5± 10.70
DEC'94	23.891	23.827	23.225	27.194	28.357	31.953	17.9± 8.48
JAN'95	17.925	24.299	17.935	17.674	26.550	27.241	15.8± 6.70
FEB'95	25.130	24.940	17.378	10.036	25.672	26.398	15.3± 7.39
MAR'95	22.122	22.009	14.995	15.297	24.170	23.606	14.2± 6.57
APR'95	21.122	20.349	16.250	14.458	24.818	22.712	14.9± 6.09
JUN'95	18.943	18.925	14.531	13.629	22.911	21.018	13.0± 5.55
AVERAGE	22.017 ± 2.381	22.894 ± 2.356	19.457 ± 5.946	19.565 ± 8.267	26.588 ± 3.499	27.043 ± 4.673	16.02 ± 5.21

Above table provides an idea about the relative strength of methane to NMVOC in relation to traffic density. The ratio varies from 0.229 to 0.331. The percentage of methane varies from 18.7 to 34.5 of total volatile organic compounds in the urban atmosphere (Figure 9).

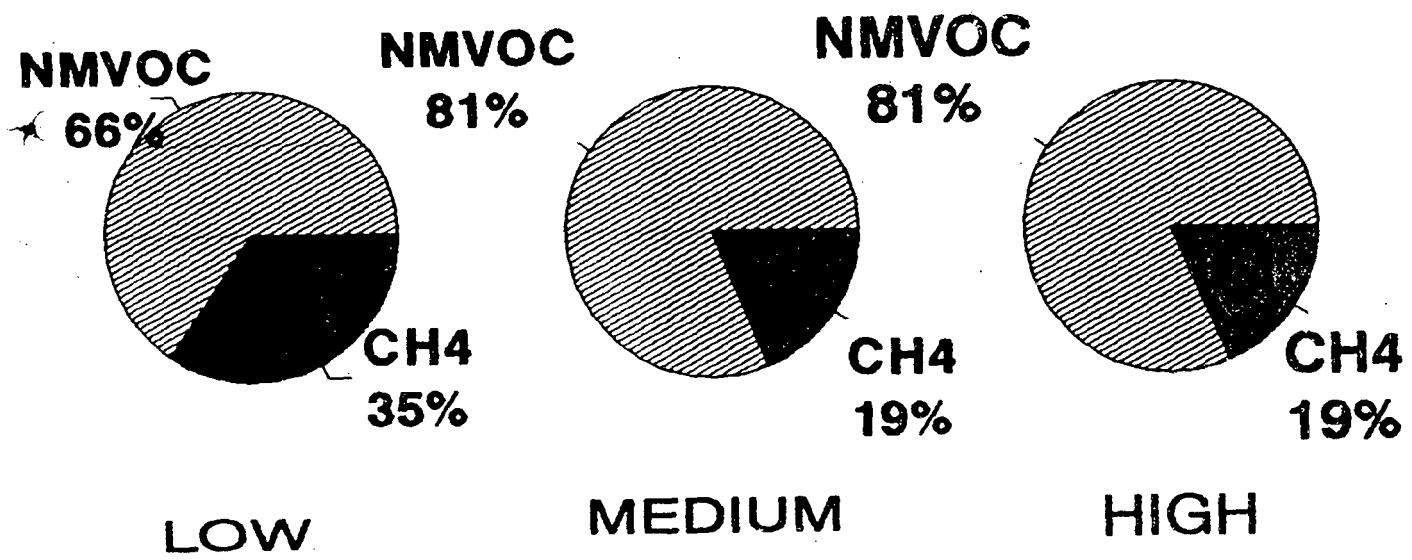
Saturated C₂-C₉ and Aromatic Hydrocarbons in Delhi

Ambient air samples from Ashram and JNU were analyzed for saturated hydrocarbons (C₂-C₉) and aromatics like toluene at the Indian Oil Corporation Ltd., Research and Development Centre, Faridabad. The values obtained (in ppm) are given in Table 16.

TABLE 16: Saturated (C₂-C₉) and Aromatic Compounds at Delhi (in ppm)

Site	Saturated (C ₂ -C ₉)	Aromatics (Toluene)
JNU	7.0 6.8	--- ---
ASHRAM	13.6 13.0	--- 0.2

The average concentration of saturated hydrocarbons (C₂-C₉) obtained in the air samples of JNU and Ashram were 6.9



TRAFFIC SITES

Figure 9. Relative Percentage of methane to NMVOC levels at different site categories (low, medium and high).

ppm and 13.3 ppm, respectively. Aromatics, in the ambient air were absent at JNU but they were detected at Ashram and the value obtained was 200 ppb or 0.2 ppm.

Diel Variation in the Ambient VOC Level at Delhi:

TVOC: Total volatile Organic compounds varied widely with the time of the day. The concentrations also differed from place to place and season to season.

The TVOC build up in the ambient environment started early in the morning and peaked at 9 am which was invariably observed except during November when the peak was at 12 o'clock midnight (Table 17). After attaining a peak in the morning (9 am) the TVOC level starts declining and continues to decline till late afternoon (Figure 10). Such variation in TVOC concentration during the course of the day was observed at AIIMS, with a slight variation at Bhikaji Cama (the maximum concentration was observed at 9 pm in the evening (Table 18).

The values obtained for JNU is given in Table 19. The build up of TVOC started from the early morning reached its maximum value during noon and thereafter it started declining and continued to decline through the night. The pattern of diel variation in ambient level of TVOC was the

TABLE:17 Diurnal Variation in the Ambient Concentration of TVOC at AIIMS (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	08.285	10.293	35.842	21.813	21.022	19.451± 9.851
9	24.010	35.490	39.988	31.243	29.142	31.974± 5.450
12	17.883	31.033	26.706	20.988	19.810	23.284± 4.863
3	20.254	18.463	23.407	11.676	12.475	17.255± 4.522
6	25.435	30.268	16.917	15.612	14.975	20.641± 6.114
9	29.153	19.073	18.985	19.007	16.789	20.601± 4.362
12	35.213	16.627	12.571	29.031	26.181	23.924± 8.255
AVERAGE	22.890 ± 7.965	23.035 ± 8.547	24.916 ± 9.285	21.338 ± 6.427	20.056 ± 5.542	22.447 ± 6.878

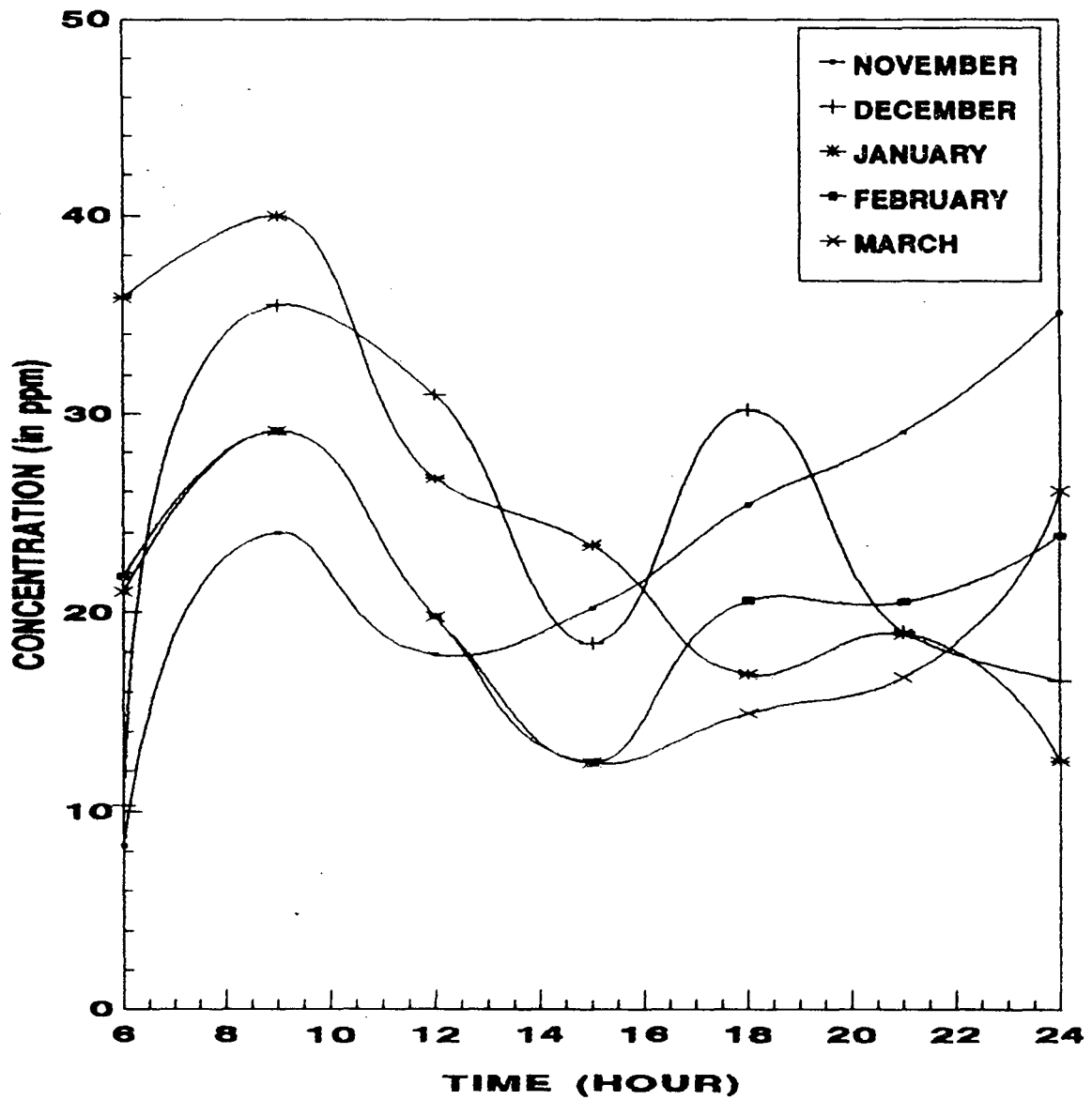


Figure 10. Diurnal variation in the ambient concentrations of TVOC at AIIMS (November'94 - March'95; in ppm).

TABLE:18 Diurnal Variation in the Ambient Concentration of TVOC at BHIKAJI CAMA (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	09.384	19.085	17.863	22.598	19.545	17.695± 4.438
9	24.564	44.429	26.984	30.023	27.198	30.639± 7.108
12	19.769	33.761	20.568	19.784	16.539	22.084± 6.600
3	21.497	23.135	21.194	12.851	12.786	18.292± 4.518
6	25.544	37.567	16.573	15.819	14.174	21.935± 8.760
9	30.737	14.095	17.374	17.401	16.672	19.255± 5.867
12	28.391	16.826	11.964	26.888	21.451	21.104± 6.140
AVERAGE	22.840 ± 6.500	26.985 ± 10.748	18.931 ± 4.314	20.766 ± 5.681	18.337 ± 4.532	21.572 ± 6.237

TABLE:19 Diurnal Variation in the Ambient Concentration of TVOC at JNU (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	07.352	08.127	07.478	04.931	03.885	06.354± 1.644
9	11.142	12.098	18.127	11.536	09.530	12.486± 2.946
12	14.773	15.550	12.689	13.999	14.887	14.379± 0.978
3	09.662	10.439	17.479	08.933	10.311	11.364± 3.103
6	06.632	07.409	07.827	05.060	06.022	06.590± 0.986
9	05.456	06.233	07.362	04.629	04.274	05.590± 1.115
12	05.420	06.197	04.387	03.579	03.230	04.562± 1.111
AVERAGE	08.633 ± 3.187	09.436 ± 3.208	10.764 ± 4.995	07.523 ± 3.717	07.448 ± 3.972	08.761 ± 2.757

same for each month except for the month of January where the maxima was reached at 9 am (Figure 11).

Diel variation in the ambient levels of TVOC exhibits a distinct peak at 9 am at both AIIMS and Bhikaji Cama. Again towards night time, there is peak in almost all months (Figure 10 and Table 18). But the diel variation in the ambient concentration of TVOC exhibited a distinct peak during noon in all months at JNU except January where two peaks were observed one at 9 am and the other at 3 pm (Figure 11).

METHANE : Methane concentration varied widely with the time of the day. Methane concentration also varied from one site to another as well from one season to another at the same site.

The CH₄ build up in the ambient environment started early in the morning and peaked at 9 am which invariably represents the methane maxima for the day except during the month of November (when it was 12 o'clock midnight for AIIMS and 12 o'clock for Bhikaji Cama) (Table 20 and 21). There was no definite trend after 9 am. At most of the sites from morning (9 am) to afternoon, methane level started declining and towards evening again increased (Figure 12 and Table 21). Such variation in methane concentration during the course of

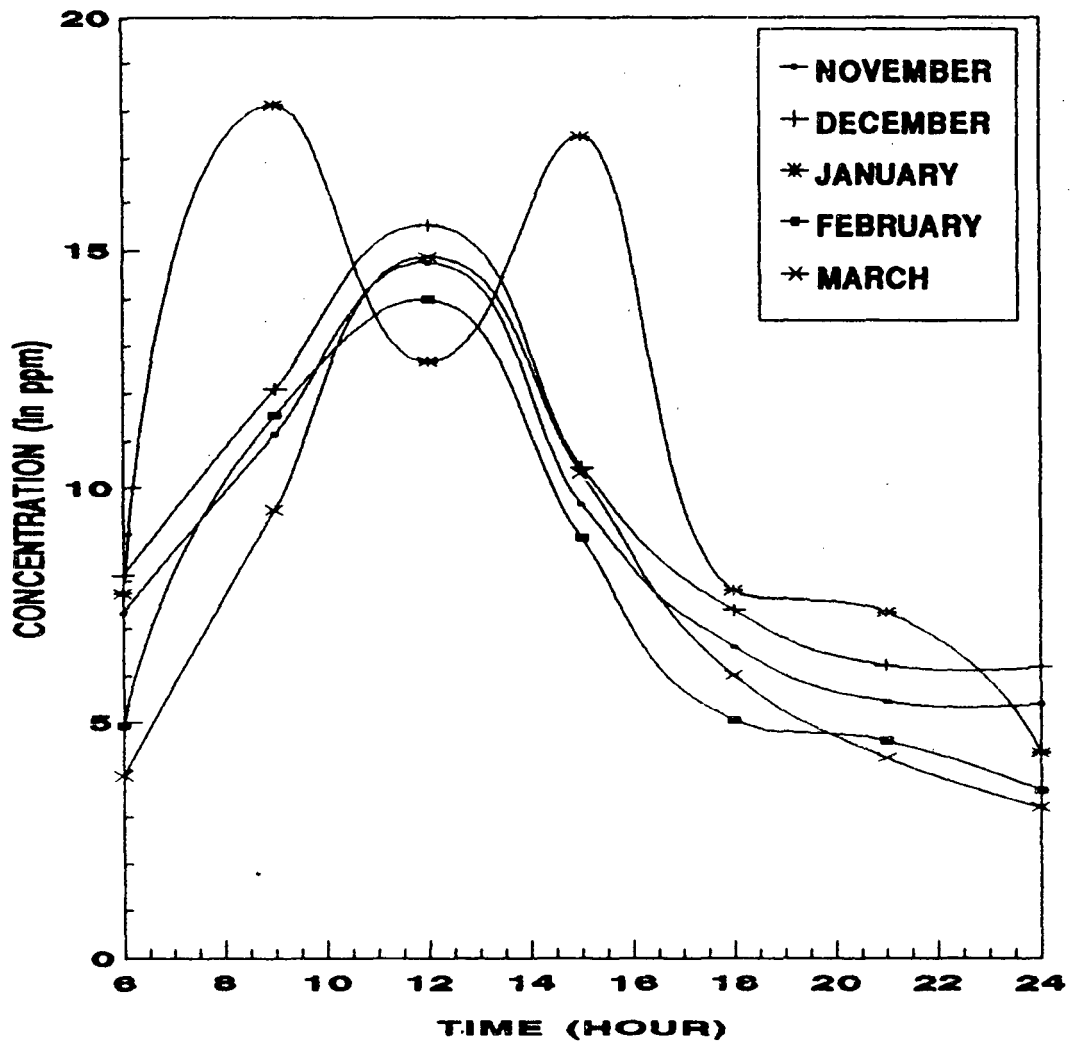


Figure 11. Diurnal variation in the ambient concentrations of TVOC at JNU (November'94 - March'95; in ppm).

TABLE:20 Diurnal Variation in the Ambient Concentration of Methane at AIIMS (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	1.635	2.279	6.127	3.564	3.410	3.403± 1.538
9	4.589	7.449	7.225	5.208	5.060	5.906± 1.188
12	3.862	6.893	4.597	3.324	3.315	4.398± 1.332
3	4.258	4.488	4.171	1.785	1.832	3.306± 1.227
6	5.192	7.325	3.099	2.404	2.360	4.076± 1.923
9	6.065	4.252	3.291	3.008	2.817	3.886± 1.195
12	6.810	3.840	2.193	4.666	4.436	4.389± 1.487
AVERAGE	4.630 ± 1.550	5.218 ± 1.860	4.386 ± 1.640	3.422 ± 1.111	3.318 ± 1.046	4.195 ± 1.427

TABLE:21 Diurnal Variation in the Ambient Concentration of Methane at BHIKAJI CAMA (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	1.928	3.923	3.100	3.744	3.398	3.218± 0.704
9	4.882	9.957	5.118	5.177	4.749	5.976± 1.996
12	3.695	7.871	3.480	3.133	2.680	4.171± 1.881
3	4.243	4.302	3.490	1.697	1.767	3.099± 1.153
6	5.778	7.521	2.930	2.404	1.857	4.098± 2.181
9	6.244	3.314	2.986	2.655	2.680	3.575± 1.355
12	5.919	3.725	2.063	4.528	3.598	3.966± 1.260
AVERAGE	4.669 ± 1.412	5.801 ± 2.413	3.309 ± 0.860	3.334 ± 1.136	2.961 ± 0.970	4.015 ± 1.431

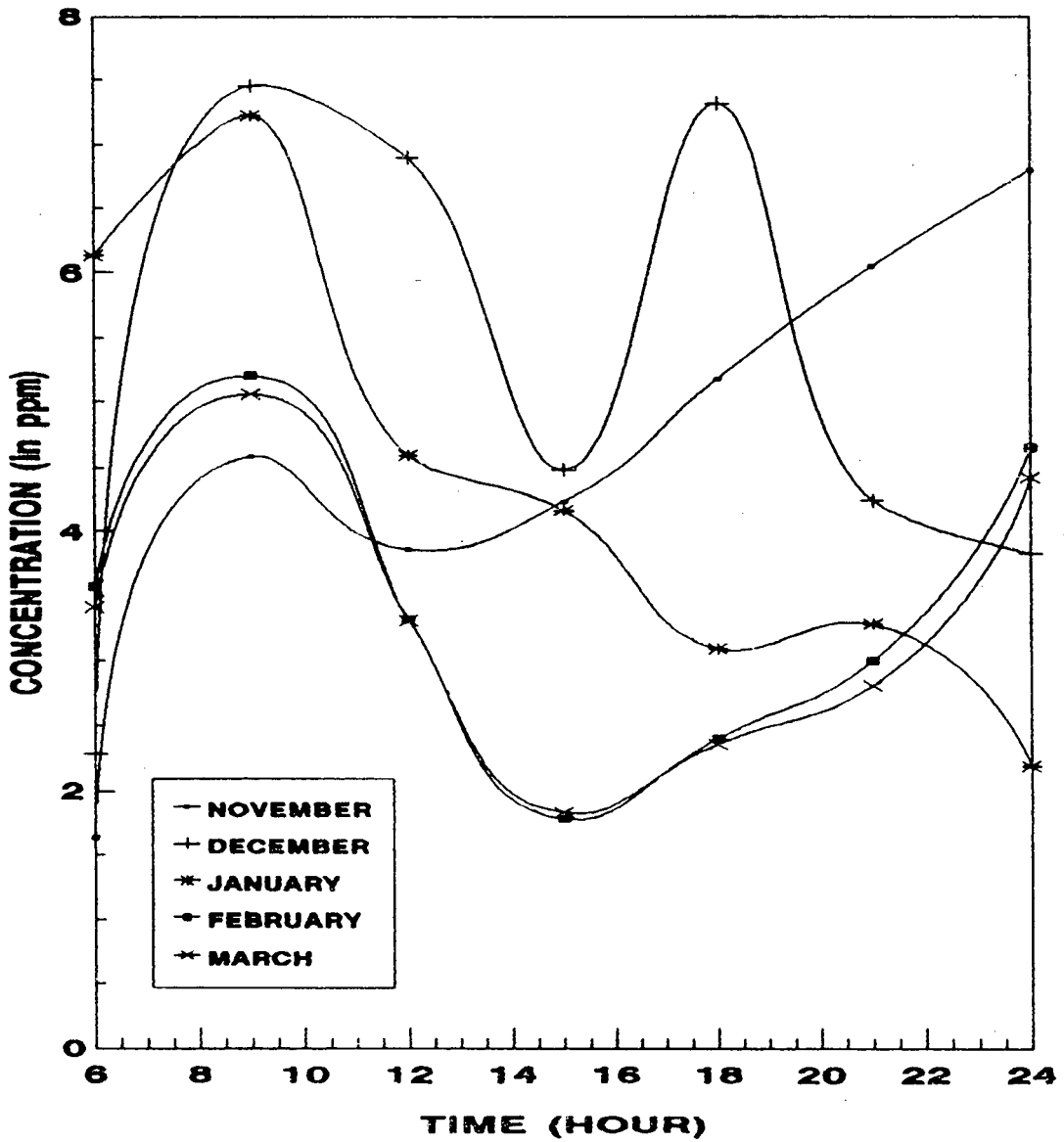


Figure 12. Diurnal variation in the ambient concentrations of methane at AIIMS (November'94 - March'95; in ppm).

the day was observed at both the sites (AIIMS and Bhikaji Cama).

The values obtained for JNU is given in Table 22. The build up of CH₄ started from morning reaching to its maximum value during noon and there after it started declining and continued to decline through the night. The pattern of diel variation in ambient level of methane was the same for each month except for the month of January where the maxima was reached at 9 am (Figure 13).

The pattern of diel variation of methane exhibits a distinct peak at 9 am both at AIIMS and Bhikaji Cama. During night there was an increase in the concentration in comparison with the late afternoon in almost all months (Figure 12 and Table 21). A distinct peak was observed during noon at JNU except in January where two peaks were observed (one at 9 am and the other at 3 pm (Figure 13)).

NMVOC : Non-methane volatile organic compounds concentration varied widely with the time of the day. NMVOC concentration also varied from one site to another as well from one season to another at the same site.

The NMVOC build up in the ambient environment started early in the morning and peaked at 9 am which was

TABLE:22 Diurnal Variation in the Ambient Concentration of Methane at JNU (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	1.526	1.822	1.624	1.188	1.023	1.436± 0.291
9	2.672	2.969	3.776	2.391	2.015	2.764± 0.595
12	3.397	3.248	2.666	2.997	3.056	3.072± 0.247
3	2.227	2.301	3.714	1.916	2.160	2.463± 0.638
6	1.631	1.719	1.769	1.183	1.332	1.526± 0.229
9	1.469	1.480	1.563	1.018	1.003	1.306± 0.243
12	1.223	1.269	1.041	0.894	0.812	1.047± 0.178
AVERAGE	2.020 ± 0.726	2.115 ± 0.697	2.307 ± 1.012	1.655 ± 0.740	1.628 ± 0.754	1.945± 0.566

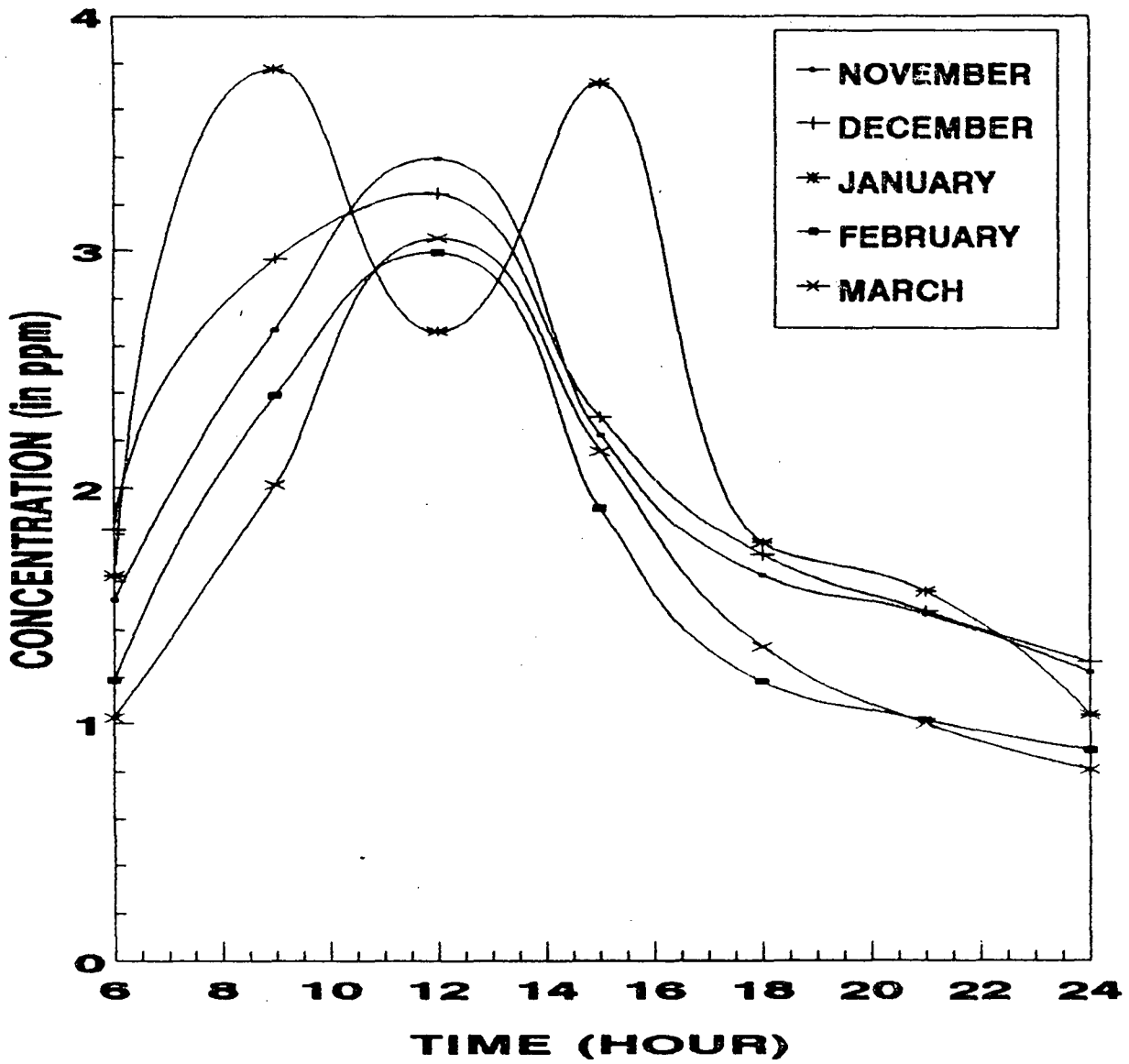


Figure 13. Diurnal variation in the ambient concentrations of methane at JNU (November'94 - March'95; in ppm).

invariably observed for the NMVOC maxima for the day except during November (when it was at 12 o'clock midnight for AIIMS and at 9 pm for Bhikaji Cama) (Table 23 and 24). Thereafter the NMVOC levels started declining and continued to decline till the late afternoon (Figure 14). Such variation in NMVOC concentration during the course of the day was observed at both the sites (AIIMS and Bhikaji Cama) (Figure 14 and Table 24).

The values observed at JNU is given in the Table 25. The build up of NMVOC started from morning reached to its maximum value during noon and thereafter it started declining and continued to decline through the night. The pattern of diel variation in ambient level of NMVOC was the same for each month except in the month of January, where the maxima was observed at 9 am (Figure 15).

Diel pattern of NMVOC fluctuation exhibited a distinct peak during 9 am at both AIIMS and Bhikaji Cama. Again towards night time, there was peak in almost all months (Figure 14 and Table 24). But the diel pattern of NMVOC fluctuation exhibited a distinct peak during noon in all months at JNU except January where two peaks were found, one at 9 am and the other at 3 pm (Figure 15).

TABLE:23 Diurnal Variation in the Ambient Concentration of NMVOC at AIIMS (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	06.65	08.014	29.715	18.249	17.612	16.048± 8.330
9	19.421	28.041	32.763	26.035	24.082	26.068± 4.400
12	14.021	24.140	22.109	17.664	16.495	18.885± 3.711
3	15.996	13.975	19.239	09.891	10.643	13.948± 3.451
6	20.243	22.943	13.818	13.208	12.615	16.565± 4.210
9	23.088	14.821	15.694	15.999	13.972	16.714± 3.264
12	28.403	12.787	10.378	24.365	21.745	19.535± 6.873
AVERAGE	18.260 ± 6.429	17.817 ± 6.718	20.530 ± 7.650	17.915 ± 5.317	16.737 ± 4.498	18.252 ± 5.503

TABLE:24 Diurnal Variation in the Ambient Concentration of NMVOC at BHIKAJI CAMA (NOV'94-MAR'95 ; in ppm)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	07.456	15.162	14.763	18.854	16.147	14.476± 3.789
9	19.682	34.472	21.866	25.134	22.449	24.720± 5.176
12	16.074	25.890	17.088	16.651	13.859	17.912± 4.140
3	17.254	18.833	17.704	11.154	11.019	15.192± 3.392
6	19.766	30.046	13.643	13.415	12.317	17.837± 6.639
9	24.493	10.781	14.388	14.746	13.992	15.680± 4.627
12	22.472	13.101	09.901	22.360	17.853	17.137± 4.998
AVERAGE	18.171 ± 5.117	21.183 ± 8.388	15.621 ± 3.471	17.473 ± 4.613	15.376 ± 3.572	17.565 ± 4.856

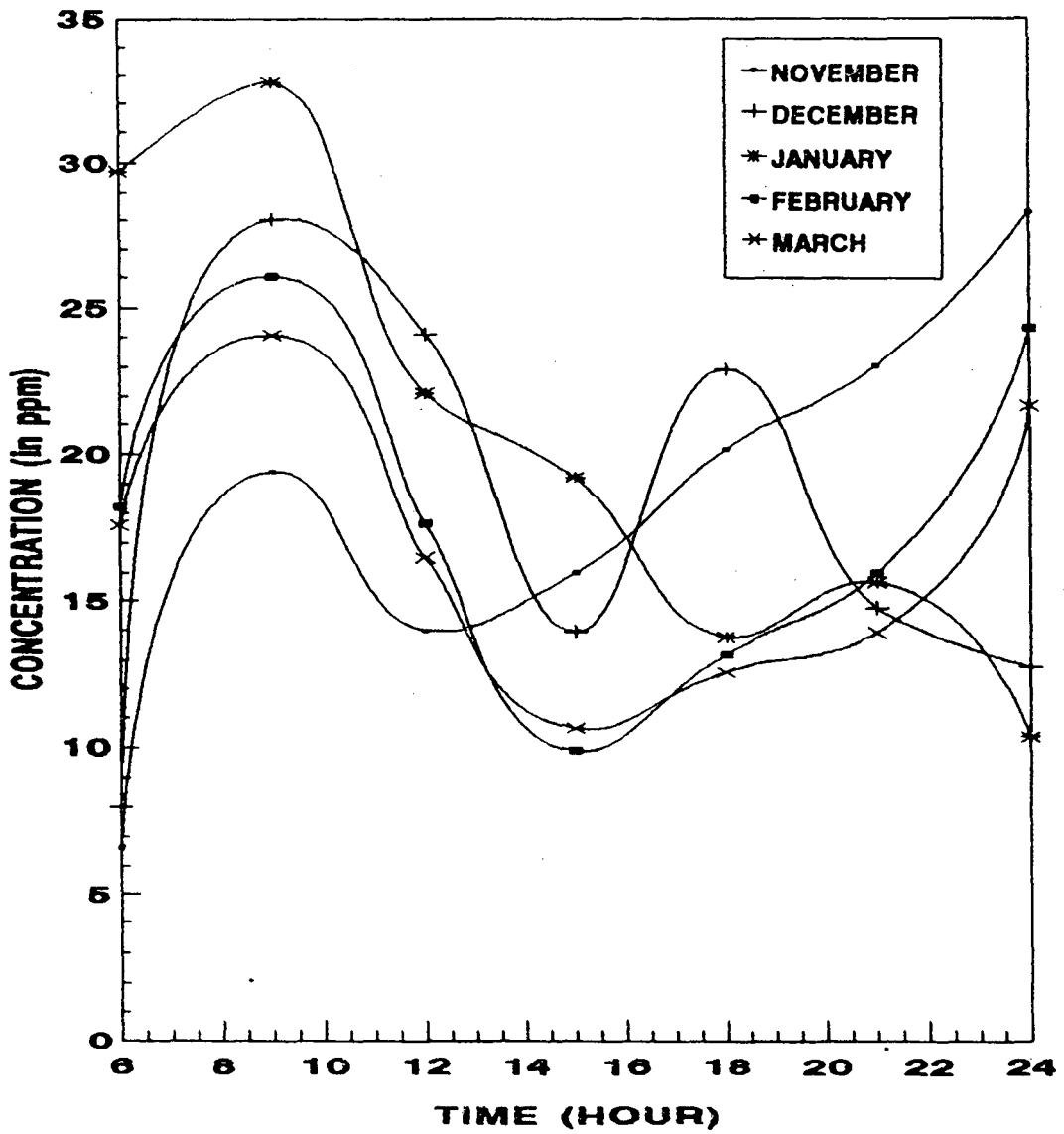


Figure 14. Diurnal variation in the ambient concentrations of NMVOC at AIIMS (November '94 - March '95; in ppm).

TABLE:25 Diurnal Variation in the Ambient Concentration of NMVOC at JNU (NOV'94-MAR'95 ; in ppM)

HOUR	NOV (9th)	DEC (20th)	JAN (30th)	FEB (20th)	MAR (20th)	AVERAGE
6	5.826	6.305	5.854	3.743	2.862	4.918± 1.358
9	8.47	9.129	14.351	9.145	7.515	9.722± 2.389
12	11.376	12.302	10.023	11.002	11.831	11.30± 0.776
3	7.435	8.138	13.765	7.017	8.151	8.901± 2.469
6	5.001	5.690	6.058	3.877	4.690	5.063± 0.765
9	3.987	4.753	5.799	3.611	3.271	4.284± 0.903
12	4.197	4.928	3.346	2.685	2.418	3.514± 0.936
AVERAGE	6.613 ± 2.471	7.320 ± 2.528	8.456 ± 3.983	5.868 ± 2.979	5.819 ± 3.219	6.815 ± 2.203

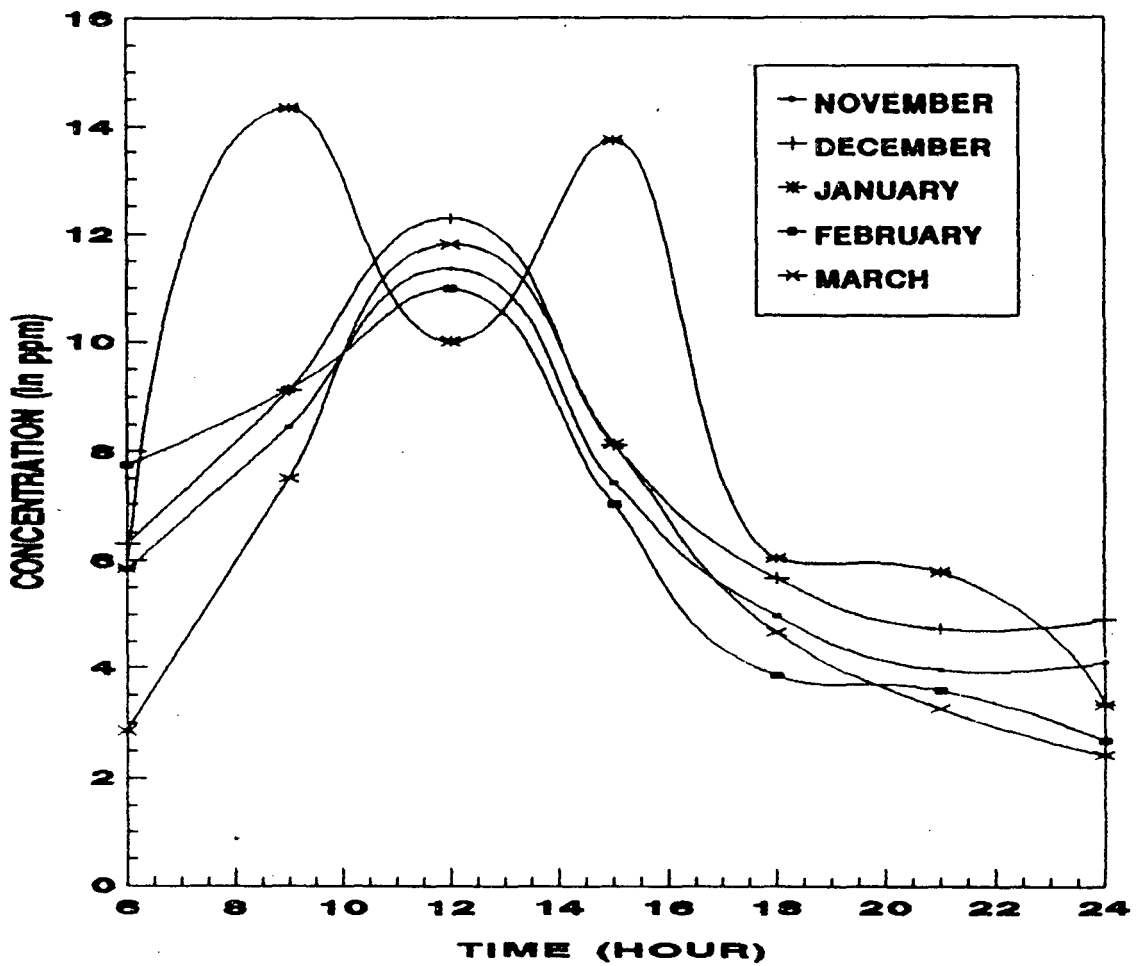


Figure 15. Diurnal variation in the ambient concentrations of NMVOC at JNU (November '94 - March '95; in ppm).

A comparative monthly variation in TVOC, methane and NMVOC levels at AIIMS, Bhikaji Cama and JNU during November to March (24 hour average) is given in Figure 16.

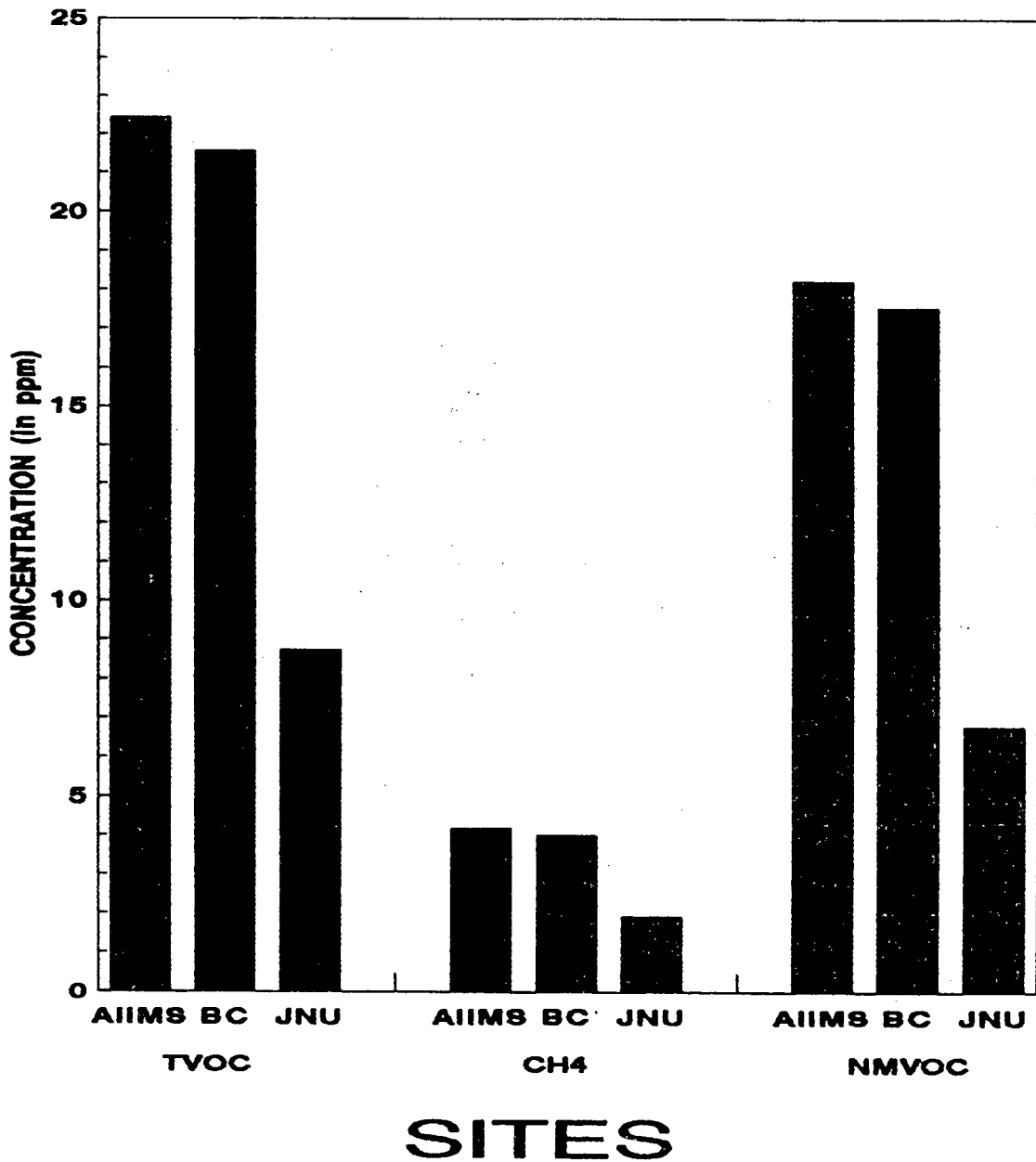


Figure 16. Comparison in the ambient levels of TVOC, methane and NMVOC among AIIMS, Bhikaji Cama and JNU during November to March (in ppm ; five months average).

Chapter IV
Estimation of Anthropogenic VOCs
Emissions for India

Emission Inventory :

Emission calculation

Identification of sources could be done by preparing inventory of various activities resulting in VOCs emission and quantification of individual activities as well as ascertaining their VOCs emission factor for each activity. In order to obtain the total quantities of VOC emission of a given activity quantified values of each activity is multiplied by the specific emission factors to provide a good estimates of VOCs emission of specific activity and summation of VOCs emission from various activities. It can provide a broad assessment of total anthropogenic VOC emission for any given region. In the case of certain activities there is no unanimity about the emission factors among different workers i.e., different emission factors have been reported by different workers. In such cases either the most likely emission factors was taken, or an average of the different emission factors for the same activity was taken for the calculation. The completeness of the inventory is given higher

priority than the accuracy of single emission factors. Thus default emission factors were introduced for emission sources in which factors were unknown.

So far no attempt has been made neither to prepare inventory of VOC emission sources nor for the assessment of VOCs emission in the country. In this study an attempt has been made to estimate the emission of VOCs from anthropogenic sources on the basis of the available data from literature using the appropriate emission factors worked out by earlier workers. VOCs emission sources are extremely wide and ever changing. Therefore making of a comprehensive and full proof list of anthropogenic sources of VOCs is a tedious and time consuming exercise and difficult to accomplish within the time frame of this study. However, efforts has been made to include all major sources of VOCs emission to get an idea of the order of magnitude of VOCs emission from the anthropogenic sources in the country. The estimate made in this study represent a broad first estimate of VOCs emission in India which may serve as a baseline information which could be improved and further refined with the availability of better quality data.

TABLE 26: An assessment of anthropogenic VOCs emission in India, 1993-94

Source Category	Emission (t/yr)	Reference/Remark
Traffic and mobile sources		
Passenger Cars	60000.6	(aa)
Scooters/mot.	426000.2	(aa)
Cycles (2 stroke)		
Mopeds	134000.6	(aa)
Diesel	172000.8	(aa)
Railways ^a	20790.0	(1)
Aircraft ^b	1367.019	(2)
Ships and boats ^c	6958.0	(3)
Stationary Combustion		
Small domestic stoves ^d	5423.137	(4)
Small commercial stoves ^e	29379.11	(5)
Large industrial use ^f	3044.952	(6)
Thermal power plant ^g (energy generation)	20466.266	(7)
Thermal power plant ^h (energy utilization)	40.068	(8)
Industrial Processes		
Plastic material production ⁱ	58.224	(9)
Chemical Industry ^j	423.036	(10)
Rubber and tyre production ^k	4053.2686	(11)
Food and drink industry ^l	21533.31871	(12)
Pulp/paper/ cellulose production ^m	3516.836	(13)
Petroleum industry ⁿ	22137.24875	(14)
Natural gas production and Distribution ^o	8633.945652	(15)
Solvents		
Solvent evaporation ^p	877490.70	(16)
Other sources		
Organic Waste ^q (including dung)	9933329.76	(17)
Tobacco smoking ^r	81.795	(18)
Agricultural straw burning ^s	292905.0	(19)
Wood combustion ^t	2872800.0	(20)
Total	14918428.19 t/yr	

Remark :

- (aa) Pundir and Kumar, 1993.
- (1) Brice and Derwent, 1978.
- (2) OECD, 1986; Mueller and Alfons, 1986.
- (3) Brice and Derwent, 1978.
- (4) Friedrich et al., 1987.
- (5) Friedrich et al., 1987.
- (6) UBA, 1981.

- (7) BMHGI, 1984.
- (8) BMHGI, 1984.
- (9) UBA, 1981.
- (10) UBA, 1981.
- (11) USEPA, 1980; Stockton and Stelling, 1987.
- (12) Nieman, 1982; USEPA, 1985; Swannel et al., 1991; Faith, 1977; Rentz et al., 1990.
- (13) Stockton and Stelling, 1987.
- (14) CONCAWE, 1986; CORINE, 1986.
- (15) CONCAWE, 1986.
- (16) CONCAWE, 1986.
- (17) US EPA, 1980, calculated after Orthofer, 1991.
- (18) Calculated as straw burning.
- (19) Calculated after Bocola and Cirilla, 1987; Brice and Derwent, 1978.
- (20) Calculated after Bocola and Cirilla, 1987.

- (^a) Indian Petroleum and Natural Gas Statistics, 1991-92.
- (^b) Air Transport Statistics, India (1992-93).
- (^c) as (^a)
- (^d) TEDDY, 1990-91.
- (^e) TEDDY, 1990-91 (derived figure).
- (^f) as (^a), TEDDY, 1990-91 (derived figure).
- (^g) as (^a) pp 64.
- (^h) --do--
- (ⁱ) Monthly production of selected industries of India, April, 1994.
- (^j) ---do---
- (^k) Statistical Abstract, 1990.
- (^l) Monthly production of selected industries of India, August 1994.
- (^m) as (^k)
- (ⁿ) UN Energy statistics yearbook, 1993.
- (^o) --do--
- (^p) Monthly production of selected industries of India, August 1994.
- (^q) Statistical Abstract, 1990, TEDDY, 1988.
- (^r) TEDDY, 1994-95.
- (^s) TEDDY, 1994-95 (derived data)
- (^t) Khoshoo, 1986.

Uncertainties

Estimation of VOCs emission on a country wide scale is bound to suffer from a large number of uncertainties. The

major handicaps are inadequate statistics about efficiency of fossil fuel use, performance characteristics of combustion devices and related activities and the absence of emission of VOC from different types of fossil fuel uses and other activities. One of the ways to overcome these difficulties is to make cross comparison of the factors given by different workers for the same activity or by computing the factors afresh after collecting field data for the given activity. In view of the time constraints, emission factors from literature have been used to arrive at a first cut estimates of annual VOCs emission from anthropogenic sources in India.

The anthropogenic total volatile organic compounds for India for the year 1993-94 was 14918428.18 t/y or 14.918 mt/yr to which about 9.933 mt (66.5 %) is contributed by organic waste (including dung) and 2.872 mt (19.25 %) by wood combustion. The percentage of share by different sectors are given below:

1. Traffic and mobile sources, 0.821117 mt/y (5.5%)
2. Stationary combustion, 58353,533 t/y (0.3%)
3. Industrial processes, 60355.87771 t (0.4%)
4. Solvents, 877490.70t (5.88%).
5. Others, 13.099 mt (87.8%).

The per capita emission of total anthropogenic

volatile organic compounds will be 17.66 kg/person/yr. And the amount of TVOC (anthropogenic) per km² per year will be 4.538t. A comparative data on total anthropogenic volatile organic compound emission, per capita emission and emission per sq km per yr is given in the following Table 27 (Molnar, 1990).

TABLE:27 Comparative anthropogenic TVOC emission, emission per capita and emission per sq km of India with other countries.

Sl.	Country	Total Anthro. Emission (t/y)	Emission per capita kg/year	Emission (t/km ² /y)
01	Albania	11499.2	3.8	0.4
02	Austria	276714.9	36.6	3.3
03	Belgium	390643.2	39.6	12.8
04	Bulgaria	244004.2	27.2	2.2
05	Czechoslovakia	370660.8	23.9	4.7
06	Denmark	219682.5	42.9	5.1
07	Finland	202876.2	41.3	0.6
08	France	2012670.5	36.4	3.7
09	German (both)	2891359.8	37.2	8.2
10	Greece	263972.0	26.5	2.0
11	Hungary	223276.8	21.1	2.4
12	Ireland	105420.0	29.7	1.5
13	Italy	1747221.0	30.5	5.8
14	Hixemburg	29997.6	81.7	11.6
15	Netherlands	607472.3	41.9	17.9
16	Norway	161947.0	38.9	0.5
17	Poland	1000585.6	26.8	3.2
18	Portugal	202367.0	20.4	2.2
19	Romania	451250.0	19.8	1.9
20	Spain	1059975.0	27.5	2.1
21	Sweden	329292.0	39.4	0.8
22	Switzerland	260114.4	40.2	6.3
23	United Kingdom	1084036.2	19.1	4.7
24	United States	2510000.0	105.2	2.7
25	Yugoslavia	143212.0	6.1	0.8
26	India	14918424.19	17.6	4.5

Chapter V : Discussion

Total volatile organic compounds in the ambient environment of Delhi at 14 sites during November' 94 to June' 95 varied between 3.889 - 42.579 ppm. The maximum TVOC concentration was recorded at South Extension (42.579 ppm) and the lower at Jawaharlal Nehru University (3.889 ppm).

The highest average concentration was at Darya Ganj (33.178 ppm) followed by Ashram (32.422, Pahar Ganj (28.245), Minto Bridge (26.972), South Extension (24.762), AIIMS (23.903), K.A. Marg (15.424), S.J. Flyover (14.504), Vijay Chowk (13.605), WWF (13.392) DLTA (11.985), Chanakya Puri (11.893) and Jawaharlal Nehru University (4.772 ppm). The TVOC level at Jawaharlal Nehru University was about seven times less as compared to the average concentration at Darya Ganj. High TVOC level at above first six sites can be attributed to high vehicular density and slow traffic movement. It is reported that during idling and deceleration, vehicle motor exhaust has high quantities of unburnt hydrocarbons i.e., 500-1000 ppm and 3000-12,000 ppm respectively as compared to acceleration and cruising (50-800 ppm and 200-800 ppm) respectively (Temple, 1971). At above first six sites, the motor vehicles are seen idling and in deceleration mode. It is

Plate 16. A scene of Ring Road traffic

Plate 17. Vehicle Showing Exhaust



Plate 18. Indraprast Thermal Power Plant Showing
Plumes

Plate 19. Plume of Rajghat Thermal Power Plant

18



19



likely that high quantities of VOCs are released into the atmosphere at these sites as compared to above second six sites (K.A. Marg to Chanakya Puri) where there is less traffic density, no congestion as well as vehicles remain at a high speed. Traffic density is time and site specific and on account of these two variables wide fluctuation of VOC level are expected.

The reasons for highest average concentration observed at Darya Ganj in addition to high vehicular traffic are : 1. It has very mixed traffic and 2. It is narrow and congested. The TVOC concentration at South Extension in some sampling day was high. This is due to the additional reasons given below. 1 Because shopping complex has developed on both sides of the road and therefore high traffic come to this place and they enter into both side complexes as well as the pedestrians. During this period the movement of the vehicle is very slow. 2. There are two crossings on both end of the market which are about 150-200m apart and acrossing the Ring Road. The vehicles enter into the complexes through these crossings and for this purpose they have to wait for long time at idling position.

At K.A. Marg the concentration of TVOC is not so high as one would expect because of rapid movement of

vehicles. S.J. Flyover being one of the busiest flyover of Delhi, with high traffic density has low TVOC level. This could be because of the fact that, 1. The site is chosen at high level where there is possibility of TVOC transfer by wind and secondly the vehicles remain at a high speed.

At JNU, low concentration of TVOC was observed this is because the site was not besides road and secondly the traffic density is very low and there is less human activity.

The rank order of 13 sites with respect to TVOC level is:

Darya Ganj > Ashram > Pahar Ganj > Minto Bridge > South Extension > AIIMS > K.A. Marg > S.J. Flyover > Vijay Chowk > WWF > DLTA > Chanakya Puri > JNU.

The ranking of site correlates well with the increasing order of human activities.

Monitoring of this period, November' 94 - June'95 is not sufficient and much longer time series measurements are needed to ascertain the trend of TVOC build up, unless longterm systematic TVOC monitoring is undertaken. However the study from 1989-1991 showed the variation of ozone between $20 \mu\text{g}/\text{m}^3$ - $243 \mu\text{g}/\text{m}^3$, which is very high (Ph.D thesis, Aggarwal,

1993). It is more likely that the ozone precursor level too increased indirectly (as it is reported that the build up of tropospheric ozone during the last two decades is largely on account of increased emission of TOPs such as VOCs including CH₄, NO_x and CO arising from increasing anthropogenic activities, Bojkov, 1984; 1986; Feister and warmbt, 1987; Liu et.al., 1980; logan, 1985; Penkett, 1984; Volz and Kley, 1988).

TVOC concentration fluctuates widely from season to season. It is observed that TVOC concentration is relatively higher in winter months as compared to spring and summer months. This is because during winter months atmosphere remains highly stable because of low light temperature high pressure, therefore the conditions (meteorological) are not conducive for O₃ build up (Shreffler and Evans, 1982; Bower et.al., 1989; Janach, 1988; Stephens, 1969). As a result the precursor level (TVOC) is likely to be high. But in summer, as the light and temperature are conducive for ozone formation, most of the VOCs emitted into the ambient environment is utilized for photochemical reaction. Therefore the TVOC level during summer months is low.

Diel fluctuation of each site is dependent upon traffic density, pattern and congestion. In high traffic areas

(AIIMS) the TVOC concentration peaks at 9 am because of regular high traffic density. By this time every body has to reach in their respective office. Therefore, the sites like AIIMS, Bhikaji Cama experience specific type of traffic density. As the day advances, the density of the traffic decreases, as well as the TVOC is utilized on photochemical reactions, leading to ozone formation. Therefore TVOC concentration decreases after 9 am upto late afternoon and as the traffic density increases towards evening, the TVOC level increases too except in January when the increase in TVOC level occurs towards late evening i.e., towards 9 pm. Towards night time in case of November the concentration of TVOC after 6 pm continuously build up. This is because during night, the automobile exhaust released into the atmosphere is used up and therefore build in TVOC level. However in December and January, there is decreasing trend towards night time. This could be explained as less traffic in Ring Road because of heavy winter (also observed in field condition while sampling). But towards February and March as the coldness decreases, the traffic density come to average and again the concentration of TVOC increases towards night.

However at JNU the pattern was different and the peak were obtained at 12 noon. This is due to the fact that, the site is inside a small forest where the source of TVOC is

basically natural (plants). The emission of VOC from plants is light temperature dependant (Yokouchi et.al., 1983; Tingey, et.al., 1979; 1980; Lamb et.al., 1985; Yokouchi and Ambe, 1984; Guenther, et.al., 1993; Lamb et.al., 1987; Robert et.al., 1993) and also photosynthetically active radiation (Guenther et.al., 1993). Therefore the emission increases as the day advances and peaks at noon. In case of JNU in the month of January two peaks (one at 9 am and other at 3 pm) were observed. There is no likely explanation to this for the behaviour of VOCs showing two peaks. However as the time did not permit to repeat the observation it is difficult to regard the behaviour of VOC obtain at JNU as a site specific characteristics. The high concentrations of TVOC were observed between 9 am to 3 pm. But thereafter it decreases because of the limiting nature of the meteorological factors. During night time the concentrations were low.

Methane levels in the ambient environment of Delhi at 14 sites during November' 94 to June' 95 varied between 0.998 - 8.974 ppm. The result showed a fluctuation of methane levels. The maximum methane concentration was recorded at Darya ganj (8.974 ppm) followed by other 11 sites to minimum at Jawaharlal Nehru University (0.998 ppm).

The highest average concentration was at Darya Ganj (6.133 ppm) followed by Ashram (5.835), Pahar Ganj (5.350), Minto Bridge (4.955), South Extension (4.453), AIIMS (4.445), K.A. Marg (2.888), WWF (2.536) S.J. Flyover (2.505), Vijay Chowk (2.442), DLTA (2.116), Chanakya Puri (2.082) and Jawaharlal Nehru University (1.152 ppm). The methane level at control site, Jawaharlal Nehru University therefore is more than 5 times lower than the Darya Ganj. High methane level at all first six sites are due to high vehicular traffic exhaust. It is reported that the exhaust gases of gasoline engine vehicle gives out 238 ppm of methane (Dimitriades et al., 1968). As at all first 6 sites, the density of motor vehicles are very high and emit high quantity of exhaust gases, it is likely that high quantities of methane would be obtained from those sites in ambient air as compared to second six sites where there is less traffic density, no congestion as well as vehicles remain at a high speed. All the sites of Delhi except JNU has crossed the global average concentration of methane (1.737 ppm, Khalil and Rasmussen, 1994)..

But this much high quantity of methane observed at Delhi atmosphere is not only because of vehicular traffic but also due to the following reasons.

1. There is no proper solid waste disposal (where the organic part of it emit methane). It is reported that

solid waste disposal sites emit methane (Hofler et al., 1986; Angrick, 1987; Bingemer and Crutzen, 1987) and one tonne of waste in landfills emit approximately 25-30 m³ of methane for 25 years of which 70% is in first 10 years (Vanni and Esposito, 1982). The solid waste disposal site of Delhi is given in Plate 20.

2. Here there is no proper management of sewers, where as a result of anerobic decomposition of organic matter high quantity of methane is produced. Some times the pressure becomes too high which could lead to powerfull blast as occured at connaught place area in April '95.
3. The sewage water treatment plants and a number of biogas plants from where also large quantity of methane is being released. Fugitive emission of natural gas in cooking, bottle filling and distribution.
4. The people used to burn the road side leaf litter after cleanning and on the process high quantity of methane is released. It is reported that methane is a major component released from biomass burnning (Crutzen et al., 1979; Westberg et al., 1981; Greenberg et al., 1984).
5. In addition there are large swampy areas in both sides of river Yamunna, large numbers of ditches, ponds and puddles which also contribute to methane emission. The swampy area besides Yamunna is given in Plate 21.

Plate 20. Solid waste disposal site near
Nizammudin

Plate 21. Swamps besides Yamunna



At JNU, low concentration of methane was observed this is because the site is a remote area and basically the traffic density is very low and less human activity.

The rank order of 13 sites with respect to methane level is:

Darya Ganj > Ashram > Pahar Ganj > Minto Bridge > South Extension > AIIMS > K.A. Marg > WWF > Vijay Chowk > S.J.Flyover > DLTA > Chanakya Puri > JNU.

Monitoring of this period, November' 94 - June'95 is not sufficient and much longer time series measurements are needed to ascertain the trend of methane build up, unless longterm systematic methane monitoring is undertaken. But rapid build up of methane occurs in the atmosphere in comparing to other VOCs as the atmospheric lifespan of methane is high and is about 16 years (Stern, 1986).

Methane concentration fluctuates widely from season to season. It is observed that methane concentration is relatively higher in winter months as compared to spring and summer months. This is because during winter months atmosphere remains highly stable because of low light, temperature and high pressure, therefore the conditions (meteorological) are

not conducive for O₃ build up (Shreffler and Evans, 1982; Bower et.al., 1989; Janach, 1988; Stephens, 1969). As a result the precussion level (methane). is likely to be high. But in summer, as the light and temperature are conducive for ozone formation, most of the VOCs emitted into the ambient environment is utilized for photochemical reaction. Therefore the methane level during summer months is low.

If we consider the concentrations of methane on diurnal variations we can observe remarkable dynamics. But the pattern of fluctuation vary from site to site with regard to vehicular traffic. In high traffic areas (AIIMS) the methane concentration peaks at 9 am because of regular high traffic density. As the day advances, the density of the traffic decreases, as well as methane is utilized on photochemical reactions, leading to ozone formation. Therefore methane concentration decreases after 9 am upto late afternoon and as the traffic density increases towards evening, the methane level increase too. After 6 pm continous build up of methane occurs. This is because during night, the automobile exhaust released into the atmosphere is not used up and therefore build in methane level.

The methane level observed at Delhi is very high and it has crossed the limits of available standard of USA, i.e.,

160 $\mu\text{g}/\text{m}^3$ (0.24ppm) both for primary and secondary standards in the ambient atmosphere. But report says that the methane in the urban areas ranges from 1.2 ppm to 15.0 ppm (SCDPH, 1967).

Non-methane volatile organic compound concentration in the ambient environment of Delhi at 14 sites during the same period varied between 2.891 - 35.312 ppm. The maximum TVOC concentration was recorded at South Extension (35.312 ppm) followed by other 11 sites to minimum at Jawaharlal Nehru University (2.891 ppm).

The highest average concentration was at Darya Ganj (27.043 ppm) followed by Ashram (26.588), Pahar Ganj (22.894), Minto Bridge (22.017), South Extension (19.565), AIIMS (19.457), K.A. Marg (12.536), S.J. Flyover (11.999), Vijay Chowk (11.158), WWF (10.856), Chanakya Puri (10.704), DLTA (9.895) and Jawaharlal Nehru University (3.614 ppm). The NMVOC level at control site, Jawaharlal Nehru University therefore is more than seven times lower than the Darya Ganj. High NMVOC level at above first six sites are due to high vehicular traffic density and slow movement as well as because of industrial activity, building construction, use of paints.

The reasons for highest average concentration observed at Darya Ganj in addition to high vehicular traffic

are : 1. It has a very mixed traffic, 2. Narrow and congested. However the NMVOC concentration at South-Extension during some days of sampling was high. This is due to 1. Because of market complex high traffic come to this place and they enter into the both side complexes. During the period the movement of the vehicle is very slow. 2. There are two crossings on both end of the market which are approximately 150-200m apart and crossing the Ring Road.

At Kamal Ataturk Marg near PM's House the concentration of NMVOC is not so high as one would expect because of rapid movement of vehicles. S.J. Flyover being one of the busiest flyover of Delhi, with high traffic density has low TVOC level. This could be because of the fact that, 1. The site is chosen at high level where there is possibility of NMVOC transfer by wind and secondly the vehicles remain at a high speed.

At JNU, low concentration of NMVOC was observed this is because the site was not besides road and secondly the traffic density is very low and less human activity.

The rank order of 13 sites with respect to NMVOC level is:

Darya Ganj > Ashram > Pahar Ganj > Minto Bridge > South Extension > AIIMS > K.A. Marg > S.J. Flyover > Vijay Chowk > WWF > Chanakya Puri > DLTA > JNU.

The ranking of site correlates well with the increasing order of human activities.

Monitoring of this period, November' 94 - June'95 is not sufficient and much longer time series measurements are needed to ascertain the trend of NMVOC build up. However the study from 1989-1991 showed the variation of ozone between 20 $\mu\text{g}/\text{m}^3$ - 243 $\mu\text{g}/\text{m}^3$, which is very high (Aggarwal, 1993). It is more likely that the precursor level too increased indirectly (as it is reported that the build up of tropospheric ozone during the last two decades is largely on account of increased emission of TOPs such as VOCs including CH_4 , NO_x and CO arising from increasing anthropogenic activities, Bojkov, 1984; 1986; Feister and warmbt, 1987; Liu et.al., 1980; logan, 1985; Penkett, 1984; Volz and Kley, 1988).

NMVOC concentration is relatively higher in winter months as compared to spring and summer months because during winter months atmosphere remains highly stable because of low light temperature high pressure, therefore the conditions (meteorological) are not conducive for O_3 build up (Shnoffer

and Evans, 1982; Bower et.al., 1989; Janach, 1988; Stepherns, 1969). As a result the precursressor level (NMVOC) is likely to be high. But in summer, as the light and temperature are conducive for ozone formation, most of the VOCs emitted into the ambient environment is utilized for photochemical reaction. Therefore the NMVOC level during summer months is low.

If we consider the concentrations of NMVOC on diurnal variations we can observe remarkable dynamics. In high traffic areas (AIIMS) the NMVOC concentration peaks at 9 am because of regular high traffic density. As the day advances, the density of the traffic decreases, as well as the NMVOC is utilized on photochemical reactions, leading to ozone formation. Therefore NMVOC concentration decreases after 9 am upto late afternoon and as the traffic density increases towards evening the NMVOC level increases too except in January when the increase in TVOC level occurs towards late evening i.e., towards 9 pm. Towards night time in case of November the concentration of NMVOC after 6 pm continuously build up. This is because during night, the automobile exhaust released into the atmosphere is not used up and therefore build in NMVOC level. However in December and January, there is decrease trend towards night time. This could be explained as less traffic in Ring Road because of heavy winter (also

observed in field condition while sampling). But towards February and March as the coldness decreases, the traffic density come to average and again the concentration of NMVOC increases towards night.

However at JNU the pattern was different and the peak were obtained at 12 noon. This is due to the fact that, 1. The site is inside a small forest where the source of NMVOC is basically natural (plants). The emission of NMVOC from plants is light temperature dependant (Yokouchi et.al., 1983; Tingey, et.al., 1979; 1980; Lamb et.al., 1985; Yokouchi and Ambe, 1984; Guenther, et.al., 1993; Lamb et.al., 1987; Robert et.al., 1993) and also photosynthetically active radiation (Guenther et.al., 1993). Therefore the emission increases as the day advances and peaks at noon. The high concentrations of NMVOC were observed between 9 am to 3 pm. But thereafter it decreases because of the limiting nature of the meteorological factors. During night time the concentrations were low.

SUMMARY AND CONCLUSIONS

Summary and Conclusions

The importance of volatile organic compounds in the ambient atmosphere is rapidly increasing. Studies on VOC are mainly from industrialised countries, but in developing countries including India, knowledge on VOC is altogether lacking. Latest studies in USA show, there is an increase in VOC levels in the atmosphere. In India, particularly at Delhi, recent studies show that, there is increase in ozone concentration in the ambient air. Therefore ozone precursors particularly VOC is expected to be high in the ambient environment of Delhi. The present study was undertaken from November 1994 to June 1995 to determine VOC levels in Delhi. Fourteen road sites in Delhi representing different traffic intensities were selected for determining the seasonal and diurnal variation in the VOC level in the ambient environment. The result of present study show:

1. The concentration of total volatile organic compounds (TVOC) in the ambient air at 13 sites varied between 3.889 - 42.579 ppm during the study period. The overall average of all sites worked out to be 19.620 ± 3.078 ppm. The maximum TVOC level was observed at South Extension (42.579 ppm) and the minimum at JNU (3.889 ppm).

2. The concentration of methane in the ambient air at different sites varied between 0.998 - 8.974 ppm during the period of study. The overall average concentration of all sites was 3.607 ± 0.787 ppm with maximum concentration being measured at Darya Ganj (8.974 ppm) and the minimum at JNU (0.998 ppm). Methane concentration in urban areas is high in general. Methane emission occur from a large number of sources within the city. The important sources are, fugitive emission of natural gas from cooking stoves; bottle filling and distribution, leakage of biogas from a number of plants, biomass burning (leaf litter), vehicular exhaust, choked sewers due to their bad management (recent explosion, in April 1995 in sewer drain in Connaught Place area indicate that, the city drains are an important source of methane), large number of landfilled sites for solid waste disposal, and swampy areas besides Yamunna.

3. The ambient level of non-methane volatile organic compound in Delhi at 13 sites and for the study period varied between 2.891 - 35.312 ppm. The overall average concentration of all sites was 16.025 ± 2.347 ppm. The maximum NMVOC was measured at South Extension (35.312 ppm) and the minimum at JNU (2.891 ppm).

4. Monthly average of TVOC in winter months (November-February) was between 19.39 ± 8.63 ppm to 25.35 ± 12.75 ppm. The maximum concentration was in the month of November. The monthly average in spring and summer (March-June) varied between 15.60 ± 6.83 ppm to 17.18 ± 7.95 ppm. At all sites the concentration of TVOC was found to be relatively higher in winter months as compared to spring and summer periods.

5. Monthly average value of methane in winter months (November-February) varied between 3.575 ± 1.393 ppm to 4.771 ± 2.093 ppm. The maximum concentration was in the month of November. The monthly average in spring and summer months (March-June) varied between 2.546 ± 1.307 ppm to 2.905 ± 1.391 ppm. The concentration of methane is relatively higher in winter months as compared to spring and summer months.

6. The monthly average NMVOC concentration in winter months (November-February) varied between 15.31 ± 7.39 ppm to 20.58 ± 10.70 ppm. The maximum concentration was in the month of November. The monthly average for spring and summer months (March-June) varied between 13.07 ± 5.55 ppm to 14.92 ± 6.091 ppm. The NMVOC concentration was

relatively high during winter as compared to spring and summer periods.

7. The rank order of TVOC at 13 sites based on the observations over seven months is as follows:

Darya Ganj > Ashram > Pahar Ganj > Minto Bridge > South Extension > AIIMS > KA Marg > S.J. Flyover > Vijay Chowk > WWF > DLTA > Chanakya Puri > JNU.

8. The rank order of methane at 13 sites based on the observations over seven months is as follows:

Darya Ganj > Ashram > Pahar Ganj > Minto Bridge > South Extension > AIIMS > KA Marg > WWF > Vijay Chowk > S.J.Flyover > DLTA > Chanakya Puri > JNU.

9. The rank order of NMVOC at 13 sites based on the observations over seven months is as follows:

Darya Ganj > Ashram > Pahar Ganj > Minto Bridge > South Extension > AIIMS > KA Marg > S.J. Flyover > Vijay Chowk > WWF > Chanakya Puri > DLTA > JNU.

10. The methane to non-methane ratio at low, medium and high traffic sites was 0.331, 0.234 and 0.229 respectively.
11. The concentration of C₂-C₉ saturated hydrocarbons were 6.9 and 13.3 ppm at JNU and Ashram respectively. The aromatics (toluene) was not detected at JNU but at Ashram the value of toluene was 0.2 ppm.
12. Invariably through out the study period VOC (TVOC, methane and NMVOC) exhibited a distinct morning peak (9 am) at AIIMS and Bhikaji Cama but for most part of the day the concentration remained low. A distinct peak was observed at JNU during noon (12 O'clock) except in the month of January where 2 peaks were observed one at 9 am and the other at 3 pm.
13. Human activities basically traffic density, vehicle speed, traffic pattern are the major source of VOC emission into the urban environment.
14. Estimation of VOC emission from anthropogenic sources, for India, calculated on the basis of emission factors for different activities given in literature, amounts to about 14.9 million tonnes of VOC per year (1993-94) on a countrywide scale. Organic wastes including cattle dung

are the major contributor to the VOC loading of the ambient atmosphere.

REFERENCES

References

- Ahlberg, M., Berghem, L., Nordgerg, G., Persson, S.A., Rudding, L. and Steen, B. (1983). Chemical and biological characterization of emissions from coal and oil-fired power plants. *Envir. Hlth Persp.*, **47**, 85.
- Aikin, A.C., Herman, J.R., Maier, F.J. and McQuillan, C.J. (1982). Atmospheric chemistry of ethane and ethylene. *J. Geophy. Res.*, **87**, C4, 3105-3118.
- Air Transport Statistics, India (1992-93). Air Transport Directorate, Directorate General of Civil Aviation, New Delhi, March 1994.
- Albert, R.E. (1978). The Carcinogen Assessment Group's Preliminary Report on Ethelene Dichloride, Perchloroethylene and Benzene. Prepared for the U.S. Environmental Protection Agency.
- Alfheim, I., Bergstrom, J.G.T., Jenssen, D. and Moller, M. (1983). Mutagenicity in emissions from coal and oil-fired boilers. *Envir. Hlth Persp.*, **47**, 177.
- Altshuller, A.P. (1980). Lifetime of organic molecules in the troposphere and lower stratosphere. *Adv. Envir. Sci. Technol.*, **10**, 181-219.
- Altshuller, A.P. and Bufalini, J.J. (1971). Photochemical aspects of air pollution: A review. *Environ. Sci. Technol.*, **5**, 36-64
- Anastasi, C., Hopkinson, L. and Simpson, V.J. (1991). Natural hydrocarbon emissions in the U.K. *Atmos. Environ.*, **25A**, 7, 1403-1408.
- Angrick, M. (1987). *Mull and Abfall* 19: 142.
- Atkinson, R., Aschmann, S.M., Winer, A.M. (1987). *J. Atmos. Chem.*, **5**, 91.
- Atkinson, R., Llyod, A.C. (1984). *J. Phys. Chem. Ref. Data* 13: 315.

- Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F.Jr., Kerr, J.A. and Troe, J. (1988). Evaluated kinetic and photochemical data for atmospheric chemistry. Supplement III. *J. Phys. Chem. Ref. Data.*, 18, 881-1097.
- Atkinson, R. and Lloyd, A.C. (1984). Evaluation of kinetic and mechanistic data for modeling of photochemical smog. *J. Phys. Chem. Ref. Data.*, 13, 315-344.
- Banerjee, S.P. (1980). Methane emission problems in Indian coal mines-some case studies. In Second International Mine Ventilation Congress, Mackay School of Mines, Reno, Nevada, pp. 15-21.
- Banerjee, B.D., Singh, A.K., Kispotta, J. and Dhar, B.D. (1994). Trend of methane emission to the atmosphere from Indian coal mining. *Atmos. Environ.*, 28, 7, 1351-1352.
- Benkovitz, C.M. (1982). *Atmos. Environ.*, 16, 1551.
- Berces, T., Demeter, A., Haszpra, L., Molnar, A., Nyitrai, L., Szilagyi, I. and Turanyi, T. (1988). Local air quality studies, Final report, Nov. 1988.
- Bertard, C., Bruyet, B. and Gunther, J. (1970). Determination of desorbable gas concentration of coal (Direct method). *Int. J. Rock Mech. Min. Sci.*, 7, 43-65.
- Beskrony, N.S. and Lobkov, V.A. (1977). Relationships of spreading of hydrocarbon gases in modern hydrothermal systems of Kamchatka. In: Geothermal process in the regions of tectonic-magmatic activity. Nauka; Moscow.
- Bingemer, H.G., Crutzen, P.J. (1987). *J. Geophys. Res.*, D92, 2181.
- BMHGI (1984). Energiebericht 1984 (Austrian energy report 1984). Federal Ministry of Economic Affairs, Vienna.
- Bocola, W. and Cirillo, M.C. (1987). Air pollutant emissions by combustion processes in Italy. ENEA report No. ENEA-RT/STUDI/87/4.
- Bojkov, R. (1984). Tropospheric ozone, its changes and possible radiative effects, *WMO Spec. Environ. Rep.*, 16, WMO Geneva.
- Bondarev, V.B. and Porshnev, N.V. (1980). *Dokl. AN SSSR*, 252, 455.

- Bower, J.S., Broughton, G.F.J., Dando, M.T., Stevenson, K.J., Lampert, J.E., Sweeney, B.P., Parker, V.J., Driver, G.S., Clark, A.G., Waddon, C.J., Wood, A.J. and Williams, M.L. (1989). Surface ozone concentration in the UK in 1987-1988, *Atmos. Environ.*, **23**, 2003-2016.
- Brasseur, G. and Hitchman, M.H. (1988). Stratospheric response to trace gas perturbation : Changes in ozone and temperature distribution. *Science*, **240**, 634.
- Bressan, R.A., Le Cureux, L., Wilson, L.G. and Filner, P. (1979). Emission of ethelene and ethane by leaf tissue exposed to injurious concentrations of sulfur dioxide or bisulphite ion. *Plant Physiol.*, **63**, 929-930.
- Brewer, D.A., Augustsson, T.R. and Levine, J.S. (1983). The photochemistry of anthropogenic nonmethane hydrocarbons in the troposphere. *J. Geophys. Res.*, **88**, C11, 6683-6695.
- Brice, K.A. and Derwent R.G. (1978). Emission inventory for hydrocarbons in the United Kingdom., *Atmos. Environ.*, **12**, 2045- 2054.
- Brief, R.S., Lynch, J., Bernath T. and Scala R.A. (1980). Benzene in the workplace. *Am. Ind. Hyg. Ass. J.*, **41**, 616-623.
- Broddin, G., Cautreels, W., Van Cauwenberghe, K. (1980). *Atmos. Environ.*, **14**, 895.
- Bruckmann, P., Kersten, W., Funcke, W., Balfanz, E., Konig, J., Theisen, J., Ball, M. and Papke, O. (1988). The occurrence of chlorinated and other organic trace compounds in urban air. *Chemosphere*, **17**, 2363-2380.
- Bucher, J.B. (1981). SO₂ - induced ethelene evolution in foresttree foliage and it's potential use as strss-indicator. *Eur. J. For. Pathol.*, **11**, 369-373.
- Bufler, U. and Wegmann, K. (1991). Diurnal variation of monoterpene concentrations in open top chambers in the Welzheim forest air, F.R.G. *Atmos. Environ.*, **25A**, **2**, 251-256.
- Carter, W.P.L. and Atkinson, R. (1987). An experimental study of incremental hydrocarbon reactivity. *Envir. Sci. Technol.*, **21**, 670-679.
- Census, (1991) Oxford School Atlas, 1994.

- Chameides, W.L., Lindsay, R.W., Richardson, J. and Kiang, C.S. (1988). The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science*, **241**, 1473-1475.
- Chameides, W.L. and Cicerone, R.J. (1978). Effect of nonmethane hydrocarbons in the atmosphere. *J. Geophys. Res.*, **83**, C2,947- 8952.
- Chevrier, N. Chung, Y.S and Sarhan, F. (1990). Oxidative damages and repair in *Euglena gracilis* exposed to O₃. II. Membrane permeability and uptake of metabolites. *Plant and Cell Physiol.*, **31**(7), 987-992.
- Churkin, S.P., Barakov, T.V., Stepen, R.A., Chernyaeva, G.N. (1976). *Khim. Prirodn. Soedin. N.2*: 260.
- Cicerone, R.J., Walters, S. and Liu, S.C. (1983). *J. Geophys.Res.*, **C88**, 3647.
- Cicerone, R.J. and Oremland, R.S. (1988). Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles.*, **2**, 299-327.
- Clark, A.I., McIntyre, A. F., Perry, R. and Lester, J.N. (1984). Monitoring and assessment of ambient atmospheric concentrations of aromatic and halogenated hydrocarbons at urban, rural and motorway locations. *Envir. Pollut.*, **7**, 141-148.
- CONCAWE (1986). Volatile organic compound emissions: an inventory for Western Europe. Report No 2/86, Den Haag.
- Colbeck, I. and Harrison, R.M.(1985). The concentrations of specific C₂-C₆ hydrocarbons in the air of NW England. *Atmos. Environ.*, **19**, 1899-1904.
- CORINE Emission Inventory Project (1986). Final Report No. 6614(85)02 11 July 1986, CITEPA, Paris.
- Crutzen, P. (1979). The role of NO and NO₂ in the chemistry of the troposphere and stratosphere. *Annu. Rev. Earth planet. Sci.*, **7**, 443-472.
- Crutzen, P.J., Heidt, L.E., Krasnec, J.P., Pollock, W.H. and Seiler, W. (1979). *Nature*, **282** : 253.

- Cuffe, S.T., Gerstle, R.W., Orning, A.A. and Schwartz, C.H. (1964). Air pollutant emissions from coal-fired power plants. *J. Air Pollut. Control Ass.*, **14**, 353.
- Darnall, K.R., Lloyd, A.C., Winer, A.M. and Pitts, J.N. Jr. (1976). Reactivity scale for atmospheric hydrocarbons based on reaction with hydroxyl radical. *Envir. Sci. Technol.*, **10**, 692-696.
- Demerjian, K.L., Kerr, J.A. and Calvert, J.G. (1974). The mechanism of photochemical smog formation. *Adv. Environ. Sci. Technol.*, **4**, 1-262.
- Dimitriades, B (1981). *J. Air Pollut. Contr. Assoc.*, **31**, 229.
- Derwent, R.G. and Hov, Q. (1979). Computer modelling studies of photochemical air pollution formation in North West Europe. AERE-R9434.
- Derwent, R.G. and Jenkin, M.E. (1990). Hydrocarbon involvement in photochemical ozone formation in Europe. United Kingdom Atomic Energy Authority, Harwell Modelling and assessments group, AEA Environment and Energy, Harwell Laboratory report AERE R 13736.
- Derwent, R.G. and Hov, O. (1979). Computer modelling studies of photochemical air pollution formation in North-west Europe. United Kingdom Atomic Energy Authority, Harwell Environmental and Medical Sciences Division, Harwell Laboratory report AERE HL 79/3237 (C 10).
- Dhar, B.B., Banerjee, B.D. and Singh A.K. (1991). Estimation of methane emission to the atmosphere from Indian coal mining. In *National Symp. on Environment and Development - A Scientific Approach*, 19-20 Dec., Meerut University, Meerut, UP, India.
- DSH (1992). Delhi Statistical Handbook, 1992.
- Duce, R.A., Mohnen, V.A., Zimmerman, P.R., Grosjean, D., Cautreels, W., Chatfield, R., Jaenicke, R., Ogren, J.A., Pellizzari, E.D. and Wallace, G.T. (1983). Organic material in the global troposphere. *Rev. Geophys. Space, Phys.*, **21**, 921-952.
- Ehhalt, D.H (1974). *Tellus*, **26**, 58.

- Engelman, R. (1994). Stabilizing the atmosphere. Population, consumption and Greenhouse Gases. Population and Environmental Programme, Population Action International.
- EPA (1986). A review of NMOC, NOx and NMOC/NOx ratios measured in 1984 and 1985. EPA-450/4-86-015.
- Faith, W.L. (1977). Agriculture and agriculture-products processing. In Air Pollution Vol. IV (ed. Stern, A.C.) 3rd edition Academic Press, New York, 645-684.
- FAO Year Book, (1991). *Fishery Statistics Commodities*, Vol. 73, 1991.
- Federal Register (1977). TSCA Interagency Testing Committee, Council on Environmental Quality, Part IV, Vol., 42, No., 197, Wednesday, October 12.
- Federal Register (1987), 52, 45060.
- Feister, U. and Warmbt, W.J. (1987). Long term measurement of surface ozone in German Democratic Republic. *J. Atmos. Chem.*, 5, 1-21.
- Field, R.A., Goldstone, M.E., Lester, J.N. and Perry, R. (1992). The sources and behaviour of tropospheric anthropogenic volatile hydrocarbons. *Atmos. Environ.*, 26A, 16, 2983-2996.
- Fishbein, L. (1979a), *STOTEN* 11:113.
- Fishbein, L. (1979b), *STOTTEN* 11;163.
- Fishbein, L. (1984). An overview of environmental and toxicological aspects of aromatic hydrocarbons. 1. Benzene. *Sci. Total Envir.*, 40, 189-218.
- Fishman, J. and Crutzen, P.J. (1978). The origin of ozone in the troposphere. *Nature*, 274, 855-858.
- Friedrich, R., Obermeier, A. and Voss A. (1987). Emissionskataster für fluchtige organische Verbindungen (Emission inventory for volatile organic compounds). Kernforschungszentrum Karlsruhe. Report No. KfK-PEF 22, Karlsruhe.
- Garcia, J.P., Beyne-Masclet, S., Mouvier, G. and Masclet, P. (1992). Emissions of VOCs by coal-fired power stations. *Atmos. Environ.*, 26A, 9, 1589-1597.

- Gotz, H. (1979). *Gas, Wasser, Warne* 33: 195.
- Greenberg, J.P., Zimmerman, P.R., Heidt, L. and Pollock, W. (1984). *J. Geophys. Res.*, D89 : 1350.
- Greenberg, M.M. and Parker, J.C. (1979). Health Assessment Document for Tetrachloroethylene. U.S. Environmental Protection Agency, External Review Document No. 1, Research Triangle Park, North Carolina.
- Greenfelt, P., Saltbones, J. and Schjoldger, J. (1988). Oxidant data collection in OECD Europe 1985-87. Report on ozone, nitrogen dioxide and peroxyacetyl nitrate. Norwegian Institute for Air Research. Report No. NILU-31, Lillestrom.
- Grosjean, D. and Fung, K. (1984). Hydrocarbon and carbonyls in Los Angeles air. *J. Air Pollut. Contr. Assoc.* 34, 537-543.
- Guenther, A. Monson, R. and Fall, R. (1991). Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. *J. Geophys. Res.*, 96D, 10,799-10,808.
- Guenther, A., Zimmerman, P., Harley, P., Monson, R. and Fall, R. (1993). Isoprene and monoterpene emission rate variability: model evaluation and sensitivity analysis. *J. Geophys. Res.*, 98D, 12, 609-12, 617.
- Gwynne, M.D. (1987). The threat from chemical pollution. In *The ozone layer, UNEP/GEMS Environment Library No 2.*
- Hampton, C.V., Pierson, W.R., Harvey, T.M., Updegrove, W.S., Morana, R.S. (1982). *Envir. Sci. Technol.*, 16: 287.
- Handbook of agriculture (1987). IARI, New delhi.
- Hansen, M., Frieswyck, T., Glover, J. and Kelly, J. (1992). The eastwide forest inventory database: user's manual. Gen. tech. rep. NC-151., U. S. Dept. Agriculture, Forest Service. St. Paul MN, pp-48.
- Hanst, P.L., Spence, J.W. and Edney, E.O. (1980). Carbon monoxide production in photoxidation of organic molecules in the air. *Atmos. Environ.*, 14, 1077-1088.

- Harborne, J. (1991). Recent advances in the ecological chemistry of plant terpenoids. In *Ecological Chemistry and Biochemistry of Plant Terpenoids* (edited by Harborne J. and Tomas-Barberan F.). Clarendon Press, Oxford.
- Hasegan, et al., (1984). *J. Tox. Env. Health.* 14 : 621.
- Hester, N.E. and Meyer, R.A. (1979). A sensitive technique for measurement of benzene and alkylbenzenes in Air, *Envir.Sci. Technol.*, 13, 107-109.
- Hofler, F., Schneider, J., Mockel, H.J. (1986). *Fresenius Z. Anal. Chem.*, 325 : 365.
- Hough, A.M. and Derwent, R.G. (1987). Computer modelling studies of the distribution of photochemical ozone production between different hydrocarbons. *Atmos. Environ.*, 21, 2015-2033.
- Hov, O., Schjoldager, J. and Wathney, B.M. (1983). Measurement and modelling of the concentrations of terpenes in coniferous forest air. *J. Geophys. Res.*, 88D, 10,679-10,688.
- Hutchinson, S.A. (1971). Biological activity of volatile fungal metabolites. *Trans. Br. mycol. soc.*, 57, 185-200.
- Hutchinson, S.A. (1973) Biological activity of volatile fungal metabolites. *Ann. Rev. Phytopath.*, 11, 223-246.
- Hutchinson, S.A. and Cowan, M.E. (1972). Identification and biological effects of volatile metabolites from cultures of *Trichoderma harzianum*. *Trans. Brit. mycol. soc.*, 59, 71-73.
- IARC. (1982). Chemicals, Industrial Processes and Industries Associated with Cancer Int. Agency. Research on Cancer, Lyons France Suppl 4, 292.
- Indian Petroleum and Natural Gas Statistics, 1991-92. Economics and statistics division, Ministry of Petroleum and Natural Gas, Govt. of India, New delhi, 54-55.
- Isaken, I.S.A. and Hov, O. (1987). Calculation of trends of tropospheric concentration of ozone, OH, CO, methane and NOx. *Tellus*, 39B, 271-285.
- Isidorov, V.A. (1990). Organic Chemistry of the Earth's Atmosphere. Springer.

- Isidorov, V.A., Zenkevich, I.G., Ioffe, B.V. (1982). *Dokl. AN SSSR*, 263: 893.
- Isidorov, V.A., Zenkevich, I.G., Ioffe, B.V. (1985). Volatile organic compounds in the atmosphere of forest. *Atmos. Environ.*, 19, 1-8.
- Jack Faucett Associates. (1986). *Methanol Prices During Transition* (USEPA, sept. 1986).
- Janach, W.E. (1988). Surface ozone: trend, details, seasonal variations, and interpretations. *J. Geophys. Res.*, 94, 289-295.
- Jones, B.M.R. (1988). The measurement of ambient hydrocarbon concentrations in the atmosphere at Harwell during the period April 1986 to March 1987. AERE-R13174.
- Kashmiura, H., Suyama, Y., Saiki, Y., Yamamoto, A., Himi, Y. (1983). *J. Jap. Soc. Air pollut.*, 18: 432.
- Kasting, J.F. and Singh, H.B. (1986). Non-methane hydrocarbons in the troposphere: impact on the odd hydrogen and odd nitrogen chemistry. *J. Geophys. Res.*, 91, D12, 13239-13256.
- Khalil, M.A.K. and Rasmussen, R.A. (1994). Global methane record derived from six globally distributed locations. *Trend'93, Acompendium of data on global change, CIAC-65, WDC*, pp 268-272.
- Khoshoo, T.N. (1986). Requirement of wood, woodland and revegetation. In Presidential address, Environmental priorities in India and sustainable development, 73rd session, Jan. 3-7.
- Kjaergaard, S.K., Molhave, L. and Pedersen, O.F. (1991). Human reactions to a mixture of indoor air volatile organic compounds. *Atmos. Environ.*, 25A, 8, 1417-1426.
- Lamb, B., Guenther, A., Gay, D. and Westberg, H. (1987). A national inventory of biogenic hydrocarbon emissions. *Atmos. Environ.*, 21, 1695-1705.
- Lamb, B., Westberg, H., Allwine, G. and Quarles, T. (1985). Biogenic hydrocarbon emissions from deciduous and coniferous trees in the U.S. *J. Geophys. Res.*, 90, 2380-2390.

- Lamb, S.I., Petrowski, C., Kaplan, I.R. and Simoneit, B.R.T. (1980). Organic compounds in the urban atmosphere: a review of distribution, collection and analysis. *J. Air Pollut. Control Ass.*, 30, 1098-1115.
- Lefon, A.S., Shadwick, D.S. and Mohenen, V.A. (1990) Characterization of ozone concentration at select set of high-elevation sites in the eastern United States. *Environ. Pollut.*, 67, 147-148.
- Littman, F.E., Grisson, R.W. and Klein, O. (1977). Regional air pollution study point source emission inventory, EPA report 600/4-77-014, USEPA, Research Triangle park, NC.
- Liu, S.C., Kley, D., MacFarland, M., Mahlman, J.D. and Levy, II. H. (1980). On the origin of tropospheric ozone. *J. Geophys. Res.*, 85, 7546-7552.
- Logan, J.A. (1985). Tropospheric ozone : Seasonal behaviour, trend and anthropogenic influences. *J. Geophys. Res.*, 90, 10482-10483.
- Lonneman, W.A., Kopczynski, S. L., Darley, P.E. and Sutterfield, F.D. (1974) Hydrocarbon composition of urban pollution. *Envir. Sci. Technol.*, 8, 229-236.
- Loveland, T., Merchant, J., Ohlen, D. and Brown, J. (1991). Development of a land-cover characteristics database for the coterminous U.S. *Photogrametric Engng Rem. Sens.*, 57, 1453-1463.
- Lubkert, B. and De Tilly, S. (1989). The OECD-MAP emission inventory for SO₂, NOx and VOC in Western Europe. *Atmos. Environ.*, 23, 3-15.
- MacDonald, R.C. and Fall, R. (1993). Detection of substantial emissions of methanol from plants to the Atmosphere. *Atmos. Environ*, 27A, 11, 1709-1713.
- McIven, M. and Phillips, L. (1975) Chemistry of the Atmosphere.
- Merkhinin, E.K. (1985). *Volcanism. Nedra, Moscow.*
- Mayer, A., Muller, and Sembdner, G. (1987). Air pollution and plant hormones. *Biochem. Physiol. Pflanzen.*, 182, 1-21.
- Mayrsohn, H. Kuramoto, M., Sothern, R.D. and Mano, S.H. (1977). Source Reconciliation of atmospheric hydrocarbons 1974. *Atmos. Environ.*, 11, 189-192.

- Menyailov, I.A., Nikitina, L.P. and Shapar, V.N. (1986).
Vulkanol. Seismol. No 4 : 43.
- Mitra, I and C.K. Varshney. (1993). Hydrocarbon emission from
cucurbit leaves under SO₂ stress. Proceedings of the 80th
Indian Science Congress.
- MOBILE 4 (1986). Mobile source emissions model (1986). USEPA.
- Molhave, L., Bach, B. and Pedersen, O.F. (1986). Human
reaction to low concentrations of volatile organic
compounds. *Envir. Int.*, 12, 167-175.
- Molnar, A. (1990). Estimation of volatile organic compounds
(VOC) emissions for Hungary. *Atmos. Environ.*, 24A, 11,
2855- 2860.
- Monthly Production of selected industries of India, April,
1994, Vol. XXVII, No. 4, Computer Center, Deptt. of
Statistic, Ministry of Planning and Programme
Implementation, Govt. of India, New Delhi.
- Monthly Production of selected industries of India, August,
1994, Computer Center, Deptt. of Statistic, Ministry of
Planning and Programme Implementation, Govt. of India,
New Delhi.
- Mueller, K.J. and Alfons, G. (1986). Schadstoffemissionen des
gewerblichen Flugverkehrs in Osterreich (pollutant
emissions of commercial air traffic in Austria).
Technical University Vienna, Institute of Stream and Gas
Turbines, Communication Series. Report No. 12/1986,
Vienna.
- NAS (1978). Chloroform, Carbon Tetrachloride and Other
Halomethanes: An Environmental Assessment. National
Academy of Sciences, Washington, D.C.
- Nelson, P.F. and Quigley, S.M. (1982). Non-methane
hydrocarbons in the atmosphere of Sydney, Australia.
Envir. Sci. Technol., 16, 650-655.
- Nelson, F., Quigley, S.M. and Smith, M.Y. (1983). Sources of
atmospheric hydrocarbons in sydney: a quantitative
determination using a source reconciliation technique.
Atmos. Environ., 17, 439-449.

- Nieman, W. (1982). Air and Water emissions from bakeries, Part 1: air emissions during backing of bread and rusk. Published by TNO (IGMB), Netherlands, Report No. 82-944.
- Niki, H., Daby, E.E. and Weinstock, B. (1972). Mechanisms of smog reactions. *Adv. Chem. Ser.*, 113, 116-176.
- NTP (1985). Technical Report on the Toxicology and Carcinogenicity. Studies of Dichloromethane, NTP 306, RTP, NC 94.
- OECD (1986). Control of major air pollutants - a status report. Report No. OECD-ENV/AIR/86.3, Paris.
- Orthofer, R. (1991). Abschätzung der Methan-Emissionen in Österreich (Estimation of methane emissions in Austria). Austrian Research Centre Seibersdorf. Report No. OEFZS-A-1965, Seibersdorf.
- Padgett, J. (1980). List of Chemicals Assessed by Weight of Carcinogenic Evidence. Memorandum from Joseph Padgett, Office of Air Quality Planning and Standards, U.S. EPA, Research Triangle Park, North Carolina.
- Peake, E. and Fong, B.D. (1990). Ozone concentrations at a remote mountain site and two regional locations in Southwestern Alberta. *Atmos. Environ.*, 24, 475-480.
- Peiser, G.D. and Shang, F.Y. (1979). Ethylene and ethane production from sulfur dioxide injured plants. *Plant Physiol.*, 63, 142-145.
- Penkett, S.A. (1988). Indication and causes of ozone increases in the troposphere. In : F.S. Rowland and I.S.A. Isaken (Eds.) *The Changing Atmosphere*, John Wiley and Sons, New York. 91-103.
- Ph.D. Thesis, Maneesha Aggarwal (1993). Characterization of ozone levels in Delhi and its phytotoxic effects, School of Environmental Sciences, JNU, New Delhi.
- Pundir, B.P. and Kumar, D. (1993). Vehicular emissions and its control -current and future trends. *J. Electrochem Soc. India*, vol 42-1, 25-34.
- Puxbaum, H. and Lanzerstorfer, Ch. (1986). Flüchtige Kohlenwasserstoffe im Raum Wien. Abteilung für Umweltanalytik, Inst. für Analytische Chemie, TU Wien. Auftrag nr. MA 22-2081/86.

- Rasmussen, R.A. (1972). What do the hydrocarbons from trees contribute to air pollution. *J. Air Pollut. Contr. Assoc.*, 22, 537-543.
- Rentz, O., Jourdan, M., Roll, C. and Schneider, C. (1990). Emissions of VOCs from stationary sources and possibilities for their control. Institute of Industrial Production, University of Karlsruhe, Germany, Report No. OBA 91-010.
- Robert, C. M. and Fall, R. (1993). Detection of substantial emissions of methanol from plants to the atmosphere. *Atmos. Environ.*, 27A, 11, 1709-1713.
- Robinson, E. and Robbins, R. (1969) *Source, Abundance and Fate of Gaseous Atmospheric Pollutants Supplement*. Stanford Research Institute, Menlo Park, CA.
- Rudolph, J., Khedim, A. and Wagendbach, D. (1989). The variation of light nonmethane hydrocarbons in the Antarctic troposphere. *J. Geophys. Res.*, 94, D10. 13039-13044.
- Rutten, G.A., Burtner, C.W.J., Visser, H. and Rijks, J.A. (1988) The determination of aldehydes in the exhaust gases of LPG fuelled engines. *Chromatographia*, 26, 274-280.
- Sanadze, J. A. (1957). Emissions of organic matters by leaves of *Robinia pseudacia* L. *Soobsh. Acad. Nauk. GSSR* 19, 83.
- Sass, R.L. (1995). Science feature: Mitigation of methane emissions from irrigated rice agriculture. *IGAC, News letter*, Issue-1, June-1995.
- SCDPH (State of California Department of Public Health, Air and Industrial Hygiene lab), (1967). Ranges of hydrocarbon values expected in urban air masses. Berkeley Recommended Method (tentative), No. 9A, July 1967.
- Seiler, W. (1982). The cycle of CH₄ in the troposphere. In: AMS-AGU-NASA Conf. Williamsburg, Va. May 25-26.
- Sexton, K. and Westberg, H. (1984). Nonmethane hydrocarbon composition of urban and rural atmospheres. *Atmos. Environ.*, 18, 1125-1132.

- Sheeton, J.W. (1981). Catalytically assisted combustion in residential wood fueled heating appliances, Proceedings of USEPA, New Orleans Conf. wood combst. Environ. Assessment, Air pollution Control Assoc., Pennsylvania.
- Sheppard, J.C., Westberg, H., Hopper, J.F., Ganesan, K. and Zimmerman, P. (1982). *J. Geophys. Res.*, C87, 1305.
- Shih, C.C. and Takata, A.M. (1981). Emissions assessment of conventional stationary combustion system, EPA report 600/57-81-003, USEPA, Research Triangle Park, NC.
- Shreffler, J.H. and Evans, R.B. (1982). The surface ozone record from the regional air pollution study, 1975-1976. *Atmos. Environ.*, 16, 1311-1321.
- Singh, H.B. and Hanst, P.L. (1981). Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides. *Geophys. Res. Lett.*, 8, 941-944.
- Singh, H.B., Salas, L.J., Smith, A., Stiles, R. and Shigeishi, H. (1981b). Atmospheric Measurements of Selected Hazardous Organic Chemicals. EPA-600/3-81-032.
- Singh, H.B., Salas, L.J., Smith, A.J. and Shigeishi, H. (1981a). Measurements of some potentially hazardous organic chemicals in urban environments. *Atmos. Environ.*, 15, 601-612.
- Singh, H.B., Salas, L.J., Smith, A.J. and Shigeishi, H. (1981). Measurement of some potentially hazardous organic chemicals in urban environments. *Atmos. Environ.*, 15, 601-612.
- Singh, H.B., Salas, L.J. and Stiles, R.E. (1982). Distribution of selected gaseous organic mutagens and suspect carcinogens in ambient air. *Envir. Sci. Technol.*, 16, 872-880.
- Singh, H.B., Salas, L.J., Cantrell, B.K. and Redmond, R.M. (1985). Distribution of aromatic hydrocarbons in the ambient air. *Atmos. Environ.*, 19, 1911-1919.
- Singh, H.B. and Zimmerman, P.B. (1992). Atmospheric distribution and sources of Non-methane hydrocarbons. Gaseous Pollutants, Characterization and Cycling. In Nriagu, JO (Ed.), *Advances in Environmental Science and Technology*, Vol. 24., pp 185.

- Skold, Y.A., Grennfelt, P. and Pleljel, K. (1992). Photochemical ozone creation potentials: A study of different concepts. *J. Air Waste Manage. Assoc.*, 42, 9, 1152-1158.
- Smith, K.K. (1981). MS Institute, East-West Center mimeographed.
- Snedecor, G.W. and Cochran, W.G. (1978). *Statistical Methods*. Iowa State University Press, Ames. IA, pp 593
- Statistical Abstract (1990). Department of Statistics, Ministry of Planning, Govt. of India.
- Stern, A.C. (1986). *Air Pollution*, Vol. VII, Third Edition. Academic Press, INC.
- Stephens, E.R. (1969). Chemistry of atmospheric oxidants. *J. Air Pollut. Control Assoc.*, 19, 181-185.
- Stephens, E.R. and Burleson, F.R. (1969). Distribution of light hydrocarbons in ambient air. *J. Air pollut. contr. Assoc.*, 19, 929-936.
- Stepen, R.A., Konev, V.A., Khrebtov, B.A. (1978). *Izvestiya Sib. Otdel. AN SSSR. Ser. biol. nauk* N 10: 34.
- Stockholm, J., Norn, M. and Schneider, T. (1982). Ophthalmologic effects of man-made mineral fibres. *Scand. J. Work. Envir. Hlth.*, 8, 185-190.
- Stockton, M.B. and Stelling, J.H.E. (1987). Criteria Pollutant emission factors for the 1985 NAPAP emission inventory. US Environmental Protection Agency. Report No. EPA-600/7-87-015.
- Swannell et al., (1991). Biodegradability and emissions of Volatile Organic Compounds from the Food, Drink and Metal Degreasing Industries. TNO Environmental and Energy Research, Netherlands, Report No. R91/381.
- Szilagyi, I., Demeter, A., Turanyi T. and Berces, T. (1991) Non-methane hydrocarbon and aldehyde measurements in Budapest, Hungary. *Atmos. Environ.*, 25A, 0, 2103-2110.
- Temple, R.G. (1971). Control of Internal Combustion Engine. In W. Strauss (ed.), "Air Pollution Control," Wiley Interscience, New York, 1971. In Seinleld, J.H. (ed.), *Air pollution physical and chemical fundamentals*, 1975.

- Teri Energy Data Directory and Yearbook (TEDDY) (1994-95). Tata Energy Research Institute, New Delhi.
- Teri Energy Data Directory and Yearbook (TEDDY) (1988). Tata Energy Research Institute, New Delhi.
- Teri Energy Data Directory and Yearbook (TEDDY) (1990-91). Tata Energy Research Institute, New Delhi.
- The State of India's Environment (1982). A citizens' report. Center for Science and Environment.
- The State of India's Environment (1984-85). The second citizens' report. Center for Science and Environment.
- Tille, K.J.W., Savelsberg, M. and Bachmann, K. (1985). Airborne measurements of nonmethane hydrocarbons over Western Europe: vertical distributions, seasonal cycles of mixing ratios and source strength. *Atmos. Environ.*, 19, 1751-1706.
- Tingey, D.T., Standley, C. and Field, R.W. (1976). Stress ethylene evolution: A measure of ozone effects on plants. *Atmos. Environ.*, 10, 969-974.
- Tingey, D.T., Pettit, N. and Bard, L. (1978). Effect of chlorine on stress ethylene production. *Env. Exp. Bot.*, 18, 61-66.
- Tingey, D.T. (1980). Stress ethylene production: A measure of plant response to stress. *Hort. Sci.*, 15, 630-633.
- Tingey, D.T. (1981). The effect of environmental factors on the emission of biogenic hydrocarbons from live oak and Slash pine, in atmospheric biogenic hydrocarbons. I, Ann Arbor, MI.
- Tingey, D.T., Manning, M., Grothaus, L.C. and Burns, W.F. (1979). The influence of light and temperature on isoprene emission rates from Live Oak. *Physiol. Pl.*, 47, 112-118.
- Tingey, D.T., Evans, R. and Gumpertz, M. (1981). Effects of environmental conditions on isoprene emission from live oak. *Planta*, 152, 565-570.

- Tsani-Bazaca, E., McIntyre, A.E., Lester, J.N. and Perry, R. (1981). Concentrations and correlations of 1,2-dibromoethane, 1,2-dichloroethane, benzene and toluene in vehicle exhaust and ambient air. *Envir. Technol. Lett.*, 2, 303-316.
- UBA (1981). *Luftreinhaltung 81, Entwicklung-Stand-Tendenzen* (Clean Air '81, development-status-trends) (Ed. The German Federal Environmental Protection Agency). Erich Schmidt, Berlin.
- UN Energy statistics yearbook, (1991). Deptt. of economics and social information and policy analysis. Statistical division, UN year book, 1993.
- USEPA (1980). Volatile organic compound (VOC) species data manual. 2nd edition. US Environmental Protection Agency. Report No. EPA-450/4-80-015.
- USEPA (1990). Methane emissions from Coal Mining Issues and opportunities for Reduction. EPA/400/9-90/008, U.S. Environmental Protection Agency, 401 M Street, SW, Washington DC. September.
- USEPA (1985). Compilation of air pollutant emission factors. Vol. 1, Stationary point and area sources. 4th edition, EPA Report AP-42, North Carolina, U.S.A.
- Varshney, C.K and Aggarwal, M. (1992). Ozone levels in the urban atmosphere of Delhi. *Atmos. Environ.*, 28, 291-294.
- Veldt, C., Huygence, C., Van Jaarsveldt, J.A. and Onderdelinden, D. (1983). Litertuuronderzoek naar de emissies van spoorcomponenten door met kolen gestookte centrales, IMG-TNO report G 1251.
- Volz, A. and Kley, D. (1988). Ozone measurements in the 19th century: Anevaluation of the Montsouris series, *Nature*, 322, 240-242.
- Wang, W.C., Pinto, J.P., Yung, Y.L. (1980). *J. Atmos. Sci.*, 37: 333.
- Wathne, E.M. (1983) Measurements of benzene, toluene and xylenes in urban air. *Atmos. Environ.*, 17, 1713-1722.
- Westberg, H., Sexton, K. and Flyckt, D. (1981). *J. Air Pollut. Contr. Assoc.*, 31 : 661.

- WHO (World Health Organisation) (1987). WHO guidelines for Europe. WHO, Geneva.
- World Health Organisation (1982). Indoor air pollutants, exposure and health effects assessment. Euro. reports and studies no. 78, working group report, Nordlinger, Copenhagen.
- Yokouchi, Y. and Ambe, Y. (1984). Factors affecting the emission of monoterpenes from Red Pine. *Pl. Physiol.*, 75, 1009-1012.
- Yokouchi, Y. and Ambe, Y. (1988). Diurnal variation of atmospheric isoprene and monoterpene hydrocarbons in an agricultural area in summertime. *J. Geophys. Res.*, 93, D4, 3751-3759.
- Yokouchi, Y., Okaniwa, M., Ambe, Y. and Fuwa, K. (1983). Seasonal variation of monoterpenes in the atmosphere of a pine forest. *Atmos. Environ.*, 17, 743-750.
- Zelinski, S.G., Pangaro, N. and Hall-Enos, J.M. (1980). Inventory of organic emissions from fossil fuel combustion for power generation, EPRI report EA 1394.
- Zimmerman, P.R. (1979). Determination of emission rates of hydrocarbons from indigenous species of vegetation in the Tampa/St. Petersburg, Fla. area, EPA 904/9-77-028, USEPA, Region 4, Atlanta, GA.
- Zimmerman, P.R., Chatfield, R.B., Fishman, J., Crutzen, P.J., and Hanst, P.L. (1978). Estimates of the production of CO and H₂ from oxidation of hydrocarbon emissions from vegetation. *Geophys. Res. Lett.*, 5, 679-682.
- Zinger, G.E. (1985). SAE Techn Pap. Ser. No 851262.
- Zor'kin, L.M., Korzenstein, Y.N., Stadnic, E.V., Kozlov, V.G., Kir'yasin, V.M., Yurin, G.A., Borodkin, V.A. (1980). Dokl. AN SSSR 252: 381.