MEASUREMENT OF AMBIENT LEVEL OF NO$_x$ IN DELHI USING PASSIVE SAMPLER

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

MASTER OF PHILOSOPHY

iv, 115p + plates + tables

ABHAI PRATAP SINGH

SCHOOL OF ENVIRONMENTAL SCIENCES
JAWAHARLAL NEHRU UNIVERSITY
NEW DELHI-110067
July, 1999

*Dedicated to all those martyrs
who laid down there lives in Kargil,
sacrificing themselves in defending
the integrity of the Mother Land.*

CERTIFICATE

The research work embodied in this dissertation entitled **"Measurement of Ambient Level of NOx in Delhi Using Passive Sampler"**, 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.

ABHAI PRATAP SINGH

(Candidate)

PROF. J. SUBBA RAO

(Dean)

PROF. C. K. VARSHNEY

(Supervisor)

ACKNOWLEDGEMENTS

CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

INTRODUCTION AND REVIEW

Chapter I : Review of Literature

Introduction

Air pollution has become an extremely serious problem in both developed and developing countries. The indiscriminate exploitation of natural resources for industrialization and urbanization, making the urban centers as a pollution zone. The air pollution problem is no longer restricted to a particular air-shed but it has become regional in character, as high air pollution level has been frequently reported even from the remote areas (Coffey and Stasiuk, 1975; Rubino et al., 1976; Rodes and Holland, 1981; Calbeck and Mackenze, 1994; Atkins and Lee, 1995; Glasius et al, 1999).

India is one of the fastest developing economies in the world. The population of country has increased from 109.5 million in 1971 to 900 million in 1994. The increased urbanization and rapid expansion of commercial activities have resulted in coming up of large number of industries and vehicles growth.

In Delhi, phenomenal growth in industries and vehicles have been reported. There is a 581 per cent increase in industrial units from 18,500 in 1961 to 1,26,000 in 1996 (DSB, 1996). At present in Delhi there are 45 large and medium industrial units. There is no count of number of small unit industries, which are scattered all over the city. An estimated 2000 metric tones of pollutants are released into the atmosphere everyday (Delhi Pollution Statistics, 1995).

Delhi has highest vehicles growth rate, two times of Bombay and three times of Calcutta and Madras. The numbers of vehicles are increasing at the rate of approximately 14,000 per month. Automobiles emissions have increased significantly over past 20 years. The good vehicles and buses which are only 7 per cent of total vehicles and contribute to 85 per cent of vehicular NO_x emission (NEERI, 1991). Presently, vehicles emit more than 1300 tones of pollutants into the Delhi air everyday. This is more than the sum of vehicular pollutants in Mumbai (659.57 tpd), Calcutta (310.62) and Bangalore (253.72 tpd). Diesel driven vehicles, which is about 7 per cent of the total vehicles population contribute about 19 per cent of total vehicular emission.

1

In Delhi, vehicular emission account for 64 per cent of total pollution load followed by power plant 16 per cent, industries 12 per cent and domestic sector 7 per cent.

NO_2 is an important pollutant and present in sufficiently large concentration in atmosphere. It is a minor component (usually < 10 per cent) of the mixture of nitrogen oxides ($NO_x = NO + NO_2$) formed during combustion processes and emitted. During recent years interest in ambient NO_2 concentration has increased, both because of its important role in the formation of photochemical oxidants and toxicity. NO_2 is also a precursor to species such as nitric acid and nitrate aerosols, which contribute to acidification of environment. It has been widely reported that NO_2 causes health hazards, in animals NO_2 causes lung edema and pulmonary congestion, edema, obliterative bronchiolitis, pneumonitis in human beings. NO_2 may cause the release of vasoactive harmones, alter bronchial tone or increase mucous secretion, such effects would tend to exacerbate preexisting disease and to accelerate the natural courts of bronchitis and asthma in man.

Most of studies on NO_2 (concentration, effect and behavior) are mainly from industrialized countries, particularly in temperate climate, by using conventional monitoring techniques. However since 1986, NO_2 spatial monitoring in western countries, especially in UK, Netherland, Sweden have been done by passive sampler (light, robust, cheap, sampling device based on diffusion of air), whilst in developing countries including India the NO_2 monitoring studies by passive sampler are almost lacking. The limited NO_2 monitoring (at few urban station) studies by CPCB have shown considerable NO_2 build up in Delhi, where NO_2 levels frequently exceeds the NO_2 standard prescribed by WHO and ISI. (CPCB, report, 1995). There is a need of spatial monitoring of NO_2 in both urban and remote area, although the costly, bulky, conventional sampling techniques, which require trained personnel, security, high level maintenance and basic infrastructure for monitoring are the mainconstrain in developing countries, particularly in India.

The present study was under taken to determine

1.   Status and behavior of NO_2 at different activity sites such as rural, urban (residential, commercial, parks/recreation, parking and road sites) and peri-urban sites.

2

2.   To evaluate the effectiveness of passive sampler in sub-tropical/tropical climate.

3.   To observe the NO_2 spatial and monthly variation trend at different activity sites.

Sources of NO_x

The oxides of nitrogen(NO_x) includes N_2O, NO, NO_2, NO_3, N_2O_3, N_2O_4 and N_2O_5. However, only three species of oxides of nitrogen namely, N_2O, NO and NO_2 are found in the atmosphere in appreciable quantities. The later two, NO and NO_2, are generally referred to as "nitrogen oxides" and represented by the symbol NO_x.

Both NO and NO_2 are considered as pollutant. Other oxides of nitrogen, such as N_2O_3, N_2O_4, NO_3 and N_2O_5 also occur in the atmosphere, but in very low concentrations and are not of much concern as air pollutants. While N_2O occurs in the ambient atmosphere in relatively high concentration (0.25ppm). Chemically N_2O is inert at ordinary temperature and is not considered as air pollutant. The atmospheric sources of NO_x are given in the following table.

Table no. 1 : Global Atmospheric Sources of NO_x.

Source	NO_x (Tg/N/Y)	N_2O (Tg/N/Y)
(a) Energy related emission		
Fossil fuel combustion	21	<0.1
Biomass burning	8	0.4
(b) Natural sources		
Oceanic processes	<1	2
Lightning	8	—
Ammonia oxidation	1	—
(c) Soil emission		
Cultivated land	7.2	1
Tropical forest	2.6	3.4
Savanna	7.7	—
Other undisturbed soil	2.7	1
Total	59	8

Source :   Levine (1991)

Tg : $= 10^{12}$ gram

NO_x emitted into the atmosphere from different sources can be broadly grouped into three major categories

1. Anthropogenic sources
2. Natural sources
3. Miscellaneous sources

The Contribution of NO_x from different sources is shown in figure no. 1.

Fig. no. 1 :   Emission of Nitrogen Oxide from Different Sources (in percentage)

Contribution of Nitrogen oxide from different sources

- Misllaneous sources
- Natural sources
- Anthropogenic sources

35.5%
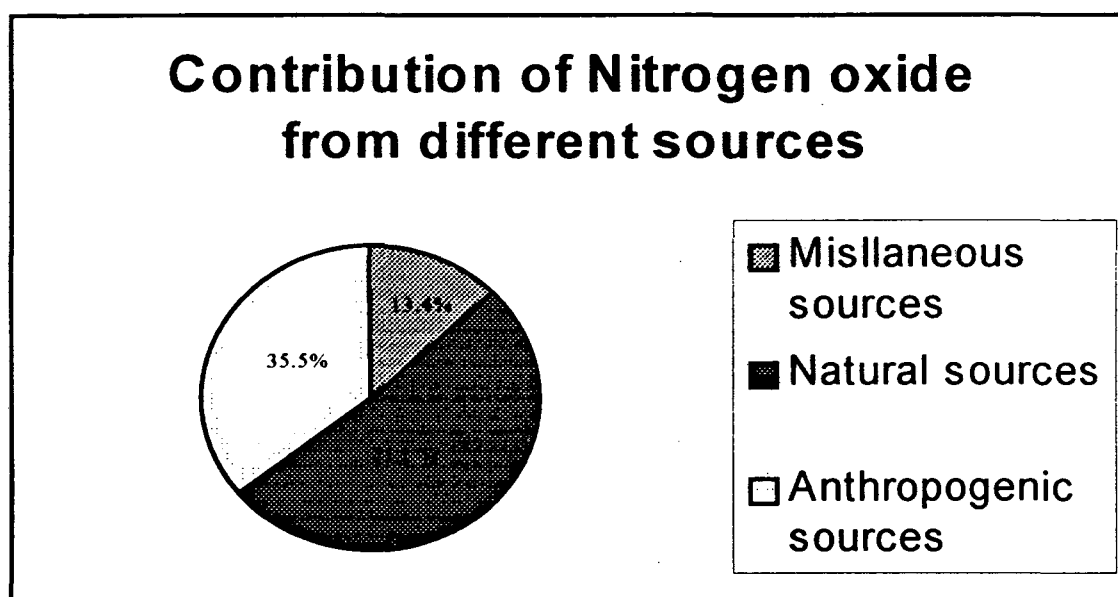
Anthropogenic Sources : Robinson and Robbins, (1968), estimated that anthropogenic sources contribute 450 Tg ($1Tg = 10^{12}$ gram) NO and NO_2 annually. However, Soderlund and Svensson (1976), have presented an estimate of 19×10^{12} g of nitrogen as the annual anthropogenic input via nitrogen oxide released to the atmosphere.

Anthropogenic sources includes a wide spectrum of different sources which can be broadly grouped into two categories

1. Stationary sources
2. Mobile sources

4

Figure no. 2 :   Sources of Oxides of Nitrogen in the Ambient Air

OXIDES OF NITROGEN

Natural   Anthropogenic   Miscellaneous

— Denitrification

— Lightning

— Stretospheric input

— NH₃ oxidation

Transportation

Vehicles —

Railways —

Aircraft —

Marine
vessels

Industrial process

— Chemicals (Nitric
acid plants and
others)

— Matals processing

— Fertilizers

Combustion

— Domestic
combustion

— Forest fire and
managed fires

— Industrial boilers &
furnaces

— Commercial
combustion

Generally, relative contributions of NO_x from motor vehicles and stationary sources range 50:50 in heavily industrialized areas and 90:10 in non industrialized areas with heavy traffic.

Stationary Sources : Stationary sources of NO_x comprises of into 2 categories :

    1.   Industrial process

    2.   Combustion

Industrial Processes : Due to expanding industrialization and industrial operations, increasing amount of NO_x is released into the atmosphere. The major polluting industries are,

- Thermal power plants,
- Chemical,
- Pesticides,
- Petro chemical industries,
- Electronics,
- Steel rerolling,
- Plastics,
- Electroplating,
- Automobiles
- Other agro-based industries including wide range of small scale industries.

The rate of thermal NO_x formation is strongly dependent on combustion temperature and to a lessor extent, on air-fuel mixture in the flame zone.

It has been found that NOx emission from NTPP (National Thermal Power Plant) is influenced by boiler size, boiler type, furnace size, burner configuration, thermal load, excess air and other variables (Doelman et al, 1975). The emission factor for NO_x during combustion of fuels and other materials in different types of activities is given in table no. 2.

Table no. 2 : **Emission Factors for Nitrogen Oxides During Combustion of Fuels and Other Materials**

Source	Average NO_2 Emission Factor	
Fuels		
Coal		
Household and commercial	4	Kg
Industry and utility	10	g/Kg
Fuel oil		
Household and commercial	5.45-32.7	g/gal
Industry	32.7	g/gal
Utility	43.7	g/gal
Natural gas		
Household and commercial	1680	$Kg/10^6 m^3$
Industry	3,100	$g/10^6 m^3$
Utility	5,650	$Kg/10^6 m^3$
Wood	5.5	g/Kg
Combustion sources		
Gas engines		
Oil and gas production	11,150	$Kg/10^6 m^3$
Gas plant	62,400	$Kg/10^6 m^3$
Pipeline	106,000	$Kg/10^6 m^3$
Refinery	64,000	$Kg/10^6 m^3$
Gas turbines	2,900	$Kg/10^6 m^3$
Waste disposal		
Open burning	5.5	g/Kg
Conical incinerator	0.33	g/Kg
Municipal incinerator	1	g/Kg
Chemical industries		
Nitric acid manufacture	28.5	g/Kg product
Adipic acid	6	g/Kg product
Terephthalic acid	6.5	g/Kg product
Nitrations		
Large operations	0.1-7	g/Kg
Small batches	1-130	g/Kg

Source : Control Techniques for Nitrogen Oxide Emission from Stationary Sources (1970).

Domestic Combustion : Domestic emission are generated from open incineration of garbage/ flammable material, domestic combustion units, standly power generators and public smoking.

In some households, there is practice of burning firewood, cowdung cakes, coal, hard coke, charcoal in stoves, kerosene oil, LPG and other combustible materials for domestic cooking and household heating processes. These combustion units are more hazardous creating indoor air pollution and various health problems.

Commercial Combustion : The commercial combustion units as angithees, tandoors and bhattis fired with wood, hard coke, steam coal, briquettes, cowdung cakes and other combustible materials are in use at various establishments like restaurants, eat outs, hotels, brick kilns & potter kilns.

The burning of steam coal, wood, cowdung and other combustible materials lead to the emission of NO_x. In addition to these, the open incineration of garbage, refuge, rubber and others also contribute NO_x.

When fossil fuel burnt at high temperature in the flame, both nitrogen in the coal and nitrogen in combustion air combines with oxygen to form NO. The NO subsequently, reacts with O_2 in the atmosphere to give NO_2.

$$N_2 + O_2 \leftrightarrow 2NO$$
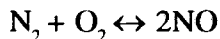
Emission of NO_x from stationary fuel combustion sources is given in table no.3.

Table no. 3 :   **Emissions from Stationary Fuel Combustion Sources (in millions of ton per year).**

Sources	NO_x (mtY^{-1})
Electric power plants	
Coal	3.4
Oil	0.6
Gas	0.7
Total	4.7
Industrial	
Coal	0.5
Oil	0.3
Gas	.3.7
Total	4.5
Other (heating etc.)	
Coal	-
Oil	0.4
Gas	0.3
Other fuels	0.1
Total	0.6
Grand Total	10.0

Source : Cavender, J.H., Kircher, D.S., Hoffman, A.J., (1973), Nation Wide Air Pollution Trends 1940-1970, EPA, (1973).

Mobile Sources

Mobile sources includes automobiles, railways, aircraft's and marine vessels.

Automobiles : Automobiles are the main contributor (70 percent) to NO_x pollution in urban areas. With population growth and urbanization the vehicle population is diversifying. The emission of NO_x from automobiles depend not only on the number of automobiles on the road but also augmented more intensely due to traffic congestion, driving habits, maintenance level, age of vehicles, traffic condition and type of engine.

In India, the vehicle number has increased manifold during the past few decades. A steady increase in total number of registered vehicles in India between 1951 to 1995 has increased over hundred folds.

Table no. 4 :   Total Registered Vehicles in India (1951-95) (in thousands).

Year	Total Vehicles	Two Wheelers	Car/Jeeps/ Taxi	Buses	Good Vehicles	Others
1951	306	27	159	34	82	4
1961	665	88	310	57	168	42
1971	1,865	576	682	94	343	170
1981	5,391	2,618	1,160	162	554	897
1991	21,374	14,200	2,954	331	1,356	2,533
1993	25,299	17,026	3,330	381	1,599	2,963
1994	29,850	24,000	3,900	—	—	—
1995	32,536	26,160	4,251	—	—	—

Source :   Transport Statistics in India, 1993, Ministry of Surface Transport and Delhi Statistics 1995.

The number of two wheelers in India increased 561 percent between 1981 to 1993. In comparison, the number of buses increased only by 135 percent. According to the Association of Indian Automobile Manufacturers, the total number of vehicles is expected to hit 53 million mark in 2000-01 AD, as compared to their present population of 32 million.

Delhi has 29 percent of the total number of vehicles in India. The registered number of total vehicles in Delhi between 1971 to 1995 are given in table no.5. The vehicle number has gone up from 6,68,000 during 1983 to 25,75,731 in 1995.

Table no. 5 :   Growth of Vehicles in Delhi (1971-1995).

Year (as on 31 March)	Number of Vehicles (no. in thousands)
1971	180.4
1972	212.2
1973	244.7
1974	278.5
1975	316.4
1976	349.9
1977	389.2
1078	425.9
1979	458.0
1980	487.2
1981	536.0
1982	592.6
1983	668.0
1984	750.0
1985	841.0
1986	961.0
1987	1,112.0
1988	1,416.0*
1989	1,590.0*
1990	1,764.6*
1991	1,923.8*
1992	2,064.7*
1993	2,198.9*
1994	2,372.9*
1995	2,575.7*

Note : * Data as on 31 Dec.

Fig.no. 3 : Vehicular Growth in Delhi (1971-1995).
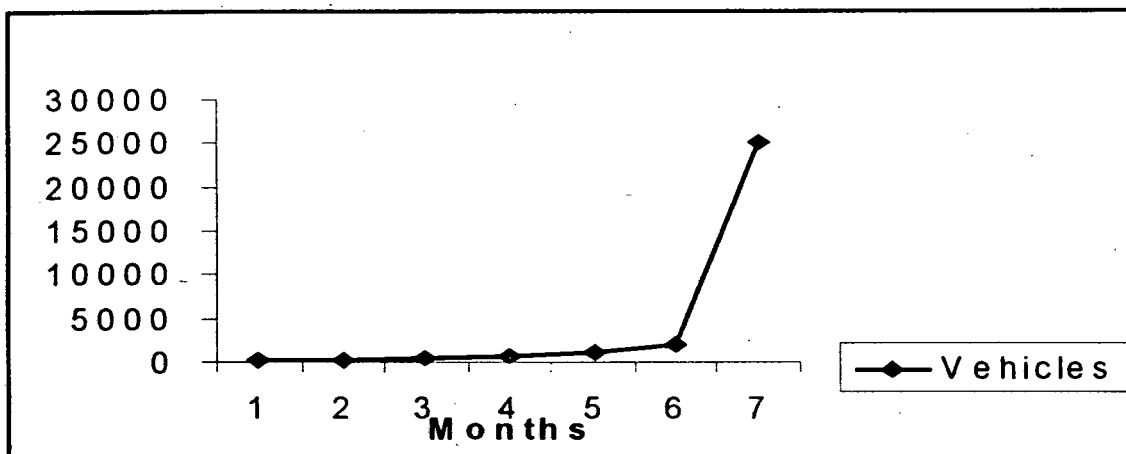
Source :   Transport Statistics in India, 1993, Ministry of Surface Transport and Delhi Statistics 1995.

Railways: The diesel driven locomotives are major NO_x contributor of rail traffic related pollution problems. Coal driven locoengine also release significant amounts of NO_x in the environment. These are line source and therefore, the emissions are dispersed in linear areas along the movement of locomotives.

There are approximately 600-700 operations of passenger and goods train departure/arrivals daily at all the railway stations located in Delhi. On the non electrified tracks, diesel and coal fired locomotives are common. The NO_x contribution by these line sources are quite smaller as compared to the emission from vehicles and industries.

Aircraft : The aircraft and passenger motor vehicles movement at the airport may be significant contributors to NO_x. High amounts of NO_x generated by a range aircraft's activities (i.e., taxing, takeoffs and landings) and airport related ground transport activities, use of heating fuels, within the airport complex and aircraft engines testing practices. The aircraft emission may be quite low as compared to other major categories of NO_x sources.

In Delhi there are three airports, two commercial airports located in south west of Delhi and a defense/non-commercial airport located amidst south Delhi residential localities. These

airports are :

1.   Indira Gandhi Airport (Domestic Terminal)

2.   Indira Gandhi International Airport

3.   Safderjung Airport (Air Force Base & Delhi Flying Club)

There are more than three hundred landing and take-off operations of various passenger and cargo aircraft's from these airports

Natural Sources: Large amount of NO_x are released via several natural mechanisms including fixation by lightning (Junge, 1958; Ferguson and Libby, 1971), inflow from stratosphere (Soderlund and Sevensson 1976), chemical conversion from ammonia in the troposphere (Crutzen, 1974; McConnel, 1973) and from denitrification (Hergreaves et al., 1992; Siba et al .,1992). The various natural sources of NO_x are discussed below.

Denitrification : The abiotic and biotic processes of denitrification globally release large quantities of nitrogen oxides to the atmosphere. Soderlund and Sevensson, (1976) have indicated that terrestrial ecosystem may release 1 to 14×10^{12} g NO_x annually. Focht and Verstraete (1977) have estimated that terrestrial denitrification may generate an annual surface flux of approximately 3 kg nitrogen per hectare.

Denitrification requires anaerobic conditions and it is greatly stimulated by high content organic matter in the soil. The highest rate of denitrification occurs during wet periods, typically during spring or early summer in the temperate climate and during rainy season in tropics. Denitrification is carried out by a diverse group of microbes, including bacteria, fungi, autotrophs, heterotrophs, aerobes and anaerobes, in a variety of habitats including poorly drained, well drained, acidic and alkaline soils (Delwiche & Bryar, 1976; Wollum and Davey, 1975; Bremner & Blackmer, 1978). The most comprehensive review of terrestrial ecosystem nitrogen oxide contribution to the troposphere has been accessed between 5-26 N^{12} g N per year by Bowden (1986).

Table no. 6 :   NO$_x$ Emission from Undisturbed Terrestrial Ecosystems.

Ecosystem	Global emission rate	
	Area (10^9 hactare)	NO$_x$ in 10^{12} g Nyr^{-1}
Temperate hardwood	1.55	1.5
Temperate conifer	0.50	1
Tropical forests	2.45	NA
Prairie/grassland	2.40	3-24
Arid lands/desert	4.20	NA
Tundra/boreal	2.00	NA
Wetlands/marsh	0.2000	NA
Total	13.30@	5-26

Source- Bowden (1986)   NA represents =   Not available data

@- Does not include cultivated land (1.4x10^9 ha) or lakes and streams (0.12x10^9 ha)

Fixation by Lightning : Earlier it was estimated that fixation of nitrogen by lightening is as much as 40-90 Tg Ny^{-1} (Noxon, 1976; Chameides et al., 1977; and Chameides, 1979). However measurement by Dawson (1980) and Hill et al. (1980) give upper limit of only 3-4 Tg Ny^{-1}. It has been reported that lightning discharge lead oxidation of atmospheric nitrogen into NO, NO$_2$ and N$_2$O.

Inflow from Stratosphere : The main source of stratosphere NO$_x$ is N$_2$O originating from nitrification and denitrification processes in the biosphere and it is subsequently transported to the stratosphere. In the stratosphere N$_2$O is chemically converted by the following reactions :

$$N_2O + O \quad = \quad N_2 + O_2$$
$$N_2O + O \quad = \quad 2NO$$
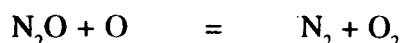
The NO formed may be partly converted to NO$_2$. Such NO$_2$ is transported to the troposphere through turbulent exchange. Actually, the exchange between troposphere and stratosphere takes place by Hadley cell circulation, eddy diffusion and polar jet stream activity, Schmeltekopf

13

et al. (1977) have calculated a yearly flux of 1.6 Tg N from the stratosphere to the troposphere.

Oxidation of NH_3 : It has been estimated that NH_3 concentration in the boundary layer of background continental air ranges from 0.1 to 0.4 ppb (Georgii, 1963; Junge, 1963; Tsunogai, 1971 and Bottger et al., 1978). NH_3 is partly converted into NO in the troposphere by a chain of chemical reactions. The first step in its conversion is the reaction between ammonia and OH radical :

$$NH_3 + OH = NH_2 + H_2O$$
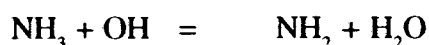
This reaction is followed by the transformation of NH_2 into NO. However, it might even be regarded as a sink for NO_x according to the following reactions :

$$NH_2 + O_2 = N_2 + H_2O$$
$$NH_2 + NO_2 = N_2O + H_2O$$
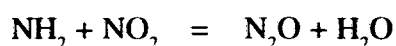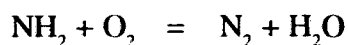
It has been calculated that globally the deduced source strength of NO by NH_3 oxidation is about 0.6 to 2.5 Tg N.

Miscellaneous Sources

These mainly include biomass burning, forest fire having natural or anthropogenic origins. Biomass burning includes : burning of wood for fuel (~15 percent), burning of agricultural wastes (~25 percent), burning related to deforestation (~15 percent), forest fire in temperate and boreal forests (less than 5 percent) and burning of grass lands (~40 percent). Current estimates suggest that over 85 percent of all biomass burning emission are produced in tropics.

Nitrogen Oxide (NO_x) Trend

The discussion in following paragraphs deals with NO_x trend related to emission its ambient concentration including seasonal and diurnal variations.

NO_x Emission Trend : NO_x in the northern hemisphere has increased significantly

during the last few decades. NO_x build up is largely associated with urban and industrial areas which actively emit NO_x. Over 90 percent of NO_x in the northern hemisphere is primarily from Europe and North America (Irwin and Williams, 1988; Hameed and Dignon, 1988). List of top five countries according to their estimated emission of NO_x are given in table no.7.

Table no. 7 : Countries with Highest NO_x Emissions from Fossil Fuel Combustion.

Country	NO_x $(Tg\ NY^{-1})$
Former U.S.S.R.	6.40
U.S.	4.40
China	1.70
Poland	0.80
West Germany	0.60

Source : Dignon, 1992. $(Tg = 10^{12}gram)$

It is reported that in UK concentration of NO_x in atmosphere has been steadly increasing since last 50 years. For UK, the total annual NO_x emission was 864 KtN in 1994, of which 50 percent is apportioned to mobile sources and 28 percent to static combustion (INDITE, 1994). However, in tropics NO_x has started increasing rapidly since 1966 (Hameed and Dignon, 1986). The NO_x emission in India is increasing at alarming rate since 1980's with increasing fossil fuel consumption. The fossil fuel (petrol + diesel) consumption in Delhi and corresponding NO_2 level increase is shown in figure no.6. The growing total NO_x emission for India has not yet been estimated, however, in Delhi total annual NO_x emission has increased from 16.12 thousand ton in 1991 to 19.95 thousand ton in 1994-95. The sector-wise emission of NO_x in Delhi is given in table no.8 and in figure no.4.

15

Table no. 8 : Sector-wise Emission of NO$_x$ in Delhi (Metric ton per day).

Sector	NO$_x$
Transport	157
Power	143
Industry	20
Domestic	3
Total	323

Source : CPCB, 1995, Pollution statistics — Delhi.

Figure no. 4 : Sector-wise Emission of NO$_x$ in Delhi (in percentage).

Industry (6.4)

Domestic (0.9)

Transport (48.7)

Power (44.3)
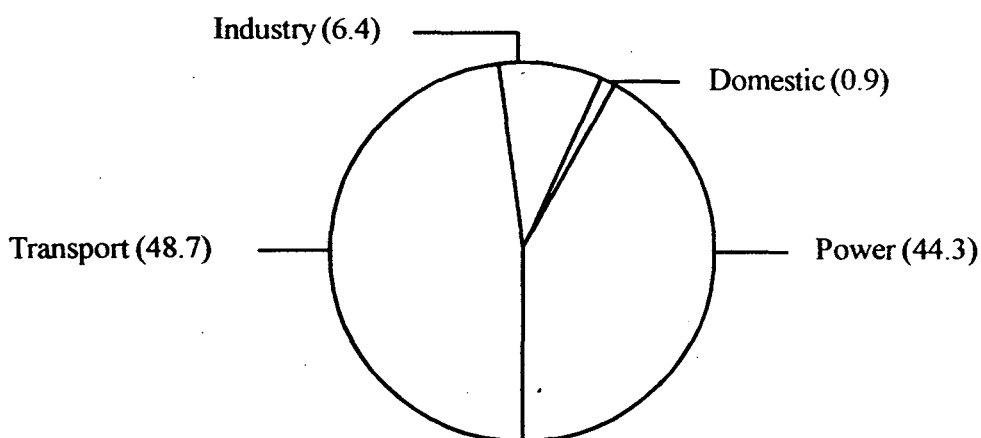
Source : CPCB, 1995, Pollution statistics — Delhi.

Ambient NO$_x$ Concentration : Measurements of NO$_x$ in the ambient environment shows a steady increase in NO$_x$ concentration over last 30 years in Europe and N. America (Martin and Barber, 1984; Sandalls and Leonard, 1986; Dignon 1988, 92; Campbell et al., 1988, 94; Bower et al., 1991; Gair et al., 1991; Irwin and Williams, 1988). In Delhi also gradual increase in NO$_2$ concentration in the ambient environment has been observed. (CPCB data 1989 to 1996) show that the annual mean concentration of NO$_x$ The annual mean NO$_2$ concentration in Delhi rose dramatically from 20.4 μg/m^3 in 1987 to 47.2 μg/m^3 in 1995. However, according to CPCB report the NO$_2$ concentrationn in Delhi during 1996 is decreased over its concentration in 1995, but in view of the projected growth in the transport, industry

16

Fig. no. 5 : Annual Mean NO₂ Concentration Variation in Delhi (1989-96).
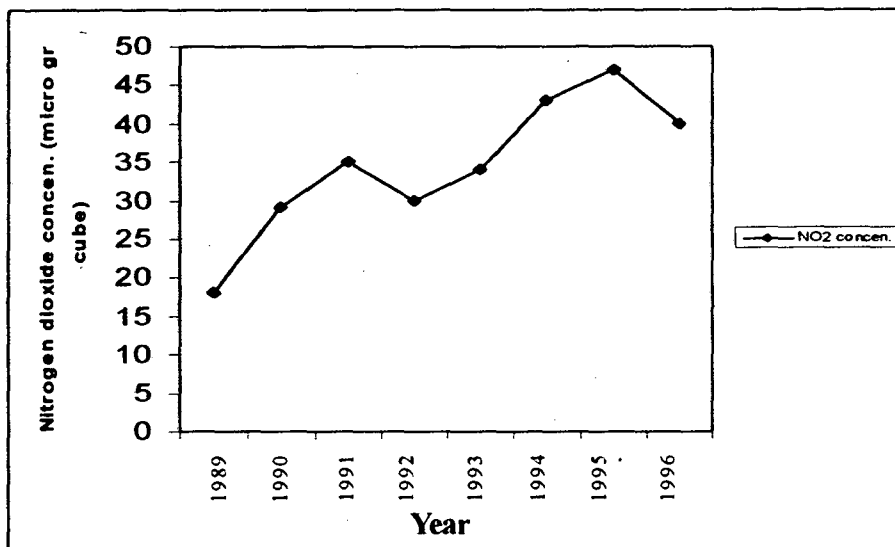
Fig. no. 6 : Fossil Fuel consumption in Delhi (1980-96).
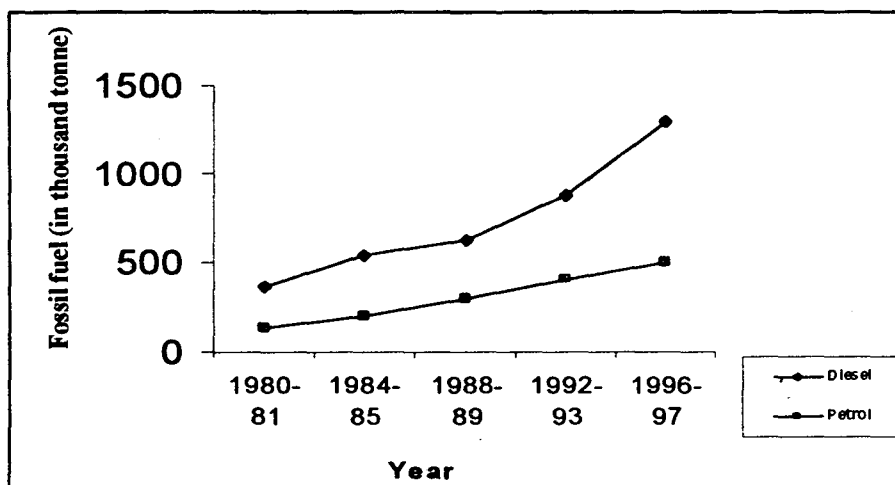
and consumption of fossil fuel, it seems the NO_x concentration in the ambient environment is bound to ascend steadily in the coming years. The annual mean NO_2 concentration trend in Delhi is given in table no.9.

Table no. 9 : Annual Mean NO_2 Concentration in Delhi (1987-1996)

Year	NO_2 Concentration ($\mu g/m^3$)
1987	20.4
1988	20.6
1989	18.5
1990	29.3
1991	34.81
1992	30.2
1993	34.25
1994	43.5
1995	47.4
1996	39.6

Source : CPCB annual report (1989-1996).

The rate of increase/decrease of NO_2 concentration in the ambient environment of Delhi has been calculated from CPCB annual mean NO_2 concentration data (table no. 10).

Table no. 10 : Annual Mean of NO_2 value in Delhi. (1987-1996)

Year	Base year	Percentage increase/decrease
1988	1987	+ 0.98
1989	1988	- 10.1
1990	1989	+ 58.3
1991	1990	+ 18.8
1992	1991	- 13.2
1993	1992	+ 13.4
1994	1993	+ 27.0
1995	1994	+ 8.5
1996	1995	- 16

Note : (+) = Sign indicate increase, (-) = Sign indicate decrease

Table no. 10 shows that 58.3 per cent increase in NO_2 concentration, in 1990 from 18.5 $\mu g/m^3$ in 1989 to 29.3 $\mu g/m^3$ in 1990 and 27.0 per cent increase in 1994 from 34.2 $\mu g/m^3$ in 1993 to 43.5 $\mu g/m^3$ in 1994. However, according to CPCB report, NO_2 concentration was decreased by 16 per cent in 1996 from 47.2 $\mu g/m^3$ in 1995 to 39.6 $\mu g/m^3$ in 1995.

Seasonal Behavior of NO_2

Ambient concentration of NO_2 undergoes seasonal change and it has been observed that winter NO_2 concentration exceeds those in summer (Campbell, 1988; Williams et al., 1988; Bower et al., 1991; Atkins et al., 1995; Delaney and Dowding, 1998; Kerby et al., 1998). However, in India on the basis of data collected by CPCB no definite pattern would discernable. Following factors are responsible for high winter and low summer NO_2 concentration.

1. A potential contributor to lower summer NO_2 concentration is chemical removal processes (wet and dry deposition), which leads to NO_2 oxidation to HNO_3 in the atmosphere. During day time following reaction takes place between OH radicals and NO_2 as :

$$OH + NO_2 \longrightarrow HNO_3 + H$$
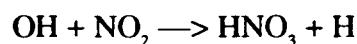
The concentration of OH redical remains high during summer, since OH generation depends on the intensity of sunlight results in relatively more NO_2 removal during summer.

2. Meteorological conditions exert a strong influence on ambient NO_2/NO concentrations. If all other factors being equal, ambient level of air pollutant (NO_2) tend to rise in winter because of generally increased atmospheric stability, reduced mixing depths and consequent poorer dispersive capacity of the atmosphere.

3. Emission pattern also influence NO_2 level. Although traffic and industrial process emissions remains reasonably constant throughout the year, but emission from space heating and power stations do rise during the winter months.

19

During summer (a) high temperature and high insolation enhances photochemical activity leads to $NO \longrightarrow NO_2$ which promotes increased O_3 formation higher temperature and insolation rate. (b) relatively low NO_2 removal by vegetation (foliage is less dense) may consequence to reduced overall seasonal variability.

It has been reported that winter/summer (W/S) NO_2 ratio are consistent in urban areas and near road side sites (Williams et al., 1988; Bower et al., 1991; Atkins & Lee, 1995; Kirby et al., 1998). However at rural locations, high seasonal variations have been observed at rural locations (Campbell et al., 1988) because rural areas have high industrial population and power station which has greater seasonality. The biomass burning in rural areas during winter is also responsible for seasonal variability.

The power plants shows seasonal variability in emission, although the plumes may be emitted above boundary layer, which is generally lower in winter due to inversion and lower mixing depth.

Diurnal Variations (Behavior) of NO_2

NO_2 levels in the atmosphere show diurnal variation (Bower et al. 1981; Delaney and Dowding, 1998). The NO_2 level throughout day are influenced by several factors (Bower et al. 1991) such as :

1. Ambient NO levels, since most NO_2 arises from oxidation of this primary pollutant.

2. Variation in NO_2 formation and removal processes during the day. This, in turn will be dependent on insolation and temperature as well as ambient concentration of NO, O_3 and reactive hydrocarbons.

3. Atmospheric stability, controlling dispersion processes.

4. The proportion of primary NO_2 emitted from sources, higher emission may occur from idling engines (for instance in congested traffic) during cold conditions (Lenner et al., 1983; Lindqvist et al., 1982).

20

The weekday, weekend and seasonal pattern for NO and NO_2 concentration are very distinct (Williams et al., 1988; Bower et al., 1991; Delaney and Dowding, 1998).

It has been observed that there are 2 peaks for NO concentrations each weekday, one in morning at approximately 9 am and other in evening around 7 pm, peaks for NO_2 weekday concentration also occur around these times, illustrating how quickly NO gets transformed into NO_2. In general weekend pattern for NO and NO_2 concentrations do not exhibit these characteristics peaks. NO_2 weekend concentration does not follow the weekday hourly trend but follows the seasonal trend. However, during spring, weekend concentrations of NO_2 is as high as weekday concentrations (Delaney and Dowding, 1998). The daily peaks during winter are some what delayed (by 1 to 2 h) with respect to summer (Bower et al., 1991). It has been reported that NO and NO_2 daily maxima coincident at most sites during the winter months. During summer, however, the NO_2 peaks at most sites occurs about 1hr. later than NO (Bower et al., 1991).

The coincident of NO and NO_2 maxima during winter reflects dominant effect of primary emissions and the production of NO_2 by O_3 together with possibly, ambient oxidation at low temperature. These reactions are fast and will not therefore cause a significant delay between daily NO and NO_2 peaks. In summer, however, chemical oxidation processes involving OH attack on hydrocarbon to form peroxyradicals are of increased importance.

NO_x Formation

The oxides of nitrogen emitted into the atmosphere are N_2O, NO, NO_2, N_2O_3. About 95 percentage of NO_x is emitted as NO. There is mainly three different kinds of NO formations depending on the individual conditions responsible for prevailing temperature, concentration, residence times and kind of fuel. They are referred as :

1.   Thermal NO

2.   Prompt NO

21

3. Fuel NO.

NO is formed during and after combustion, only a small fraction of it's converted to NO_2 which in most of the cases is formed later in the atmosphere.

Formation of Thermal NO : NO which is formed in high temperature zone is called thermal NO. The mechanism of thermal NO formation discovered by Zeldovich (1946) consist of following two reactions :

$$K_1^+$$
$$NO_2 + O = NO + O$$
$$K_1^-$$

$$K_2^+$$
$$N + NO_2 = NO + O$$
$$K_2^-$$
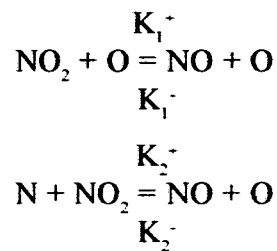
K_1^+, K_1^-, K_2^+ and K_2^- represent the forward and backward reaction rate constants. It is normally assumed that the formation of one of NO molecule in the forward step automatically leads to the formation of the second NO molecule.

Formation of Prompt NO : Fenimore (1976) called the nitrogen monoxide produced within reaction zone of a pre-mixed flame "Prompt" NO. In premixed flames, burning with excess of air, there is surplus of oxygen atoms in the reaction zone which reacts with molecular nitrogen according to Zeldovich reaction scheme.

NO Formation from Fossil Fuels Containing Nitrogen Compounds : The combustion of nitrogen containing fuel such as coal, heavy fuel oil results in NO formation due to oxidation of organic compounds like amines and others. In contrast to thermal NO, this NO is formed at relatively low temperature.

Mechanism of NO_2 Formation

NO_2 is an orange colored gas with a broad absorption band. In ambient air NO gets converted into NO_2 through following routes :

1. Thermal Oxidation of NO by Molecular Oxygen :

$$2NO \quad + \quad O_2 \quad = \quad 2NO_2$$

It has been proposed that reaction mechanism includes 2 steps (Heicklen and Cohen, 1968; Lindqvist et al., 1982), either

$$NO \quad + \quad O_2 \quad = \quad ONOO$$

$$ONOO + \quad NO \quad = \quad 2NO_2$$

Or

$$NO \quad + \quad NO \quad = \quad N_2O_2$$

$$N_2O_2 \quad + \quad O_2 \quad = \quad 2NO_2$$
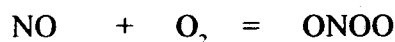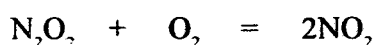
The presence of any specific substance in polluted air does not rest help in high rate of NO oxidation (Judeikis et al., 1977). On other hand, it is evident that the oxidation rate is increased by surface adsorption of NO (Lindqvist et al., 1982).

2. Direct Reaction with Ambient Ozone :

In the atmosphere chemical oxidation of NO to NO_2 occurs rapidly due to its reaction with ozone.

$$O_3 \quad + \quad NO \quad = \quad NO_2 + O_2$$
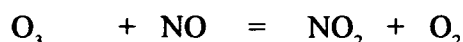
For typical O_3 concentrations (30 ppb) NO has a lifetime of 1 minute with respect to its oxidation reaction. However, if NO exceeds the local concentration of O_3 the reaction rate will be limited by the diffusion or advection of ozone into the air parcel.

Photochemical Oxidation of NO

In daylight NO is also oxidized photochemically producing peroxy redicals (HO·, CH_3CO, O_2· etc.)

$$NO_2 \quad + \quad NO· \quad = \quad RO \quad + \quad NO_2$$
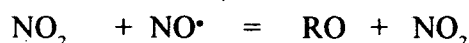
But net conversion of NO to NO_2 is limited on account of rapid photodissociatiion of NO_2 which reforms NO by light wavelength 400nm.

$$NO_2 \quad + \quad hv \quad = \quad NO \quad + \quad O$$
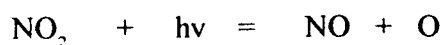
This gives rise to photostationary state governing the concentrations of NO, NO_2 and O_3, the later being produced by fast recombination of O with NO_2.

$$O + O_2 + \quad M \quad = \quad O_3 + M$$
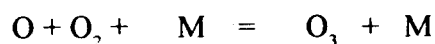
These two reactions, together with the NO + O_3 reaction from the so-called "Photostationary Equilibrium".

$$NO \quad + \quad O_3 \quad = \quad NO_2 + O_2$$
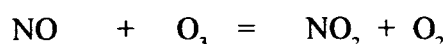
The Hydroxy (HO_2) oxide reacts with NO in following manner.

$$OH \quad + \quad CO \quad = \quad H \quad + CO_2$$
$$H \quad + \quad O_2 \quad = \quad HO_2$$
$$HO_2 \quad + \quad NO \quad = \quad OH \quad + NO_2$$
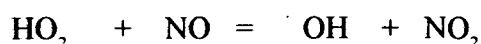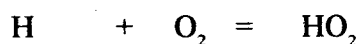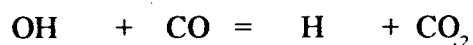
In polluted atmosphere, organics such as propane plays a role similar to CO in carrying on the chain reactions. In this cycle organics such as propane is oxidized to propanadehyde (C_2H_5CHO), two molecules of NO are converted to NO_2 and OH is regenerated. The propanaldehyde can itself then is attacked by OH and a similar cycle occurs leading to further NO oxidation. The chain reactions are terminated by such reactions as :

$$HO_2 \quad + HO_2 \quad = \quad H_2O_2 \quad + \quad O_2$$
$$RO_2 \quad + HO_2 \quad = \quad ROOH \quad + O_2$$
$$OH \quad + NO_2 \quad = \quad HNO_3$$
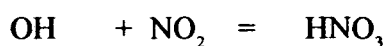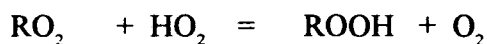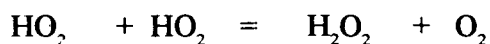
NO_2 Atmospheric Chemistry

NO_2 is a highly reactive species occurring in atmosphere. It has an intense absorption band over most of the visible and ultraviolet regions having a maximum at 400 nm.

NO_2 plays an important role in determining chemistry of atmosphere by reacting with various atmospheric constituents. NO_2 atmospheric chemistry can be discussed under following two aspects:

24

a.   Chemical transformation

b.   Removal

Chemical Transformation

In atmosphere NO_2 reacts with various atmospheric constituents resulting in the formation of O_3, PAN and other products.

Ozone : NO_2 serve as torpospheric ozone precursor within planetary boundary layer. Ozone is formed through a series of complex photochemical reactions among NO_2 and other primary pollutants such as volatile organic compounds. The only feasible route for the production of ozone in the polluted troposphere is the photolysis of NO_2.

$$NO_2 \quad = \quad NO \quad + \quad O$$
$$O + O_2 + \quad M \quad = \quad O_3 \quad + \quad M$$
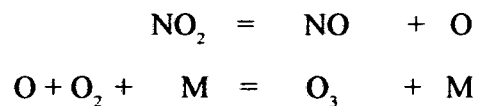
However, rapid formation of NO by NO_2 maintains an overall balance between oxidizing and reducing chemical species.

$$NO \quad + \quad O_3 \quad = \quad NO_2 \quad + \quad O_2$$
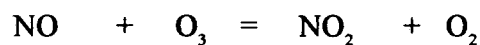
The presence of peroxy redicals (RO_2) produced by degradation of hydrocarbons leads to new O_3 formation as per the following reactions :

$$RO_2 \quad + \quad NO \quad = \quad RO \quad + \quad NO_2$$
$$NO_2 \quad + \quad hv \quad = \quad NO \quad + \quad O$$
$$O \quad + \quad O_2 + \quad M \quad = \quad O_3 \quad + \quad M$$
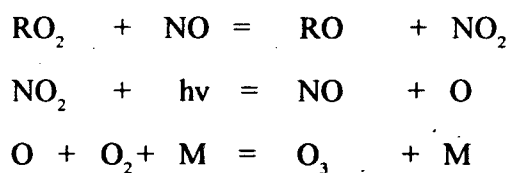
According to Crutzen and Zimmermann (1991) ozone formation from NO_x occurs through the following reactions :

$$CO \quad + \quad OH \quad = \quad H \quad + \quad NO_2$$
$$H + NO_2 + \quad M \quad = \quad NO_2 \quad + \quad M$$

$$HO_2 + NO = OH + NO_2$$

$$NO_2 + hv = NO + O \ (\lambda < 400nm)$$
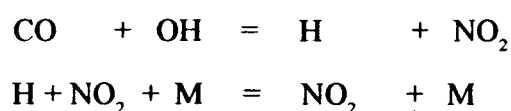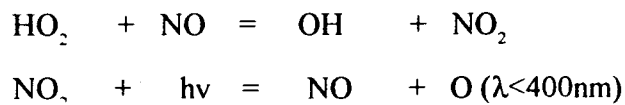
and by CH_4 in atmosphere as follows :

$$CH_4 + OH = CH_3^- + H_2O$$

$$CH_3^- + O_2 + M = CH_3O_2^- + M$$

$$CH_3O_2^- + NO = CH_3O^- + NO_2$$

$$CH_3O^- + O_2 = HCHO + HO_2$$

$$HO_2 + NO = OH + NO_2$$

$$2 \ [NO_2 + hv = NO + O]$$

$$2 \ [O + O_2 + M = O_3 + M]$$
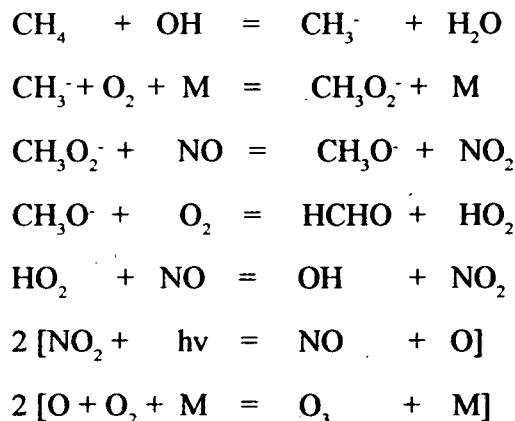
PAN Formation : (Peroxyacylnitrate) Peroxyacylnitrate is the principle component of photo-chemical smog. The first known member of this group is peroxyacetyl nitrate or simply PAN.

The PAN formation takes place through the reactions between acetyl redical with O_2 and NO_2.

$$CH_3CHO + OH = CH_3C = O + H_2O$$

$$CH_3CHO + NO_3 = CH_3 - C = O + HNO_3$$

$$CH_3C = O + O_2 = CH_3COOO$$

$$CH_3COOO + NO_2 = CH_3COOONO_2$$
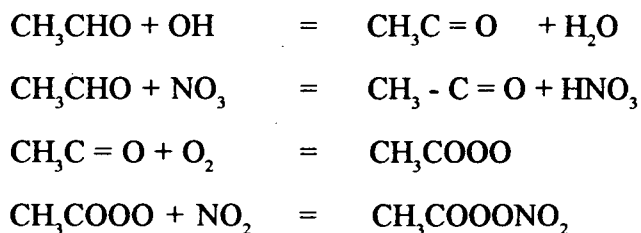
In troposphere atmospheric oxidation of ethane also results in PAN formation through the following reactions :

$$C_2H_6 + OH = C_2H_5 + H_2O$$

$$C_2H_5 + O_2 = C_2H_5O_2$$

$$C_2H_5O_2 + NO = C_2H_5O + NO_2$$

$$C_2H_5O + O_2 = CH_3CHO + HO_2$$
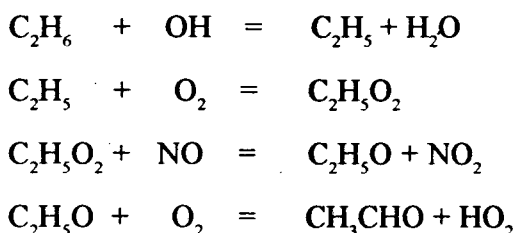
An equilibrium exists between the formation and decomposition of PAN. PAN acts as a storage reservoir of NO_x. When NO_2/NO ratio is high and or temperature is low, the decomposition

reaction is inhibited, hence, PAN concentration can build up.

Other Reactions of NO_x in the Atmosphere : The predominant atmospheric fate of NO is oxidation to NO_2. The atmospheric nitrogen dioxide undergoes photodissociation as well as it reacts with OH, O_3, NO_3, O, HO_2 and RO_2.

Nitrogen dioxide reacts with OH during daytime and forms nitric acid.

$$NO_2 \; + \; OH \; = \; HNO_3$$

In the presence of O_3, conversion on of NO_2 to nitric acid can also occur throng its reaction with O_3 (Richard, 1983).

$$NO_2 \; + \; O_3 \; = \; NO_3 + O_2$$
$$NO_3 \; + NO_2 \; = \; N_2O_5$$
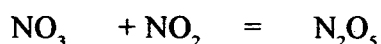
N_2O_5 reacts heterogeneously with liquid water from HNO_3.

$$N_2O_5 \; + \; H_2O \; = \; 2HNO_3$$

The efficiency of this reaction is much reduced during day time.

Formation of peroxy nitric acid, alkyl peroxy nitrate and alkyl nitrate is also significant reaction pathways. Atmospheric nitrogen dioxide reacts with the hydroxyl radical and forms peroxy nitric acid.

$$HO_2 \; + NO_2 \; = \; HO_2NO_2 \; .$$
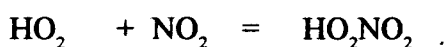
Nitrogen dioxide reacts with alkylperoxyradicals and forms alkyl peroxy nitrate

$$NO_2 \; + \; RO_2 \; = \; RO_2NO_2$$

RO_2NO_2 is thermally unstable. Hence, decomposes back into reactants. The lifetime of RO_2NO_2 $\leq$ 1 sec.

NO$_2$ can aslo react with alkoxy radicals to form alkyl nitrate or if an abstructable hydrogen is available, nitrous acid and carboxyl compund may be formed.

$$NO_2 + RO_2 = RO_2NO_2$$
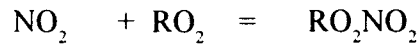
This reaction is too slow to contribute significantly in the removal of NO$_2$ from the troposphere.

Removal of Nitrogen Dioxide from Atmosphere

In principle, the available route for removal of atmosphere pollutant from the atmosphere may be separated through :

(a)   Deposition

(b)   Conversion to normal atmospheric constituents.

Any pollutants not eliminated by the above-mentioned mechanisms accumulates in the atmosphere. In the atmosphere most important nitrogenous compunds are nitric oxide, NO$_2$, HNO$_3$, nitrates and proxy acyl nitrates. Most of this compound (substances), directly or after transformation, removed from atmosphere by deposition (Irwin & Williams, 1988).

The deposition is broadly classified into two types :

a)   Wet deposition

b)   Dry deposition

Table no. 11 : Disposition Velocities of NO$_2$ on Surfaces.

Depositon Surfac	Deposition Velocity (m/s)	Reference
Alfalfa	0.4-1.9	Hill; 1971
Sea water	0.015	Bottger et al., 1978
Water	0.010	Bottger et al., 1978
Forest Soil	0.30	Bottger et al., 1978
Sand, dry	0.6	Bottger et al., 1978
Sand,	0.28	Bottger et al., 1978
Sand foam sold	0.60	Judeikis et al., 1978
Soyabeen	0.05-0.3	Wesely et al., 1982

Table no. 12 :Estimated Budget of Nitrogen Species deposition for the Atmosphere of Terrestial Tropics (between 30^{0}N and 30^{0}S) Unit TgN per year (1Tg-10^{12}g).

Deposition	Nitrogen species	
	NO_x	N_2O
Wet deposition	12-42	-
Dry deposition	12-22	-
Stretospheric photolysis	-	10.5
Atmospheric accumulation	-	3.5
Other nitrogenous compunds	1-5	-
Total	59	14

Source : Levine (1991)

Wet Deposition : Pollutants may be dissolved in clouds, fog, rain or snow when these water droplets impact the settling surfaces (which include soil, grasses, trees and building etc.) is termed wet deposition. NO_x removed from the atmosphere is found in precipitation as NO_3^- and NO_2^-. Leaitech et al. (1985) observed that considerable amount of NO_3 in cloud water is formed by NO_2 oxidation both winter and summer.

Different stages involved in wet removal are as follows :

    a) Removal of those aerosols which act as cloud condensation nuclei.

    b) Removal of particles by clout droplets and hydrometers.

    c) Removal of gas by cloud droplets and hydrometers.

Dry Deposition : Pollutants either gases or small particles can also travell to ground level and settle on ground or other surfaces without first getting dessolved in the atmospheric water droplets, is called dry deposition. The term dry deposition only refers to the mechanism of deposition on collection surface irrespective of the nature of surfaces. The depstion velociteis of NO_2 on natural surfaces given in table no.11. Ehhalt et al. (1981) have estimated that world wide $(24 \pm 9) \times 10^6$ tonnes of nitrogen per year is removed as NO_3 or HNO_3, through dry and wet deposition where as a masimum of 7×10^6 tonnes nitrogen/year could be removed by dry deposition of NO_2.

NO$_x$ Effect on Plants

The studies on the NO$_x$ pollution effect on plants, dates back to 1950s, when Middleton et al. (1950) reported that the exposure of NO$_2$ induces injury. Early NO$_x$ studies were mainly focussed on symptomology of NO$_2$ injury (Middleton et al., 1950; Czeck and Nothdurft, 1952; Heck, 1964; MaClean et al., 1968; Spierings, 1971). A number of experiments were carried out to study the effect of NO$_x$ on plants over a wide range of NO$_2$ concentration (0.1 - 60 ppm) but, in most of studies plants have been exposed to the narrow range of 0.2-6 ppm NO$_2$. Certain species such as *Helianthus annuus, Lycopersicon esculentum, Phaseolus vulgaris, Medicago sativa* have been subjected to broad range of NO$_2$ concentration (0.1-30 ppm), while, other species such as *Glycine max, Pisum sativum, Nicotiana tabacum, Zea mays, Lactuca sativa, Hordeum vulgare and Gossypium hirsutum* NO$_2$ damage has been assessed over a short range of concentrations. In experiments, plants have been subjected to low as well as high concentration for short or long term exposure.

A review of studies on phytotoxic effect of NO$_2$ reveals that most workers considered 0.1 - 0.01 ppm NO$_2$ as low concentration. Similarly, exposure duration of less than or equal to 3 week is considered as short term exposure while the long term exposure may range from months to years. The effect of NO$_2$ stress has been evaluated at following level :

1. Morphological level in terms of visual fall or injury and plants yield;

2. Physiological level in relation to net photosynthesis, respiration and enzyme activity;

3. Biochemical level involving chlorophyll, protein, sugar content, Lipids and Fatty acids.

Literature review shows that most of studies of NO$_2$ effect on plants have been carried out on angiosperms as compared to gymnosperms, bryophytes and algae, mainly on growth parameters, symptomology, photosynthesis and yield. However, information is scanty on few important parameters of plant's life-cycle such as pollen grain, flowering and also on ultrastructural level etc.

Threshold Dose : Nitrogen oxides are much less phytotoxic than O_3 and PAN. Leaf symptoms would be expected at doses approximately 1.6-2.6 ppm (3000-5000 $\mu g/m^3$) for a period of upto 48 hrs. The National Academy of Sciences (1975) concludes that an exposure of 1 ppm may requires upto 100 hrs. to produce symptoms. It has been reported that the threshold concentration of 0.3 ppm to 1.0 ppm induces negative physiological responses. (Furukawa and Totsuka, 1979; Hill and Bennett, 1970; Saxe, 1986).

NO_x Injury Symptoms : Initial NO_x injury symptoms involve the development of diffuse discolored spots of grey, green or light brown colour. These spots eventually weather and dry before getting bleached. In angiosperms, the acute foliar symptoms produced by high concentration of NO_2 exposure are characterized by water socked lasions, which first appear on upper leaf surface, followed by rapid tissue collapse. In gymnosperm initial symptoms are characterized with red brown discoloration at the distal portion of needle base. High doses of NO_2 may cause net necrosis and leave only "fingers of green" along the veins. However, at lower concentration NO_x may interfere with physiological processes and reduce growth rate without producing easily identificable physical damage (Capron and Manasfield, 1976, 1977; Ashenden and Manasfield, 1978)

Mechanism of NO_x Action : Atmospheric NO_2 can enter the leaves by diffusion through stomata into substomatal cavity (Wellburn, 1990). From this compartment, NO_2 dissolve rapidly into the aqueous phase of the apoplastic space and can either undergoes the disproportionation reaction to nitrite and nitrate (Lee and Sichwartz, 1981).

$$2NO_2 + H_2O \quad = \quad H^+ + NO_2^- + HNO_3^-.$$
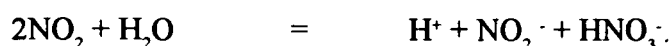
Nitrite ions is known to be toxic and the accumulation of nitrite ion causes damage.

The uptake of nitrite by plants and its assimilation can leads to alkalization :

$$3NO_3^- + 45CO_2 + 37H_2O \quad = \quad C_{45}H_{72}N_3O_{32}^- + 51O_2 + 2OH^-$$
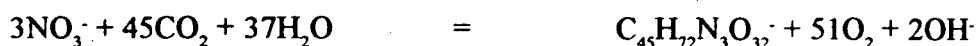
Each nitrogen molecule assimilation produces 0.78 mole OH⁻.

The nitrate accumulation occurs if nitrate reduction pathway becomes unable to cope with raised level of nitrate resulting from atmospheric NO, in presence of adequate supplies of NO_3^- from soil. There is well defined pathway in plants for the reduction of nitrate and nitrite (Beevers, 1976)

$$NO_3^- \xrightarrow{\text{nitrate reductase}} NO_2^- \xrightarrow{\text{nitrite reductase}} NH_4^+$$
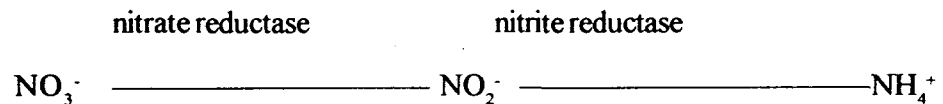
Under favorable conditions of growth, it is possible that small amount of nitrate resulting from low level of NO_2 pollution might be removed by the action of nitrate reductase. The activity of nitrate nitrite reduction pathway is thought to be controlled by nitrate not nitrite reductase and thus excess of nitrite from the external sources might effectively bypass normal points at which, the cellular pool of the toxic ion is controlled.

Studies have shown that NO_x can be metabolized by plants (Yoneyama, et al., 1979; Roger et al., 1979). It has been found that under condition of low nitrogen availability, NO_x exposure induces plants growth (Troiano et al., 1977; Anderson et al., 1979). This is probably due to incorporation of NO_2 in amino acids in the form of NH_2 (Zeevaart et al., 1974). It has been observed that the wet deposition leads to acid base perturbation in leaf tissues (Raven, 1988).

$$3HNO_3 + 45CO_2 + 35H_2O \quad = \quad C_{45}H_{72}N_3O_{32}^- + 45O_2 + H^+$$
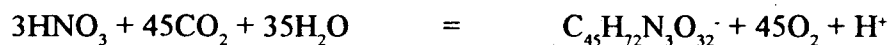
Raven, calculated that each HNO_3 leads to an excess of 0.22 mole H^+/mole N assimilation. However, the uptake of NO_3^- and its assimilation can lead to alkalization.

$$3NO_3^- + 45CO_2 + 37H_2O \quad = \quad C_{45}H_{72}O_{32}^- + 51O_2 + 2OH^-$$
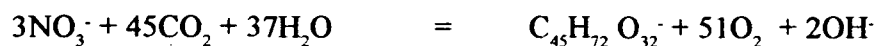
Pearson and Stewart (1990) found that tree species differ greatly in their ability to assimilate nitrate in their leaves.

The flux of atmospheric NO_2 in plants depend on atmoshperic NO_2 concentration, as atmosphere NO_2 concentration increases NO_2 fluxes increases (Johansson, 1987; Thoene et al., 1991; Rondon et al., 1993). In some cases it has been found that with temperature increase NO_2 deposition flux increases (Webber and Rannenberg, 1996). The high atmospheric humidity also increase NO_2 deposition rate as compaerd to low atmospheric concentration. (Thoene et al., 1991; Webber et al., 1996).

Effect of NO_x on Enzyme : It has been reported that NO_x exposure produces change in enzymatic activities of plants. (Horsman and Wellburn, 1975; Zeevaart, 1976; Wellburn et al., 1980; Besford and Hand 1989, 1990; Srivastava et al., 1994)

Ribulose bis-phosphate carboxylase (RUBISCO) is an important enzyme helps in CO_2 fixation, during C_3 cycle of photosynthesis. Enhanced RUBISCO activity under low level of NO_2 exposure (0.2 to 1 ppm for 2 weeks) has been observed in *Pinus banksiana and Picea*. Short exposure (48 hours) to a relatively high concentration (2 ppm) of NO_2 stimulates activity of RUBISCO in *Pinus banksiana*. In contrast, inhibition in activities of RUBISCO is reported, in *Betula papyrifera and Alnus crispa*, even at a low NO_2 concentration (0.2 ppm) (Khan and Malhotra, msd).

Nitrate reductase (Nak) is an enzyme that exhibits a diurnal rhythm in Nak activity (Melzer et al., 1989; Becker et al., 1992). It has been found that NO_2 exposure increases Nak activities in the shoots and needles of many species (Zeevaart, 1976; Norby et al., 1989; Wellburn, 1980; Srivastava et al., 1994), but not in Peppers and Tomato-cultivars in CO_2 enriched glass houses (Murray and Wellburn, 1985). NO exposure in presence of little NO_x has also been reported to increase NIR activities in Lettuce and Tomato (Wellburn et al., 1980; Besfard and Hand, 1989). In 1989, Besford and Hand, reported that increase in NIR activities is associated with NIR protein.

NO_x Effect on Amino acids and Proteins : NO_2 has been found to stimulate amino acid synthesis from CO_2 (Motsushima, 1972), plants have ability to metabolize the dissolved NO_x through their NO_3^- assimilation pathway :

$$NO_x \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \rightarrow \text{Amino acids} \rightarrow \text{Proteins.}$$

33
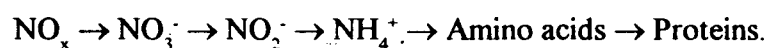
Table no. 13 : Effect of Short Term Exposure of NO_2 on Plants (<3 weeks).

Species	NO_2 concen. (ppm)	Effect	Reference
Avena sativa (Oat)	< 7	Reduction in photosynthesis rate	Hill et al., 1970
Beta vulgaris	30	Leaf damage	Thompson et al., 1970
Cichorium endivia (Endive)	< 7	Necrotic spots on leaf	Heck, 1964
		Marginal, intercostal leaf necrosis and shoot dieback	MaClean et al., 1968
Glycine max		NO stomatal effect	Aumundson et al., 1982
Gossypium hirsutum		Necrotic spots on leaf	Heck, 1964
Helianthus annuus		Increase in dry weight of root, stem and leaves	Fowler and Cape, 1982
		Increase in photosynthetic efficiency, net assimilation rate and in growth	Okano and Totsuka, 1985
		Reduction in dry weight and S/R ratio	Okano and Totsuka, 1985
Hordeum vulgare		Stimulation in shoot and root dry weight	Ronland et al., 1987
Lycopersicon esculentum		Decrease in dry weight and leaf area	Taylor and Eaton, 1966
		Increase in dry weight of root, stem and leaves	Troiano and Leone, 1977
		Reduction in photosynthesis rate	Capron et al., 1976
	40	Reduction in dry weight and leaf area	Capron and Manasfield, 1977

Species	NO$_2$ concen. (ppm)	Effect	Reference
Lycopersicon	40-60	Reduction in growth and photosynthesis rate	Hill and Bennett, 1970
Lactuca sativa (Lettuce)	30	Leaf damage	Czeck and Nothdurft, 1952
Medicago sativa (Alfalfa)	< 7	Reduction in photosynthesis rate	Hill et al., 1970
	30	Leaf stomatal damage	Czeck and Nothodurft, 1952
Phaseolus vulgaris (Bean)	< 7	Reduction in photosynthesis and respiration rate	Srivastava et al., 1990
		Reduction in dry weight and chlorophyll content	Taylor and Eaton, 1966
		Necrotic leaf spot	Heck, 1964
		Leaf injury	Middleton et al., 1958
	10	Increase in number of pods, relative growth rate	Sandhu and Gupta, 1989
Pisum sativum	< 7	Increase in transpiration rate	Ashenden, 1979
Secale cerale	30	Leaf damage	Czeck and Nothdurft, 1952
Vicia faba	< 7	Ultrastructural change in chloroplast	Wellburn et al., 1972
Zea mays		Reduction in dry weight and S/R ratio	Okano and Tosuka, 1985

Table no. 14 : Effect of Long Term Exposure of NO_2 on Plants (> 3 weeks).

Species	NO_2 concen. (ppm)	Effect	Reference
Citrus sps. (Naval orange)	< 3	Increase in leaf drop and fruit yield.	Thompson et al., 1970
		Leaf necrosis and leaf drop	Czeck and Nothdurft, 1952
Dactylus golemerata	≤ 6.8	Reduction in number of leaves, leaf area, number of tiller and in dry weight	Ashenden, 1979
Helianthus annuus (sun flower)	< 3	Increase in dry weight of root, stem and leaves	Fowler and Cape, 1982
Lycopersicon esculentum (Tomato)		Reduction in leaf, petiole, weight, stem size and fruit yield	Speirings, et al., 1971
		Reduction in fresh weight	Speirings et al., 1971
		Stimulation in growth	Troiano and Leone, 1977,
		Inhibition in growth	Hufton et al., 1996
Lolium multiflorum		Reduction in number of leaves, leaf area and number of tiller	Ashenden and Williams, 1980
Phaseolus vulgaris (Bean)		Increase in relative growth rate and total plant weight	Sandhu and Gupta, 1989
Pisum sativum		Stimulation in growth	Edelbauer and Maier, 1988
Poa pratensis		Reduction in number of leaves and leaf area	Ashenden and Williams, 1980
P. pratensis monopoly		Increase in number of leaves, number of tiller and decrease in shoot dry weight	Whitemore and Manasfield, 1983

NO_x exposed plants can accumulate and metabolize various products of the above pathway (Zeevaart, 1976; Yoneyama and Sasakawa, 1979; Kaji et al., 1980). It has been observed that most of the absorbed NO_x is transformed into reduced organic compounds.

NO_2 effect on Fatty acids and Lipids : There are limited informations available in literature about the effect of NO_x on the lipid metabolism in vascular plants. The Fumigation of *Pinus banksiana* seedling with 2 ppm NO_2 for 8 hrs. showed inhibition in lipid biosynthesis of chloroplast membranes. Young and Mudd, 1966, reported inhibition of lipid synthesis by NO_2^- in *Chlorella pyrenoidosa*. It has been found that inhibition is greater in dark than light, this is due to an increased supply of NADPH in the light stimulated reaction of NO_2^- to NH_4^+, which does not affect biosynthesis even in dark (Yung and Mudd, 1966).

Effect of NO_x on Photosynthesis : Suppression of photosynthesis by NO_x has been reported in literature. It has been found that NO_2 concentration applied up to 90 nll^{-1} does not affects photosynthesis of wheat plants (Saxe, 1986, Thoene et al., 1991, Webber and Rennenberg, 1996). inhibition of photosynthesis was observed only in long term exposure (720 hrs.) experiments, by using high concentration of (0.5 ppm - 9.0 ppm) (Hill and Bennett, 1970; Saxe, 1986; Darell, 1989), even at high concentration of NO_2, inhibition of photosynthesis seems to be restricted to few plant species (Saxe, 1986).

It has been found that NO_2 with SO_2 shows synergistic effect on photosynthesis (Hill and Bennett, 1970; White et al., 1974; Wellburn et al., 1976; Furukawa and Totsuka, 1979; Reinert and Gray, 1981).

Effect of NO_x on Ultrastructural Level : There are limited studies available on NO_x effect on ultrastructural level. Wellburn et al. (1972) showed that NO_2 causes swelling of chloroplast membranes. It has been also reported that NO_2 inhibits pigment synthesis in leaves (Zeevaart, 1976).

Relative Susceptibility of Plants to NO_x Pollution : The information on relative susceptibility

of plants to NO_x (primarily NO_2) is limited and entirely based on experimental fumigation. A relative ranking of plants are given in table no. 15, on the basis of work done by several scientists (MaClean, et al., 1968; Heck, 1964; Tingey, 1969; Taylor and Eaton, 1966; Wellburn, 1976; Saxe, 1994).

NO_2 Interaction : Heck (1968) first, reported foliar injury due to SO_2 and NO_2 mixture in *Nicotiana tabacum*. Later, Tingey et al. (1971) published first important paper on synergistic effect of SO_2 and NO_2. They found that mixture of SO_2 and NO_2 at a concentration of less than 200 ppm 25 parts 10^{-8} causes substantially more damage than the same amount of either of the pollutants alone, and more than sum of their separate effects. The synergistic effect have been reported in a number of plant species, *Lolium multiflorum Dactylus glomerata, Phelum pretense and Poa pratensis* (Ashenden and Manasfield, 1978; Ashenden, 1979; and Ashenden and Williams, 1980; Wellburn et al., 1981) *Phaseolus vulgaris*, (Ashenden, 1979), *Medicago sativa* (White et al., 1974) *Pisum sativum*, (Bull and Manasfield, 1974; Harshum and Wellburn, 1975) *Populus nigra* (Freer-smith, 1984), *Betula pendula* and 13 *B. pubescens* (Neighbour et at., 1988).

However, in contrast Hill et al. (1974) studied the effect of $SO_2 + NO_2$ combination on 10 species of plants native to Mojave desert and found no synergism. It has been reported that annuals are more severely affected than perennials, and tended to show antagonistic effect rather than additive effect.

Most of studies on synergistic effect of SO_2 and NO_2 have been carried out in concentration range 0.001 to 25 ppm. A comparative list of various studies on NO_x synergistic effect on plants, under and long term exposures are given in table no. 16 and 17.

Table no. 15 : Relative Suseptibility of Plants to NO$_x$ Pollution.

Sensitive plants	Moderately sensitive	Relatively insesitive
Field and Horticultural Crops	**Field and Horticultural Crops**	**Field and Horticultural Crops**
Vicia sativum	Secale cereale	Brassica oleracea var. gongylodes
Pisum sativa	Petunia multiflora	Allium cepa
Medicago sativa	Rhododendron catawbiense	Brassica oleracea var. capitata rubra
Trifolium incarnatum	Dahlia varibilis	Brassica oleracea acephala
Trifolium pratense		Brassica oleracea var. capitata rubra
Daucus carota		
Lactuca sativa		
Nicotiana tabacum		
Sinapis alba		
Lupinus augustrifolius		
Avena sativa		
Petroselinum hortense		
Allium porrum		
Scorzonera hispanica		
Hordeum distichon		
Rheun rhubarbarum		

Sensitive plants	Moderately sensitive	Relatively insesitive
Ornamental plants	**Ornamental plants**	**Ornamental plants**
Antirrhinum majus	Fuchsia hybrida	Chrysanthemum leucanthemum
Begonia multiflora	Petunia multiflora	Convallaria majalis
Rosa sp.	Rhododendron catawbiense	Gladiolus communis
Lathyrus odoratus	Dahlia variabilis	Hosta sp.
Callistephus chinensis		
Coniferous trees	**Coniferous trees**	**Coniferous Trees**
Larix europea	Picea pungenus glauca	Taxus baccata
Larix leptolepis	Picea alba	Pinus austriaca
	Chamaecyparis lawsoniana	Pinus montana mughus
	Abies homolepis	
	Abies pectinata	
Deciduous trees	**Deciduous trees**	**Deciduous trees**
Betula pendula	Acer platanoides	Robinia pseudoacacia
Malus sp.	Acer palmatum	Carpinus betulus
Pyrus sp.	Tilia parvifolia	Fagus sylvatica
	Tilia grandiflora	Sambucus nigra
		Ginkgo biloba
		Ulmus montana
		Fagus sylvatica atropurpurea
		Quercus pendunculata

Table no. 16 : Effect of Short Term Exposure of NO_2 + SO_2 on Plants (<3 weeks).

Species	NO_2 concen. (ppm)	Effect	Reference
Glycine max	<2	Decrease in photosynthesis and stomatal conductance	Carlson, 1983
Hordeum vulgare		Reduction in growth rate	Pandey and Manasfield, 1985
		Decrease in stomatal closure speed	Atkins, Wooky and Manasfield, 1991
Medicago sativa		Inhibition in apparent photosynthesis	White, Hill and Bennett, 1974
Pisum sativum	10-25	Inhibition of photosynthesis	Bull and Manasfield, 1974
Phaseolus vulgaris	< 2	Visible injury	Bennett et al., 1975
		Inhibition in apparent photosynthesis	White, Hill and Bennett, 1974
		Reduction in transpiration rate	Ashenden, 1979
		Reduction in growth	Taylor and Eaton, 1966

Table no. 17 : Effect of Long Term SO$_2$ + NO$_2$ Exposure on Plants (>3 weeks).

Species	NO$_2$ + SO$_2$ Concentration (ppm)	Effect	Reference
Betula pendula B. pubescens	< 1.0	Increase in transpiration rate	Neighbour et al., 1988
Dactylus glomerata	≤ 6.8	Reduction in leaf area, leaf number and dry weight	Ashenden, 1979
Helianthus annuus	< 1.0	Increase in dry weight of root, stem and leaves	Fowler and Cape, 1982
Hordeum vulgare		Reduction in all growth parameters	Pandey and Manasfield, 1985
		Reduction in growth	Kasana and Lea, 1994
Lolium multiflorum	≤ 6.8	Reduction in number of leaves, leaf area, number of tiller and dry weight	Ashenden and Williams, 1980
Phellum pratence /		Reduction in all growth parameters like, number of leaves, leaf area and dry weight	Ashenden and Williams, 1980
Populus nigra	< 1.0	Reduction in translocation of assimilates to root system	Freer-smith, 1984
Poa pratensis	≤ 6.8	Reduction in number of leaves, dry weight, and number of tiller	Whitemore and Manasfield, 1983
		Reduction in number of leaves, number of tiller, leaf area and dry weight	Ashenden, 1979
Triticum vulgare		Reduction in growth	Murray et al., 1994

42

Literature review shows that most of the NO_2 interaction studies have been carried out on angiosperms for long term exposures and for a concentration range of 0.1 ppm to 25 ppm on growth parameters and on few plants species such as :

1.   Phaseolus vulgaris,   3.   Hordeum vulgare

2.   Glycine max   4.   Hellianthus annuus

There is limited studies of NO_x synergistic effect on important plant parameters such as reproduction, biochemical, ultrastructural etc. and also on plant groups such as pteridophytes, gymnosperms, bryophytes and algae.

Development of NO_x Passive Sampler

The conventional techniques such as high volume passive sampler, handy sampler, continuous sampler etc., have been predominantly used throughout world for NO_2 monitoring in the ambient environment. The conventional sampling techniques are bulky, expensive, complex in operation, require on site power and specialist maintenance. These techniques cannot be used for large scale air quality monitoring specially in remote rural areas, having no electricity and other basic infrastructure.

It was felt that there is a need for a new, cheap, small, light weight, robust, easy and simple techniques, to overcome problems associated with conventional methods to determine spatial distribution of air pollutants .

The method of sampling by means of cheap, simple diffusion tube first developed in America as on - person air sampler by Palme et al. (1976), and subsequently, used widely for the study of indoor environment (Palme et al., 1977; Melia et al., 1978; Atkins et al., 1978, 1980; Boleij et al., 1978; Ramijn et al., 1984; Noy et al., 1984), outdoor environment : urban environment (Bower et al., 1991; Hewitt, 1991; Campbell et al., 1994; Heal et al., 1997) Rural environment (Goldsmith, 1986; Campbell, 1988; Ashenden and Bell, 1989; Gair et al.,

1991; Atkins and Lee, 1995) and both in urban and rural environment (Perkauskas and Mikelinskience, 1998; Ferm and Svanberg, 1998).

The Palme sampler is a tube type passive sampler consist of 7.1 cm long and 1.08 cm diameter acrylic tube, two TEA coated stainless steel wire mesh of 0.2 mm mesh size and 0.1 mm wire diameter and of two polyethylene caps. The palme passive sampler is shown in figure no. 7.
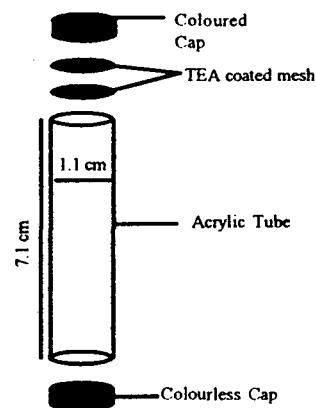
Figure no. 7 : Palme Passive Sampler

In Palme passive sampler TEA employed as absorbing agent, it has low sampling rate, due to slow rate of NO_2 absorption by TEA. Consequently, it requires many hours or days to obtain an adequate sample, at low ambient levels of NO_2.

In order to overcome slow sampling rate of tube type passive sampler (Palme sampler). Cadoff and Hodgeson (1983) designed a high sampling rate passive sampler.

This passive sampler consist of a nucleopore 47mm aerosol holder. The base of holder is attached with a sampling pump. Which is capped with a polyethylene cap. A gelman type-A glass fibber filter is used. The effective sampling rate is 110ml/min and the lower limit of estimation is 0.001ppmh exposure.

Amaya and Sugiura (1983) devised a Badge type sampler. It was reported that wind velocity and air temp seriously affect the accuracy and efficiency of the sampler. (In the range of upto 3m/s of wind velocity an over 150 per cent growth in the mass of NO_2 collected in sampler as nitrite was noted Krochmal and Gorski, 1991).

Later on Mullik et al., (1989) devised a high efficiency passive sampling device (fig. no.8). It is a dual faced sampler made up from a series of diffusion barriers placed on either side of cavity with a protective case and a O-ring sealed cap for closure before and after exposure. The whatman GF/B filter paper is used as trapping medium. The effective sampling rate is 154cm3/min and the lower limit of estimation is 25mg/m^3 for one hour.

Membrane Support   *Porous Membrane*

Internal Diffusion Path

NO2 Collector
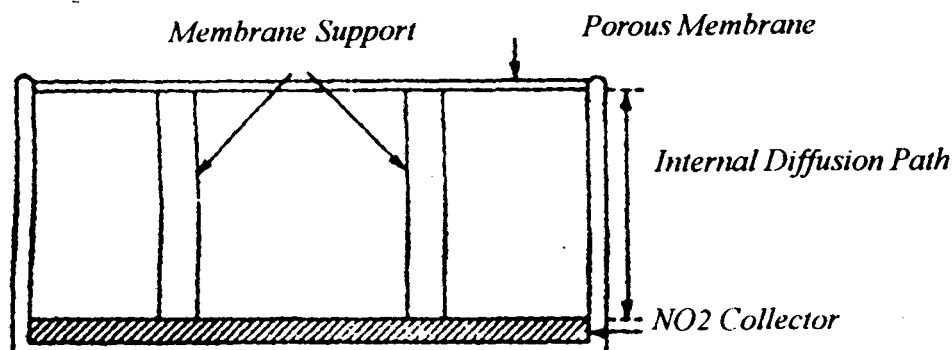
Fig. no. 8 : Diagram of a high efficiency passive sampler.

To diminish wind effect on Amaya and Sugiura Passive Sampler (badge type), a modified sampler was constructed by Krochmal and Gorski, (1991). Sampler is shown in figure no.9.

Holder

Middle Part

Career Coated with TEA Solution

Ring with porous membrane

Cap
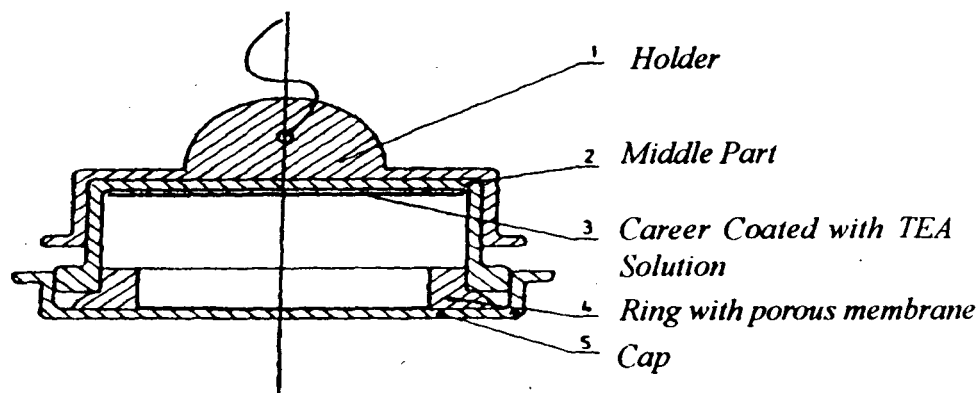
Fig. no. 9 : Modified Passive Sampler (badge type).

In modified sampler, a disk of polypropylene fibber is welded to the ring and a 25mm disk of polyamide textile is applied as a carrier of absorbent. The modification leads wind effect diminished from about 150 per cent to maximum 20 per cent, while the relative precision of method characterized by RSP is 10 per cent. The lower limit of estimation is 10mg/m^3 for 24 hours exposure. In order to improve its collection efficiency Krochmal and Kalina (1997)

45

used Whatman 1 chr filter at the place of polyamide disk. It has been observed that the sampler with Whatman GF/B disk as TEA carrier has 50 per cent higher collection efficiency than that of sampler with a nylon textile disk. The use of this type of sampler has minimized the influence of several meteorological factors like sunlight, precipitation, wind velocity and temperature on the sampling rate, and can be regarded in most situation insignificant. The precision of method as RSD is 6 per cent and the lower determination limit for monthly exposure of sampler is 0.5 to 0.7 mg/m^3.

In order to diminish wind effect on tube type passive sampler (Palme sampler), Ferm and Svanberg (1998) modified Palme sampler (Fig. no.10.).

Fig. no. 10 : Diagram of Modified Palme Passive Sampler.

It consist of 50mm long polypropylene vial with a threated cap at one end. An impregnated filter is placed in solid cap. The second end is protected using a fine stainless steel screen, to avoid turbulence diffusion inside the tube. The mixture of potassium and sodium arsenite is used to trap NO_2. The tube has lower detection limit around $4mg/m^3$ for a week and monthly range of sampling between 0.1 to 400 mg/m^3.

A list of various studies which is contributed to the development of sampler are given in table no.18.

Literature review shows that majority of the studies (approximately 98 per cent) have been carried out by tube type passive samplers, using stainless steel mesh and TEA solution as absorbent. It has been found that in majority of studies that passive samplers result has good agreement with continuous monitor results. A number of experiments have shown that suitable

Table no. 18 : Details of Various Studies Which have Contributed to the Development of NO$_x$ Passive Sampler.

Type of sampler	Place of study	Climatic zone	Filter used (mesh)	Absorbent used	Exposure duration	Reference
T. type	Indoor env., U.S.A.	Temperate	Stainless steel	TEA solution	1 W	Palme et al., 1976, 1977
T. type	Urban, U.K.	Temperate	Stainless steel		2 W	Atkin et al., 1978
H.R.S.	Lab., U.S.A.	—	Gelman type A		1 - 13 D	Cadoff and Hodgeson, 1983
T. type	Indoor, Netherland	Temperate	Stainless steel		1 - 7 D	Boleij et al., 1986
T. type	Street Canyon, U.K.	Temperate	Stainless steel		1 W	Laxen and Noordally, 1987
T. type	Rural, U.K.	Temperate	Stainless steel		2 - 4 W	Campbell, 1988
T. type	Lab, U.S.A	—	Stainless steel		66 - 106 D	Miller, D.P., 1988
T. type	Rural, U.K.	Temperate	Stainless steel		2 W	Ashenden and Bell, 1989
H.E.S.	Lab., U.S.A.	—	Whatman GF/B glass micro filter		1- 13 D	Mullik, Lewis & MaClenny, 1989
T. type	Urban, U.K.	Temperate	Stainless steel		4 W	Bower et al., 1991
T. type	Remote site, Sweden	Taiga	Stainless steeel		4.5 - 8.7 D	Gair et al., 1991
T. type	Urban, U.K.	Temperate	Stainless steel			Hewitt, 1991
B. type	Lab., Poland	—	Polyamide disk of textile		1 - 7 D	Krochmal and Gorski, 1991

Type of sampler	Place of study	Climatic zone	Filter used (mesh)	Absorbent used	Exposure duration	Reference
T. type	Urban and Rural, U.K.	Temperate	Stainless steel		4 W	Campbell et al., 1994
T. type	Rural, U.K.	Temperate	Stainless steeel		2 W	Atkins and Lee, 1995
T. type	Urban, U.K.	Temperate	Stainless steel			Heal and Cape, 1997
B. type	Lab and field, Poland	Temperate	Stainless steel		10 - 30 D	Krochmal and Kalina, 1997
T. type	Indoor, U.K.	Temperate	Stainless steel		1 W	Colbeck, 1998
M.T. type	Urban, Swedan	Taiga	Sintered glass filter	Mixture of Potacium iodid and sodium arsenate		Ferm & Svanberg, 1998
T. type	Urban, U.K.	Temperate	Stainless steel	TEA solution		Kirby et al., 1998
T. type	Urban, Lithuania		Stainless steel		4 W	Perkauskas and Mikelinskiene, 1998
T. type	Denish Island, Denmark	Temperate	Stainless steel			Glasius et al., 1999
T. type	Urban, U.K.	Temperate	Stainless steel		1- 4 W	Heal et al., 1999

Note :   T. type =   Tube type   H.R.S. =   High Rate Sampler   M.T. type   =   Modified Tube type
             B. type =   Badge type   H.E.S. =   High Efficiency Sampler   D   =   Days
             W   =   Weeks

length of exposure in urban and rural areas is 7days and 15days respectively. About 90 per cent studies with passive sampler have been done in temperate climate, remaining in taiga and subtropical climate, there are no studies from the tropical areas.

Principle of Passive Sampler

The basic principle underlying passive diffusion tube operation is that a concentration gradient is established along the length of the tube.

The atmospheric NO_2 diffuses up the tube where it gets absorbed on TEA coated mesh. This establishes a NO_2 concentration gradient along the length of the tube consequently NO_2 defuses up the tube where it is absorbed on TEA coated meshes. The reaction product of TEA and NO_2 have been studied. Levaggi et al. (1972) proposed that NO_2 reacts with TEA to give triethanolamine nitrite and triethanolamine nitrate, and later Gold (1977) found that with concentrated NO_2 gas the reaction products were nitrite and triethanolammonium nitrate (1:1) Aoyama and Yashiro (1983) detected nitrosodiethanolamine as reaction product but recently Glasius et al. (1999) identified as triethanolamine N-oxide.

$$2NO2 + N(CH_2CH_2OH)_3 + 2OH^- \text{-------} > 2NO_2 + ON^+(CH_2CH_2OH)_3 + H_2O_2.$$
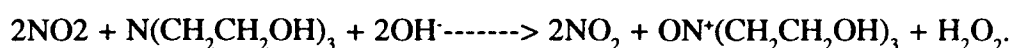
This is supported by observations of Palmes and Johnson (1987)

A steady state, molecular diffusion along the gradient is determined by Fick's first law of diffusion. The unidirectional flow of a gas_1, through a gas_2 is given by Fick's law.

$$F_1 = -D_{12}dc_1 / d_z \qquad (1)$$

where F_1 is the flux of gas (mol $cm^{-2}s^{-1}$), D_{12} is the diffusion coefficient of gas_1 in gas_2 ($cm^{-2}s^{-1}$), C_1 is the concentration of gas_1 in gas_2 (mol cm^{-3}) and z is the length of diffusion (cm). The quantity of gas transferred (Q_1 mol) in t second for a cylinder of r radius given by eq. 2 and 3.

$$Q_1 = F_1 (\pi r^2) t \text{ mol.} \qquad (2)$$

Therefore

$$Q_1 = -D_{12} (C_1 - C_0) (\pi r^2) \, 1/z \text{ mol.} \qquad (3)$$

where C_0 is the concentration experienced at the absorber surface, therefore $(C_1 - C_0/z)$ is concentration gradient along the cylinder length(z). If an efficient absorber is used to remove gas_1 then C_0 effectively becomes zero. For using diffusion tube samplers the number of moles of NO_2 collected is given by eq.(4), where C_1 is the concentration (mol. cm^{-3}) of NO_2 in ambient air and the diffusion coefficient for NO_2 in air is 0.154 cm^2s^{-1} (Palmes et al., 1976).

$$Q = -0.154(C_1) (0.92) \, 1/7.1 \text{mol.} \qquad (4)$$

Therefore in one hour (3600s) the diffusion tube absorbs $72C_1$ mole of NO_2 (eq.5), the negative sign is ignored as it arises from the direction of the flux flow from high to low concentrations.

$$Q = 72.C_1 \text{cm}^3\text{h}^{-1} \qquad (5)$$

It can be shown that the atmospheric concentration of NO_2 (Yppbv) is :

$$Y = 7.3099WX \, / \, t \ \text{ppbv } NO_2$$

where W is the volume of solution (ml) used to dissolve TEA, X is the concentration of NO_2^- in the TEA solution (ppbm) and t is the exposure time (h).

Validation of NO_x Passive Sampler

A number of attempt have been made to validate NO_x passive sampler. For validation experiments, passive samplers were deployed along with continuous NO_x monitor, at various sites (urban, rural, road site), under different weather conditions (summer, winter) with exposure time ranging from 1-2 weeks. Most of the validation studies for passive samplers have been carried out with the continuous monitors (chemiluminescent analyser) (Apling et al., 1979; Cadoff et al., 1979; Hoen et al., 1984; Boleij et al., 1986; Atkins et al., 1986; Wilson, 1987; Campbell et al., 1988; Bower et al., 1991; Gair et al., 1991; Heal and Cape, 1997; Krochmal et al., 1997; Heal et al., 1999; Glasius et al., 1999).

Comparison of the passive sampler performance with techniques other than continuous monitor such as, TGS-ANSA method (Gair et al., 1991), Saltzman Arsenic method (Krochmal and Kalina, 1997) are very few and have been carried out in temperate climate. Only one such study has been attempted in arctic climate and so for none has attempted in tropical region.

Out of the 15 studies carried out for validation, 10 studies have shown that there is good agreement between the result of NO_x passive sampler and continuous NO_x monitors in urban areas in summer. However, in winter passive samplers found to overestimate (Hoen et al., 1984; Bower et al., 1991; Gair et al., 1991; Campbell, 1994).

A number of studies have shown that difference in the result between passive sampler and continuous monitor is within 5 to 10 per cent (Atkins et al., 1986; Bower et al., 1991; Gair et al, 1991; Krochmal and Kalina, 1997; Glasius et al., 1999). However, Heal and Cape, 1997; Heal et al., 1999, have shown 27 per cent over estimation by passive samplers. Results of various validation experiments have been compiled in table no.19.

Most of the studies have shown that the precision of these methods varied between 5 to 8 per cent (Atkins et al., 1986; Gair et al., 1991; Atkins and Lee, 1995; Krochmal and Kalina, 1997), however according to Campbell (1988) the precision of the method is about 10 per cent.

Effect of Wind on the Performance of Passive Sampler : Effect of wind velocity on the performance of passive sampler has been studied (Atkins et al., 1986; Krochmal an Gorski, 1991; Gair et al., 1991; Campbell et al., 1994; Gair and Penkett, 1995; Ferm and Svanberg, 1998).

Earlier reports of passive sampler studies have suggested that there is no significant effect of air turbulence on the performance of passive sampler (Atkins et al., 1986). These reports were based on a comparison between the result of NO_2 measurements obtained using passive sampler

Table no. 19 : A Compilation of the Results of Studies Dealing with Validation of NO$_2$ Passive Sampler.

S. N.	Techniques used for validation	Land use/activity	Climatic zone	Result	Precision of P.S.	Reference
1.	Continuous monitor	Indoor environment, U.K.	Temperate	Difference in result between two techniques were within a range of 8-9 percent	Better than 2 ppb for a week	Apling et al., 1979
2.	Continuous monitor	Indoor environment, Sweden	Taiga	Good agreement between result of the two techniques	—	Hoen et al., 1984
3.	Continuous monitor	Urban, other Urban and Rural, U.K.	Temperate	Good agreement between result of the two techniques at urban sites, However P.S. result were 1.26 time of C.M. result at rural site	—	Campbell, 1994
4.	Continuous monitor	Urban and Rural, U.K.	Temperate	Difference in result between two techniques were < 5 percent	About ± 7 percent	Atkins et al., 1986
5.	Continuous monitor	Indoor environment, Netherland	Temperate	The readings with P.S. were higher than C.M.	Better than 4 μg/m^3 for a week exposure	Boleij et al., 1986
6.	Continuous monitor	Urban and Rural, U.K.	Temperate	Good agreement between result of two techniques	About 10 percent and accuracy ± 7 percent	Campbell, 1988
7.	Continuous monitor	Urban, U.K.	Temperate	Difference in result between two techniques were within ± 5 percent		Bower et al., 1991
8.	Continuous monitor	Remote site, Sweden	Taiga	Good agreement between result of two techniques. However the readings with P.S. were higer in winter (app. : ± 15 percent)	About 6.5	Gair et al., 1991

S. N.	Techniques used for validation	Land use/activity	Climatic zone	Result	Precision of P.S.	Reference
9.	Luminitol based chemiluminisent NO$_2$ monitor	Arctic, Sweden	Taiga	Results of P.S. without blank value substraction were similar to L.C.M. results	About ± 6.5 per.	Gair et al., 1991
10.	T.G.S.-ANSA method	Remote site, Sweden	Taiga	two techniques during summer. However. readings with P.S. were higher in winter (± 15 percent)	± 6.5 percent	Gair et al., 1991
11.	Saltzman - Arsenic, method	Urban, Poland	Temperate	Difference in result between two techniques were 10 percent	± 6 percent	Krochmal and Kalina, 1997
12.	Continuous monitor	Urban, Poland	Temperate	Difference in result between two techniques were 10 percent	± 6 percent	Krochmal and Kalina, 1997
13.	Continuous monitor	Urban and Rural, U.K.	Temperate	P.S. overestimated 8-14 percent in urban area, during winter and 28 percent during summer.	—	Heal & Cape 1997
14.	Continuous monitor	Urban, U.K.	Temperate	27 percent overestimation by P.S. The mean ratio between result of P.S. and C.M. was 1.06.	< ± 5	Heal et al., 1999
15.	Continuous monitor	Denish island, Denmark and Itly	Sub-tropical (Meditterranean region)	10 percent overestimation by P.S.	—	Glasius et al., 1999

Note : P.S. = Passive sampler   L.C.M. = Luminital based continious monitor

C.M. = Continuous monitor   T.G.S.-ANSA =

(diffusion tube) with those obtained using a chemiluminescent NO_x monitor at varying wind speeds (1-5m/s).

However, later it has been observed that wind speed leads to reduction in the diffusion length of tube (Campbell et al, 1994; Gair and Penkett, 1995; Ferm and svanberg, 1998). For outdoor exposures, a reduction in diffusion length of passive sampler was estimated between 7-38 per cent. (Gair and Penkett, 1995). The results of the studies of wind effect on diffusion length of passive sampler are given in table no.20.

Table no. 20 : Effect of Wind on Diffusion Length of Passive Sampler.

S.N.	Length of sampler (in cm)	Diameter of sampler (in cm)	Type of sampling	Reduction in diffusion length (in cm)	Reference
1.	4-14	—	Outdoor	2.3	Gair et al., 1993
2.	7.0	1.1	Outdoor	2.0	Campbell, 1994
3.	7.1	1.2	Outdoor	12.6 ± 1.4	Gair and Penkett, 1995
4.	5.0	1.2	Outdoor	2.3	Ferm and Svanberg, 1998

Gair and Penkett (1995) reported that wind speed and turbulence are not directly comparable and the relationship between wind speed and reduction in molecular diffusion length is non-linear. There is a need of further research to determine the type and significance of the relationship between the reduction in diffusion length and turbulence. Gair et al. (1993) reported that the tubes mounted in sheltered location shows negligible effect of wind i.e. wind effect is site dependent.

It has been proposed that wind effect on passive sampler can be minimised by using protective screen at the open end of sampler (Ferm and Svanberg, 1998) or by mounting tubes at sheltered location (Gair et al., 1993). The use of longer tube would be to reduce effect of turbulence. However, this would decrease the sampling rate of the sampler.

Literature review shows that no consensus has yet been reached on the exact nature or magnitude (if any) of wind effects and systematic correlations for such an effect have not been applied to passive sampler data.

Effect of Temperature on Passive Sampler : The effect of temperature on the performance of passive sampler has been studied (Palme et al., 1976; Kring et al., 1981; Girman et al., 1983; Motsumo and Mizoguchi; 1988; Krochmal and Gorski, 1991).

Palme et al. (1976) claimed insignificant influence of temperature on the performance of passive samplers. However, a number of studies have shown considerable increase in passive sampler uptake, with temperature rise. Effect of temperature on passive sampler uptake is shown in table. no.21.

Table no. 21 : Effect of Temperature on NO_2 Passive Sampler Uptake.

S.N.	Increase in temp. (°C)	Increase/decrease in passive sampler uptake (percentage)	Reference
1	5	+1	Palme et al.,1976
2	10	+15.5	Kring et al., 1981
3	10	+12.3	Girman et al., 1983
4	10	+18	Motsumo and Mizoguchi, 1988
5	10	+21	Krochmal and Gorski, 1991.

Note : + = increase

Krochmal and Gorski (1991) reported that in the temperature range of 0 to 30°C, sampler uptake increases on average by 21 per cent per 10°C temperature increase, for Nylon as TEA carrier. However for Whatman GT/C disks 11 per cent. It has been reported that in low temperature range of -22°C to 10°C, passive sampler underestimates NO_2. In fact, the process is even more complicated due to two reasons. First, TEA solidifies at 21.2 °C; second aqueous TEA used in passive samplers absorb or desorb water in such quantities that an equilibrium

concentration, appropriate to relative humidity, is reached in period of several hours.

Effect of Humidity on the Performance of NO_x Passive Sampler : There are few studies in which humidity effect on passive sampler performance have been reported (Boleij et al; 1986, Krochmal and Gorski, 1991).

It has been reported that 25 per cent increase in mass of NO_2 absorbed, when the relative humidity rose from 0 to 100 per cent (Krochmal and Gorski, 1991) A comparison was made using samplers prepared following the usual procedure and the sampler that were additionally dried did not show any significant difference in air collection efficiency because at 20°C the concentration of TEA in absorbing solution reach equilibrium value in several hours, corresponding to the relative humidity.

In the practical use of passive samplers, the humidity effect should be of lesser significance because the relative humidity of ambient air usually exceeds 40 per cent. Nevertheless, further work is necessary to establish the optimum concentration of TEA solution could be affected by the relative humidity of ambient air to the most limited extent.

Effect of Interference from Gases on the Performance of Passive Sampler : The effect of interference from gases on the performance of passive sampler has been studied by Gair et al., 1991; Heal and Cape, 1997; Heal et al., 1999. The atmospheric constituents which can interfere with the diffusion tube techniques are gaseous HNO_2, PAN, NO and O_3. These gases likely to efficiently produce nitrite on hydrolysis. The concentration of HNO_2 in the atmosphere is unlikely to significantly affect the measurement of NO_2 since, it is readily photolysed by sunlight and present only at insignificant levels in the remote atmosphere. (Gair et al., 1991).

Gair et al., (1991) studied the PAN interferences on diffusion tube sampler. He found that, there was

a very small response of diffusion tube sampler to PAN (less that 6per cent). The actual response to PAN could be even lower than observed in the experiment because thermal equilibrium exists between PAN and NO_2.

Experimental studies have also shown that PAN can complex with TEA and with as an additional source of NO_2 during extraction of the adsorbent (Hisham and Grosgean, 1990). It has reported than when PAN is greater than about 20 per cent of NO_2 input, then it contribute more than a few per cent of total NO_2 collected (Heal & Cape, 1997).

In a recent publication (Heal & Cape, 1997) it has highlighted that the reaction between NO and O_3 within tube lead overestimation of NO_2. Although the effect of chemical overestimation is likely to be significant only in urban environment, where direct local sources of NO increase substantially the fraction, on average, of NO to total NO_x ($= NO + NO_2$). In rural environment, where NO < NO_2, N < O_3 and total NO_x ($NO + NO_2$), the diffusion tube measures NO_x rather than, NO_2. However, in practice the differences between NO_2 and NO_x is likely to be within the measurement uncertainty.

Advantage of Passive Sampler : The advantage of diffusion tube sampler are following :

1) It is a cheap, light weight, robust and simple technique, which is easy in operation and handling.

2) It is ideally suited for wide spatial measurement of NO_x in the field.

3) Passive samplers can be mailed before and after exposure.

4) All parts of the sampler are reusable.

5) Diffusive sampling has many advantage in field over conventional sampling technique because it does not requires calibration, electricity and maintenance.

6) Passive samplers can also be used to measure background concentrations at places where other techniques cannot be used.

7) In urban areas, the passive samplers can be place on street lamps, at highways,

traffic tunnels, parks and office buildings, on persons etc. depending on the purpose of measurement.

8)   Diffusion tube sampler are stable for several months before as well as after sampling therefore, it can be used in very remote areas.

Disadvantage of Passive Sampler : The principle disadvantages of passive sampler can be discussed under following points :

1)   Poor temporal resolution

2)   Diffusion tube measure cumulative dose and typically must remain in the field for several days or weeks to collect sufficient NO_2 in the TEA, to extract and quantify reliably.

3)   Lack of complete specificity towards NO_2.

4)   Sampling problems caused by meteorological conditions.

5)   There are conflicting results from a number of previous studies, which have compared measurement of NO_2 in parallel trials between passive diffusion samplers and real time continuos techniques such as chemiluminescence (Atkins et al., 1986; Campbell et al., 1999). In particular, Campbell et al. (1994); Gair and Penkett found that NO_2 concentration overestimated by upto 40 per cent by diffusion tubes in exposed positions. This was attributed to a shortening of the position effective diffusion length of the tube, although a number of scientists (Atkins et al., 1986; Bower et al., 1991; Gair et al., 1991; Krochmal & Kalina, 1997; Glasious et al., 1999) observed no significant difference for NO_2 concentrations measured during validation trials in the field.

6)   Mosehandreas et al. (1990) reported that low temperature in the range 251-283 K results underestimation of NO_2 because of possible anomalous behavior of the TEA below its freezing point of 294 K.

7)   Under certain conditions, chemical reactions within the tube lead to a significant increase in average NO_2 concentration in passive samplers, and may be one factor contributing to the experimental discrepancies.

Information Gap

The foregoing literature review has revealed the following loopholes :

1. A number of studies have been carried out on the development of passive samplers, whilst the studies on effect of wind, temperature, pressure, humidity and interference from atmospheric gases on passive sampler are limited.

2. The NO_2 monitoring studies with passive sampler in sub-tropical/tropical climate are almost lacking. However, most of the studies with passive samplers have been carried out in temperate climate.

3. There is complete lack of any attempt to validate passive sampler under sub-tropical/tropical climate.

4. In India NO_2 problem is becoming severe day by day. However, there is limited information available on NO_2 behavior and effects. There is a need for research in India about NO_x background concentration, seasonal and diurnal variation as well as assessment of annual total NO_x emission.

5. The review also shows that studies pertaining to the effect of NO_2 on plants are extremely limited in the Indian context.

MATERIALS AND METHODS

Chapter II - Materials and Methods

The Study Area:

Delhi and its neighbouring Faridabad, which comes under the state of Haryana are almost like a twin city. 25 sites have been selected for the study. Out of this 22 sites fall in Delhi state region and 3 in Faridabad (Haryana). The exact location of the sites are given in the figure no. 11. Delhi, the capital of India located between 76°50 E - 77°23 E longitude and 28°12 N - 28°53 N latitude on the west bank of river Yamuna. The study area 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 and mild wind prevails throughout the year except the month of June ,where on few occasions the city is lashed by severe dust storms. For most of the year wind direction remains W to NW, however, in the rainy season it is from S to SE.

Faridabad is bounded by Delhi in north and by state of UP in north-east and south-east and by Gurgaon district in west.

The criteria for selection of specific sites were based on following broader parameters:

1. Different activity zones

2. Traffic density

3. Wind pattern of the city

NO_x was monitored using passive sampler in and around Delhi at 25 sites. The sites are given in table no.22.

Plate 1: Passive sampler exposed in the field.

Plate 2: Passive samplers exposed at different sites.
   a)   Libaspur site.
   b)   IOC, Faridabad.
   c)   Africa Avenue site.

Plate 3: Spectrophotometer (JASCO Model 7800 UV/VIS
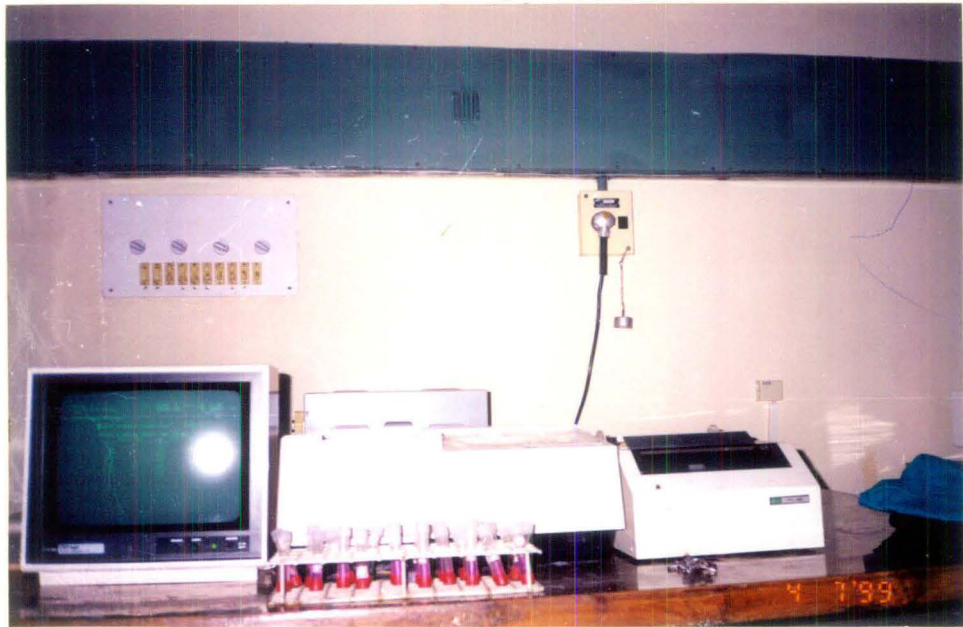
Table No. 22 : Classification of NO$_x$ Sampling Sites.

NO$_x$ Sampling sites		
Urban sites		**Rural/Periurban sites**
Commercial sites	11) CP 12) Azadpur	1) MGIIPD, Bakoli
Residential sites	13) Ashok Vihar	2) SS College, Bodhpur-I
		3) AVJSSN, Bodhpur-II
Parks/Recreation sites	14) Deer Park 15) Lodhi Garden	4) DEDA, Libaspur
		5) JNU
Parking sites, C.P.	16) Underground Parking, Palika 17) Open Parking, Bank of Baroda 18) Underground Parking, Jivan Bharti 19) Open Parking, Jivan Bharti	6) Poorvanchal Colony
		7) NTPC, Badarpur
Road sites	20) Janpath 21) Lodhi Road 22) Inner Ring Road 23) Africa Avenue 24) Vivekanand Marg 25) Aruna Asaf Ali Marg	8) IOC, Faridabad
		9) CRI, Ballabhgarh-I
		10) AIIMS, Ballabhgarh-II

Site Description

The description of individual sites are given below :

Site 1 - Mahatma Gandhi Institute of Integrated Planing and Developments (MGIIPD), Bakoli, Alipur (Delhi) : An academic complex, in a rural location, surrounded by agricultural fields, at a distance of approximately 2Km from G.T. Karnal Road (National Highway, NH-1). It is relatively free from pollution and is least polluted among the selected peri-urban study sites.

Site 2 - Swami Shradhanand College, Bodhpur, Alipur (Delhi) : An academic institution having experimental botanical garden, approximately 250 meter away from the National Highway, NH-1. This site is relatively less polluted.

Site 3 - Shri Atma Vallabh Jain Smarak Sikshan Nidhi Bodhpur (Bodhpur-II), Alipur (Delhi): It is a temple complex, besides NH-1. This area is surrounded by farm houses.

Site 4 - Delhi Energy Development Agency, Libaspur, Delhi : This site is an old research center of the DEDA and is not under use for research purpose now. It is approximately 200m away from the National Highway, NH-1. This site is highly polluted.

Site 5 - JNU : It is located inside a vast tract of natural vegetation in the southern part of Delhi. It is secluded area, relatively free from pollution and is regarded as control site. In recent years many peri-urban localities in the vicinity of university campus are developing rapidly.

Site 6 - Poorvanchal Colony : Poorvanchal colony is an area laying in extreme south of Delhi inside JNU (near IIMC). It is a near to the A.A. Marg. The colony is completely surrounded by vegetation cover.

Plate 4: J.N.U. site.

Plate 5: Poorvanchal Colony site.

Site 7 - Badarpur, (NTPC) : Badarpur situated in south east of Delhi, near Delhi-Haryana border at Mathura Road. It is a 720 MW NTPC unit. Out of which three of 100 MW and two of 210 MW units, coal is used as fossil fuel. The Badarpur Road (Mathura Road) is very congested so frequently traffic jam (congestion) takes place.

Site 8 - Indian Oil Corporation Limited, Sector 13, Faridabad : This is a large research and development complex, developed for the studies of petroleum and petroleum products. The site is situated about 2 Km east of Delhi-Agra National Highway (NH-2) and near to Escorts tractor factory.

Site 9 - Cement Research Institute, Ballabhagarh, Ballabhgarh-I : This is an academic cum research center for the growth and development of different quality of cement. The samplers were kept in the nursery of the institute, which is about 600 m east of Delhi-Agra-Mathura, National Highway (NH-2).

Site 10 - AIIMS, Ballabhagarh-II (Ballabhgarh) : This is a hospital campus, which is a branch of AIIMS, New Delhi, meant for rural projects. The samplers were kept in the nursery of the hospital, which is about 300m south-east of the Delhi-Agra-Mathura, National Highway (NH-2).

Site 11 - Azadpur : Azadpur is a busy commercial area (biggest Sabji Mandi of the Asia). It is having high traffic density dominated by trucks, buses and auto, which carry maximum traffic going out from Delhi to other states and vice versa. It is supposed to be one of the most polluted area of Delhi.

Site 12 - CP (Connaught Place) : Connaught Place is a modern shopping complex having high traffic density with a distinct peaks in the morning and evening. It is also termed as queen of Delhi's.

Legends

a. Bakoli
b. Bodhpur-I
c. Bodhpur-II
d. Libaspur
e. Azadpur
f. Ashok Vihar
g. Connaught Place
　　U.P., Palika
　　U.P., J.B.
　　O.P., B.B.
　　O.P., J.B.
h. Janpath
i. Lodhi Raod+Lodhi Garden
j. Bhikaji Cama Place
k. Africa Avenue
l. Deer Park
m. Vivekanand Marg
n. J.N.U.+Poorvanchal
o. Aruna Asaf Ali Marg
p. Badarpur
q. I.O.C., Faridabad
r. C.R.I., Ballabhgarh-I
s. AIIMS, Ballabhgarh-II
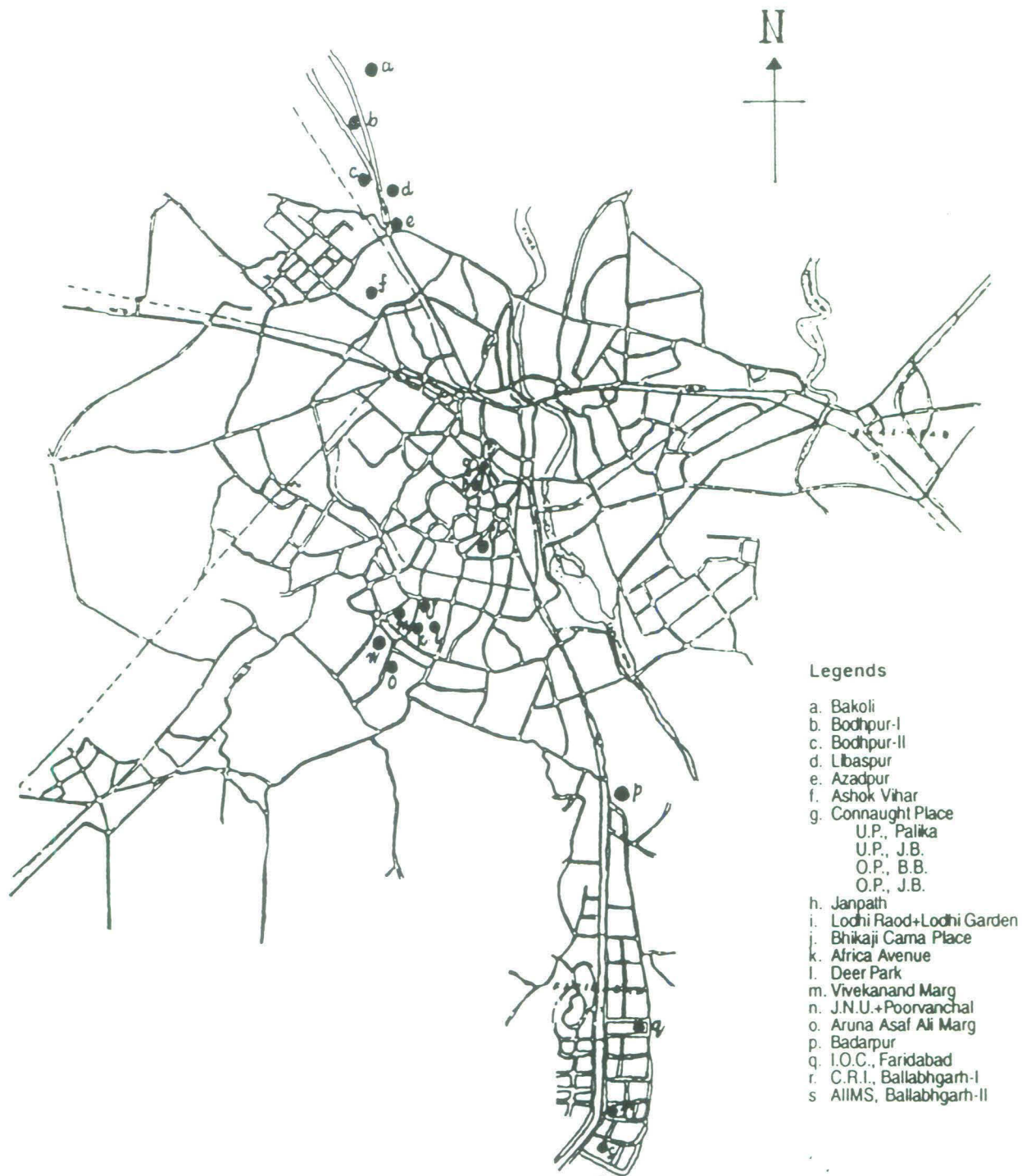
Figure no. 11 : Map of Delhi and Faridabad Showing Exposure Sites.

Site 13 - Ashok Vihar Colony : Ashok Vihar is a residential area, in north west direction of Wazirpur industrial area, adjacent to Laxmi Bai College. The surrounding area is open.

Site 14 - Deer Park : It is situated at the Junction of the Africa Avenue and Gamel Abdul Naseer Marg at Hauzkhas. Park has a big play ground, surrounded on two sides by natural vegetation. Passive samplers were placed inside the vegetation patch of the park.

Site 15 - Lodhi Garden : Lodhi Garden is a big urban park having various plant species, situated about 10 meter away from the Lodhi Road. Lodhi Garden is the final resting place of 15th century Sayyid and Lodhi rulers. It is a beautiful composition of historical monuments set amidst beautifully landscaped garden.

Site 16 - Underground Parking, Palika : It is situated at the nucleus of the Connaught Circle. Having a capacity of 1,000 vehicle and mostly populated by cars. It is open 6 days a week between 8 am to 10 pm.

Site 17 - Open Parking, Bank of Baroda : This parking site is located in the capital busy Connaught Place in front of the NDMC office building. Used solely for parking the cars and two wheelers by the employees of the Bank of Baroda. It is open throughout the week.

Site 18 - Open Parking, Jeevan Bharti : It is situated just behind Jeevan Bima building. It is open through out the week thought the frequency of the vehicles is less on weekends. The parking lot mostly houses the two wheelers.

Site 19 - Underground Parking, Jeevan Bharti : This parking site is housed within the Bank of Baroda building-an underground site, shows a preponderance of cars than two wheelers. This is also availed by the bank employees and used during office hours on their working days (5 days of a week).

Plate 6: Photograph showing vehicular traffic at Badarpur site.

Plate 7: Photograph showing vehicular traffic at C.P. site.

Plate 8: Photograph showing vehicular traffic at Azadpur site.

GREEN DELHI

CLEAN DELHI

6 29 '99

Site 20 - Janpath : It is an important traffic corridor, wide enough road and fast moving. It has high traffic density and free from any traffic jam. The traffic density is very high during morning and evening in all working days. The samples were taken near National Museum.

Site 21 - Lodhi Road : It connects Shri Aurobindo Marg (near Jorbag) and Mathura Road (near Nili Chatri). It is wide, fast moving and having medium traffic density. The samples were taken near India Habitat Center about 15m away from road.

Site 22 - Ring Road : It is the main traffic artery of the city with fast moving heavy traffic throughout the day and traffic congestion especially during peak hours. Ring Road is vital link between various parts of the city. The samples were taken near Bhikaji Cama commercial complex.

Site 23 - Africa Avenue : It connects Outer Ring Road (near Munirka) with Vinay Marg (near Chanakya Puri) It is fast moving with mild traffic density and is free from any traffic jam. The samples were taken near Mohammadpur.

Site 24 - Vivekanand Marg : It connects Outer Ring Road (near Munirka) and Inner Ring Road (near Hyatt agency). It has low traffic density and is normally free from any traffic jams. It passes through the R.K. Puram residential area. The samples were taken near R.K. Puram Sector 4.

Site 25 - Aruna Asaf Ali Marg : It connects Outer Ring Road (near Munirka) with Mehrauli Road (near Vasant Kunj, Sector 13). It has the least traffic density among the selected road sites. The traffic is fast moving and free from traffic jam. It passes through the institutional areas and has a vegetation cover on either sides with building scattered along the way. The samples were taken near IIMC.

Table no. 23 : A comprehensive Discription of the Exposure Sites.

S. N.	Site	Location	Land use/activity	Traffic density
1.	MGIIPD, Bakoli	Rural, North-West	Academic Complex	+
2.	SS College, Bodhpur-I	Peri-urban, North-West	Academic Complex	++
3.	AVJSN, Bodhpur-II	Peri-urban, North-West	Temple Complex	++
4.	DEDA, Libaspur	Peri-urban, North-West	Academic Complex	+++
5.	JNU	Rural, South	University Campus	+
6.	Poorvanchal Colony	Rural, South	Residential Complex	+
7.	NTPC, Badarpur	Peri-urban, South-East	Thermal Power Station	+++
8.	IOC, Faridabad	Rural, South-East	Research Institute	+
9.	CRI, Ballabhgarh-I	Peri-urban, South-East	Research Institute	+++
10.	AIIMS, Ballabhgarh-II	Peri-urban, South-East	Hospital Complex	+++
11.	CP, Delhi	Urban, Central	Commercial Complex	+++
12.	Azadpur	Urban, North-West	Commercial Complex	+++++
13.	Ashok Vihar	Urban, North-West	Residential Complex	+
14.	Deer Park	Urban, South	Park/Recreation Zone	++
15.	Lodhi Garden	Urban, South	Park/Recreation Zone	++
16.	U.P., Palika, C.P.	Urban, Central	Parking Zone	+
17.	O.P., BB, C.P.	Urban, Central	Parking Zone	+++
18.	U.P., J.B, C.P.	Urban, Central	Parking Zone	+
19.	O.P., J.B, C.P.	Urban, Central	Parking Zone	+++
20.	Janpath	Urban, Central	Road Site	++++
21.	Lodhi Road	Urban, South	Road Site	+++
22.	Ring Road (Near B.C.P.)	Urban, South	Road Site	++++
23.	A. Avenue	Urban, South	Road Site	+++
24.	Vivekanand Marg	Urban, South	Road Site	++
25.	A.A. Ali Marg	Urban, South	Road Site	++

Note : +   =   Represents the traffic density,   U.P.   =   Underground parking,
       O.P.   =   Open parking   A.A. Ali Marg =   Aruna Asaf Ali Marg

Plate 9 : Underground Parking site, Palika, C.P.

Plate 10 : Open Parking site, Jeevan Bharti, C.P.

Plate 11 : Open Parking site, Bank of Baroda, C.P.

Sampler Preparation : The passive sampler consist of an acrylic tube (approximately 7.1 cm long and 1.1 cm diameter), two push polyethylene caps (one coloured and other colourless) and two stainless steel mesh (0.2mm mesh size and 0.1mm wire diameter).

To assemble each sampler, 2 stainless steel mesh were coated with 50ml of 50 percent v/v tri ethanol amine (TEA) aq. solution (in deionized water). To aid the coating of meshes 0.5ml of brij-35 (a wetting agent) was added to 20ml of the TEA-aqueous solution, making it viscous. Both mesh were placed in coloured plastic cap immediately after the treatment and it was fitted to the tube on one side. The other end was then capped.

Sampling Schedule : Sampling was carried out in ten peri-urban/rural sites from Dec. 1998 to June 1999 (except the month of May) and in fifteen urban sites from January 1998 to June 1999, twice in a month at each site. Passive samplers were exposed for 7 days at 15 days interval at each urban site, where as for peri-urban/rural sites 15 day's exposure with no interval between two consecutive sampling except one peri-urban site (Poorvanchal colony), where sampling was carried out from January 1998 to June 1999, twice in a month with 7 day's exposure period.

Sampling Procedure : The freshly prepared diffusion tubes were taken to the field and were fixed by a cellotape to a 5 cm wooden block on trees and walls, vertically with colourless cap in downward direction. The wooden block serves to distance the sampler from surfaces. The tubes were placed at height of 1.5 m from the ground level and lower colourless plastic cap was removed to start NO_x sampling. Triplicate tubes were exposed at each site, out of which colourless plastic cap of one tube was not removed and it served as field blank (the TEA coated unexposed tube called as blank). In laboratory few tubes were kept in unexposed condition that served as lab. blank. After definite period of exposure the open end of tubes were resealed by colourless cap and collected with field blank tubes in sealed polyethylene bags and brought to the laboratory for analysis.

Measurement

The diffusion tube samplers analyzed by Griess Saltzman Method (Shinn, 1941; Palme et. al., 1976; Atkins et al., 1978, 1992; Campbell et al., 1988)

Reagents : Saltzman solution : It was prepared by dissolving 5 g of sulphanilic acid in 600 ml of warm re-distilled water, after cooling adding 30ml of 85 percent phosphoric acid and 50mg of N (napthylethylenediaminedihydrochloride) and making mark with redistilled water in 1 litter volumetric flask.

Procedure : For the NO_x analysis the colourless plastic cap from the diffusion tube was removed and 3.15ml of saltzman reagent containing 20 part of 2 percent W/v solution of sulphanilamide in 5 percent v/v orthrophosphoric acid to 1 parts of 0.14 W/V N-1, napthyl ethylene diamine dihydrochloride (NEDA) solution were added directly by means of a dispenser. The nitrite in solution reacted with sulphonilamide to form diazonium compound that coupled NEDA to form purple Azodye.

$$NH_2SO_2C6H_4N=NCl+C_{10}H_7NHCH_2CH_2NH_2 \cdot 2HCL = NH_2SO_2C_6H_4N=NC_{10}H_6NHCH_2CH_2NH_2 \cdot 2HCl + HCl$$

$$(NEDA) \qquad\qquad (Azodye)$$

(At pH 3.7, it changes its colour to red.)

Phosphoric acid was added to the reagent to increase acidity, and enhance colour development. The samplers closed with cap and allowed to stand for 15 minutes for full colour development, in the meantime samples were shaken gently 2 or 3 times.

The optical absorbance of a range of nitrite standard and sampler solution was measured at 543nm on JASCO-7800 UV/UIS spectrophotometer. First the spectrophotometer was zeroed against blank then the readings for different samples were taken. Both, 'lab' and 'field blank' analyzed at the same time as exposed tubes. The absorbance reading from the blank

diffusion tubes were averaged for each preparation set and the value subtracted from the reading of exposed tubes. The amount of extracted nitrite found for each tube was used to calculate ambient NO_2 concentration for its exposure location and time period.

Calculation : The concentration of NO_2 in ambient environment can be calculated by following formula.

$$NO_2 \text{ concentration (ppb)} = \frac{10437.8 \times Q \text{ (ppm)}}{t}$$

Q = mass of nitrite extracted in ppm

t = time of exposure of the tubes (hours) assuming 1 atm. pressure and 20°C temperature.

The amount of nitrite ion (Q) in the sample is obtained with the help of calibration plot derived from the measurements made with standard nitrite solution of different concentration.

Chapter III - Results

NO_2 in the ambient environment of Delhi

NO_2 levels at the 25 sites in Delhi and Faridabad during December'98 to June'98 varied between 24.2 ppb to 186.1 ppb (table no.24). The maximum NO_2 concentration (186.1 ppb) was observed as Badarpur site and minimum (24.2 ppb) at Bakoli site. The average NO_2 concentration was found to be between 37.67 ± 3.70 ppb to 160.32 ± 6.98 ppb. The maximum average NO_2 concentration was measured at Azadpur site, where the concentration was 160.32 ± 6.98 ppb (table no. 33). The minimum average NO_2 concentration of 37.67 ± 3.70 ppb observed at Poorvanchal Colony (table no.30).

The Concentration of NO_2 at urban site varied between 32.1 ppb to 169.40 ppb. Maximum NO_2 concentration (169.40 ppb) was observed at Azadpur site and minimum 32.1 ppb at Ashok Vihar site (table no. 26 and 27).

Among the selected six urban road sites, the NO_2 concentration varied between 49.55 ppb to 140.20 ppb (table no. 29). The maximum concentration (140.2 ppb) was at inner ring road site while minimum (49.55 ppb) at Aruna Asaf Ali Road site (table no. 29). On the basis of traffic density road sites are devided in to 3 catagories :

1.   High traffic density road sites (Janpath and Ring Road)

2.   Medium traffic density road sites (African Avenue, Lodhi Road and Vivekanand Marg)

3.   Low traffic density road sites (Aruna Asaf Ali Marg)

The NO_2 concentration at high traffic density road sites was about 1.79 times over its concentration at low traffic density road sites.

Table no. 24 : Ambient Levels of Nitrogen Dioxide at Different Rural Sites of Delhi and Faridabad (Dec.'98-June'99; in ppb).

Site	Dec	Jan	Feb	March	April	May	June	Average	S.D.
Bakoli	70.8	48.1	37.9	27.6	38.8	—		44.64	16.32
	68.1	42.2	24.2	39.1	38.2	—	40.9	42.11667	14.29
Bodhpur-I	80.45	65.1	58.6	41.8	60.5	—		61.29	13.86
	100.2	62.1	34.1	55.6	61.5	—	60.2	62.28333	21.36
Bodhpur-II	58.5	59.6	41.8	34.8	48.5	—		48.64	10.67
	78.8	50.1	27.4	47.6	47.5	—	50.9	50.38	16.44
Libaspur	96.94	87.7	89.9	89.2	100.4	—		92.82	5.52
	115.3	69.3	81.1	99.8	104.8	—	86.6	92.81	16.89
JNU	70.4	35.5	39.7	32.4	37.4	—		43.08	15.50
	58.8	30.9	35.6	36.1	38.2	—	30.2	38.3	10.51
P. C.		38.7	46.2	35.2	39.72	40.1	28.4	38.05	5.91
		35.1	38.2	37.04	43.24	34.3	32.4	36.71	3.79
Badarpur	186.1	77.2	101.8	78.1	97.3	—		108.1	44.98
	153.2	72.1	68.4	96.2	98.7	—	60.8	91.56	33.86
IOC	105.2	46.2	70.9	63.4	45.8	—		66.3	24.32
	71.8	48.7	69.5	59.2	48.6	—	52.6	58.4	10.26
CRI	153.6	71.4	97.3	82.1	90.7	—		99.02	32.01
	96.5	76.7	84.4	87.3	92.5	—	77	85.73333	8.04
AIIMS	147.4	66.1	96.9	78.1	108.9	—		99.48	31.47
	96.4	63.8	83.5	80.7	111.3	—	75.6	85.26	16.61
Average	126.27	65.27	84.08	78.13	86.72	37.2	66.5	67.24	10.81
S.D.	37.13	16.28	25.89	24.25	28.66	4.10	20.03		

Note :   P.C.   =   Poorvanchal Colony

Table no. 25 : Ambient Levels of Nitrogen Dioxide at Different Parking Sites of Delhi (Jan'99-June'99; ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
U.P., Palika	100.6 106.4	101.2 107.6	131.1 148.6	172.7 190.1	210.4 226.5	214.9 198.7	155.15 162.98	51.75 50.04
U.P., J.B	106.1 108.2	104.35 106.25	123.3 128.2	129.4 130.3	127.4 128.3	119.89 117.69	118.40 119.82	10.74 10.73
O.P., B.B.	133.6 139.2	148.2 140.6	136.41 142.35	144.3 145.4	135.62 139.4	127.4 118.2	137.58 137.52	7.51 9.74
O.P., J.B.	130.9 136.7	143.4 136.9	132.35 139.05	140.1 142.9	132.4 135.1	124.47 116.97	133.93 134.60	6.80 9.04
Average	120.21	123.56	135.17	149.4	154.39	142.27	137.50	19.40
S.D.	16.23	20.32	8.12	21.16	39.96	40.21	—	—

Note : U.P. = Underground Parking B.B. = Bank of Baroda
O.P. = Open Parking J.B. = Jeevan Bharti

Table no. 26 : Ambient Levels of Nitrogen Dioxide at Two Different Residencial Sites of Delhi. (Jan'99-June'99; ppb)

Site	Jan	Feb	March	April	May	June	Average	S.D.
A. Vihar C.	42.6 38.2	49.1 45.2	38.56 47.04	44.2 48.41	40.69 43.09	38.5 32.1	42.27 42.34	3.67 5.62
P. C.	38.7 35.1	46.2 38.2	35.2 37.04	39.72 43.24	40.1 34.3	28.4 32.4	38.05 36.71	5.40 3.46
Average	38.65	44.67	39.46	43.89	39.54	32.85	39.84	1.12
S.D.	3.07	4.62	5.23	3.57	3.72	4.18	—	—

Note : P.C. = Poorvanchal Colony
A. Vihar C. = Ashok Vihar Colony

Table no. 27 : Ambient Levels of Nitrogen Dioxide at Two Different Commercial Sites of Delhi (Jan'99-June'99; ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
C.P.	126.28	138.4	128.6	136.45	129.33	120.6	129.9433	6.58
	134.27	132.3	135.25	137.85	131.03	109.8	130.0833	10.21
Azadpur	162.8	167.4	155.6	167.2	158.3	150.6	160.3167	6.69
	160.3	162.3	165.8	169.4	160.1	144.9	160.4667	8.41
Average	145.91	150.1	146.31	152.72	144.69	131.47	145.2025	1.71
S.D.	18.37	17.33	17.34	18.01	16.78	19.44	—	—

Note :   C.P.   =   Connaught Place

Table no. 28 : Ambient Levels of Nitrogen Dioxide at Two Different Parks/Recreation Sites of Delhi (Jan'99-June'99; ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
Lodhi G.	61.88	75.34	64.86	72.5	65.3	61.94	66.97	5.64
	67.52	65.87	72.25	75.7	69.7	57.66	68.11	6.19
Deer Park	83.6	96.6	85.45	90.3	87.25	68.07	85.21	9.55
	88.2	89.4	89.25	95.6	82.65	72.75	86.30	7.81
Average	75.3	81.80	77.95	83.52	76.22	65.10	76.65	1.76
S.D.	12.59	13.81	11.36	11.17	10.40	6.65	—	—

Note :   Lodhi G.   =   Lodhi Garden

74

Table no. 29 : Ambient Levels of Nitrogen Dioxide at Different Road Sites of Delhi (Jan'99-June'99; ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
Janpath	118.7	138.81	120.52	134.6	125.3	122.2	126.68	8.16
	124.8	121.21	133.12	128.3	131.9	110.5	124.97	8.35
Lodhi Road	80.2	93.45	74.95	88.8	84.4	84.1	84.31	6.45
	84.4	77.95	96.5	92.36	89.82	75.7	86.12	8.22
Ring Road	119.8	140.2	127.8	136.1	129.7	123.7	129.55	7.59
	125.3	130.4	135.6	137.3	131.4	115.7	129.28	7.87
Africa A.	94.2	113.8	99.9	107.2	102.35	95.5	102.15	7.39
	98.6	106.6	112.39	110.01	105.65	88.5	103.62	8.76
V. M.	77.6	94.5	83.6	98.8	81.72	81.7	86.32	8.34
	54.3	85.9	101.9	103.4	89.35	89.5	87.39	17.73
A.A.A. M.	60.7	78.9	67.3	75.3	65.5	60.15	67.97	7.66
	58.3	68.3	74.2	71.68	71.4	49.55	65.57	9.62
Average	91.40	104.16	102.31	106.98	100.70	91.4	99.49	2.90
S.D.	26.38	24.73	23.92	23.09	24.04	23.54		

Note :   Africa A.   =   Africa Avenue
          V.M.   =   Vivekanand Marg
          A.A.A.M.   =   Aruna Asaf Ali Marg

The maximum NO_2 concentration (226.5 ppb) was at underground parking site, Palika and minimum (100.6 ppb) also at underground parking site, Palika (table no. 25). The NO_2 concentration in open parking sites, varied between 116.97 ppb to 148.20 ppb and in underground parking sites varied between 100.62 to 226.5 ppb (table no. 25). The NO_2 concentration at open parking sites was 1.03 times over its concentration at underground parking sites. It was observed that the NO_2 concentration at open parking site was 0.93 times and 3.45 times over its concentration at commercial and residentail sites repectively (table no. 39c).

The concentration of NO_2 at commercial sites varied between 109.80 ppb to 169.40 ppb (table no. 27). Maximum concentration (169.40 ppb) was at Azadpur site and minimum (109.80 ppb) at Connaught Place site (table no. 27).

The NO_2 concentration at commercial sites was 3.67 times over its concentration at residential sites (table no. 36) and 1.88 times over its concentration at parks/recreation zones (table no. 39b).

The NO_2 concentration at two different residential sites, (one in urban and other one in peri-urban localities) varied between 28.4 ppb to 49.1 ppb (table no. 29.6). The maximum concentration of NO_2 (49.1 ppb) was at Ashok Vihar site and minimum concentration (28.4 ppb) at Poorvanchal Colony site (table no. 26). The NO_2 concentration at residential sites was 3.67, 2.52, 1.95, 1.61 times less than its concentration at commercial, road site, parking and rural sites respectively (table no. 36, 39 a).

At parks/recreation sites NO_2 concentration varied between 57.66 ppb to 96.6 ppb (table no. 28). The maximum concentration (96.6 ppb) was at Deer Park site and minimum (57.66 ppb) at Lodhi Garden site. The NO_2 concentration at parks/recreation sites was 1.88 times less its concentration at commercial and 1.95 times over than its concentration at residential sites (table no. 39 a).

The concentration of NO_2 at rural sites varied between 24.2 ppb to 186.1 ppb (table no. 24). The

maximum concentration (186.1 ppb) was observed at Badarpur site and minimum concentration (24.2 ppb) at Bakoli site (table no. 24). The selected rural sites can be grouped into three catagories

1. South-east sites : It includes Badarpur, IOC, CRI and AIIMS site.

2. North-west sites : It includes Bakoli, Bodhpur-I, Bodhpur-II, Libaspur.

3. South sites : It includes JNU and Poorvanchal Colony.

The NO_2 concentration at rural sites was 1.61 times over to its concentration at residential sites (table no. 36). The NO_2 concentration at north-west rural sites was 1.33 times less than its concentration at south-east rural sites (table no. 38).

Seasonal Variation

The monthly variation in NO_2 concentration at different sites in Delhi and Faridabad is given in table no. 30-35. The monthly average concentration of NO_2 during Dec.'98 to June'99 varied between 30.05 ppb. to 169.65 ppb. The maximum monthly average NO_2 concentration (169.65 ppb) was observed at Badarpur site in the month of December and minimum (30.05 ppb) at JNU site in the month of June. At rural sites, the monthly average of NO_2, during December'98 - June'99 varied between 30.25 ppb to 169.65 ppb (table no. 30). However, at urban sites, the monthly average of NO_2, during Jan.'99 to June'99 varied between 35.25 ppb to 168.3 ppb.

The avarage monthly NO_2 concentration varied between 54.85 ppb to 136.70 ppb at road sites (table no. 31). The maximum concentration (136.70 ppb) was observed at inner ring road site in the month of April and minimum (54.85 ppb) at Aruna Asaf Ali road site in the month of June (table no. 31).

The NO_2 monthly average concentration at underground parking sites varied between 101.12 ppb to 226.5 ppb. Where, the maximum NO_2 concentration (226.5 ppb) and minimum (101.1 ppb) observed at underground parking, Palika in the month of May and February repectively

Table no. 30 : Monthly Variation in NO_2 Levels at Different Rural Sites of Delhi and Faridabad (Dec'98 - June'99; in ppb).

Site	Dec	Jan	Feb	March	April	May	June	Average	S.D.
Bakoli	69.45	45.15	31.05	33.30	38.50	—	40.90	43.05	13.89
Bodhpur-I	90.32	63.60	46.30	48.70	61.02	—	60.22	61.69	15.69
Bodhpur-II	68.65	58.80	34.60	41.20	47.91	—	50.91	50.34	12.20
Libaspur	105.92	78.50	85.20	94.50	102.20	—	86.51	92.13	10.60
J.N.U.	64.60	32.20	37.65	34.25	37.70	—	30.25	39.44	12.67
Poorvanchal C.		36.90	42.20	36.12	41.46	37.20	32.15	37.67	3.70
Badarpur	169.65	74.60	85.10	87.15	98.06	—	60.80	95.89	38.26
IOC, Faridabad	88.50	47.50	70.20	61.30	47.23	—	52.63	61.22	16.01
CRI, Ball.-I	125.05	74.05	90.85	84.70	91.45	—	77.12	90.53	18.31
AIIMS, Ball.-II	121.90	64.95	90.20	79.40	110.11	—	75.60	90.36	21.76
Average	100.44	57.62	61.33	60.06	67.56	37.2	56.70	62.99	19.01
S.D.	34.25	16.39	25.17	24.36	29.38	—	19.13	24.78	6.53

Note: Poorvanchal C. =   Poorvanchal Colony
          Ball.   =   Ballabhgarh

78

Table no. 31 : Monthly Variation in NO_2 Levels at Different Road Sites of Delhi (Dec'98-June'99;in ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
Janpath	121.75	130.51	126.82	131.45	128.60	116.35	125.91	5.80
Lodhi Road	82.31	91.0	85.7	90.58	87.10	80.10	86.13	4.37
Ring Road	122.55	135.3	131.7	136.70	130.5	119.70	129.40	6.86
Africa A.	96.40	110.2	106.15	108.60	104.0	92.2	102.92	7.13
V.M.	80.95	90.2	87.80	101.1	85.60	76.5	87.02	8.46
A.A.A.M	59.5	73.6	70.75	73.49	68.45	54.85	66.77	7.81
Average	93.91	105.13	101.48	106.98	100.70	89.95	99.69	6.56
S.D.	24.85	24.48	24.32	24.12	25.02	24.88	24.61	0.35

Note :   Africa A.   =   Africa Avenue
          V.M.   =   Vivekanand Marg
          A.A.A.M.   =   Aruna Asaf Ali Marg

Table no. 32 :   Monthly Variation in NO_2 Levels at Two Different Parks/Recreation Sites of Delhi (Jan'99 - June'99; in ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
Lodhi G.	64.70	70.62	68.15	74.10	67.5	59.80	67.47	4.91
Deer Park	85.9	93.0	87.35	92.95	85.2	76.90	86.88	5.96
Average	75.3	81.81	77.75	83.52	76.35	68.35	77.18	5.37
S.D.	14.99	15.82	13.57	13.32	12.51	12.09	13.73	1.43

Note :   Lodhi G.   =   Lodhi Garden

Table no. 33 : Monthly Variation in NO_2 Levels at Different Commercial Sites of Delhi (Jan'99 - June'99; in ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
C.P.	130.28	135.35	131.91	137.15	130.18	115.2	130.01	7.77
Azadpur	161.12	164.85	160.7	168.30	159.20	147.75	160.32	6.98
Average	145.7	150.01	146.30	152.72	144.69	131.47	145.16	7.35
S.D.	21.80	20.85	20.35	22.02	20.52	23.01	21.43	1.03

Note :   C.P.   =   Connaught Place

Table no. 34 : Monthly Variation in NO_2 Levels at Two Different Residential Sites of Delhi (Jan'99-June'99; in ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
A. Vihar C.	40.40	47.15	42.80	46.30	41.89	35.35	42.31	4.28
P.C.	36.9	40.20	37.80	40.15	36.80	30.40	37.04	3.58
Aaverage	38.65	43.67	40.30	43.22	39.34	32.87	39.67	3.90
S.D.	2.47	4.91	3.53	4.34	3.59	3.50	3.72	0.83

Note :   A. Vihar C.   =   Ashok Vihar Colony
               P.C.   =   Poorvanchal Colony

Table no. 35 : Monthly Variation in NO_2 Levels at Different Parking Sites of Delhi (Jan'99 - June'99; in ppb).

Site	Jan	Feb	March	April	May	June	Average	S.D.
U.P.. Palika	103.5	104.4	139.9	158.9	218.45	206.5	155.27	49.26
U.P.. J.B	107.15	105.3	125.75	129.85	132.25	118.7	119.83	11.51
O.P.. B.B	136.4	144.4	139.38	144.85	137.51	122.75	137.54	8.04
O.P.. J.B.	133.8	140.14	135.7	141.5	133.75	120.72	134.26	7.38
Average	120.21	123.56	135.18	143.77	155.49	142.16	136.73	20.22
S.D.	17.28	21.67	6.56	11.95	42.03	42.92		

Note :   U.P.   =   Underground Parking
               J.B.   =   Jeevan Bharti
               B.B   =   Bank of Baroda
               O.P.   =   Open Parking

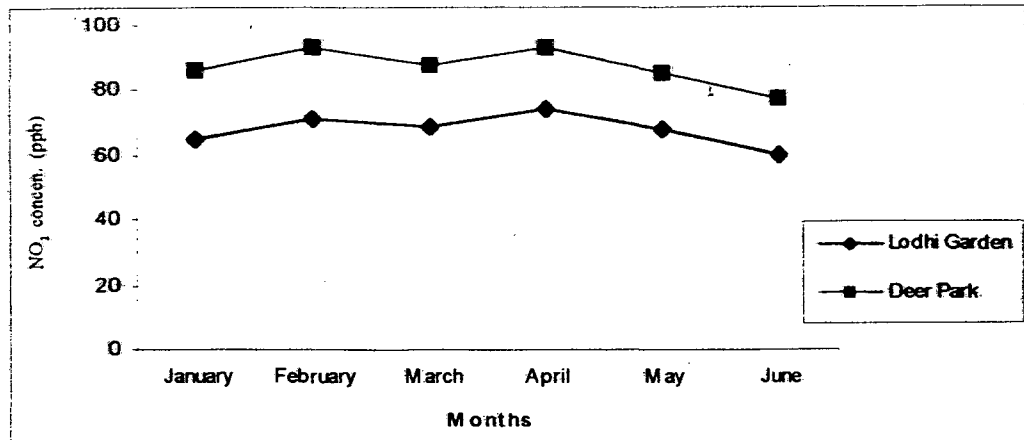**Figure no. 12 : Comparison of Monthly NO$_2$ Variation at Two Parks/Recreation Sites.**

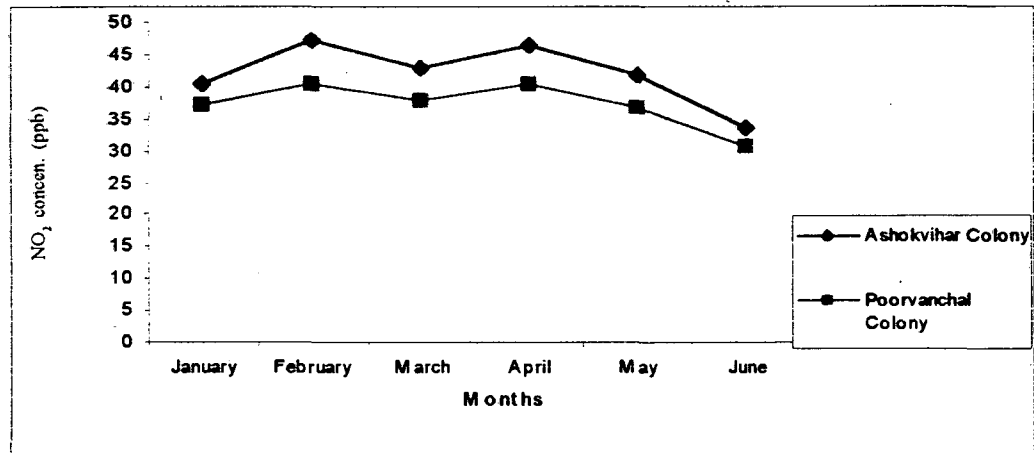**Figure no. 13 : Comparison of Monthly NO$_2$ Variation at Two Residential Sites.**

Figure no. 14 : Comparison of Monthly NO$_2$ Variation at Different Road Sites.
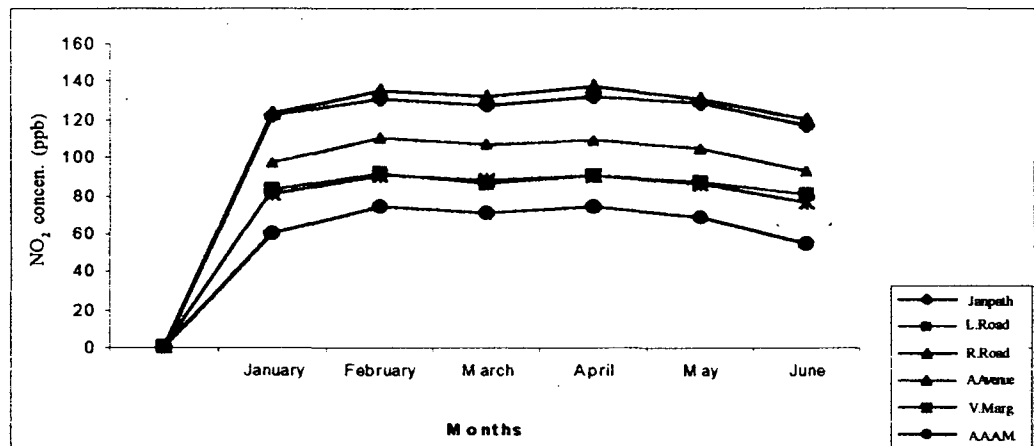
Figure no. 15 : Comparison of Monthly NO$_2$ Variation at Different Parking Sites.
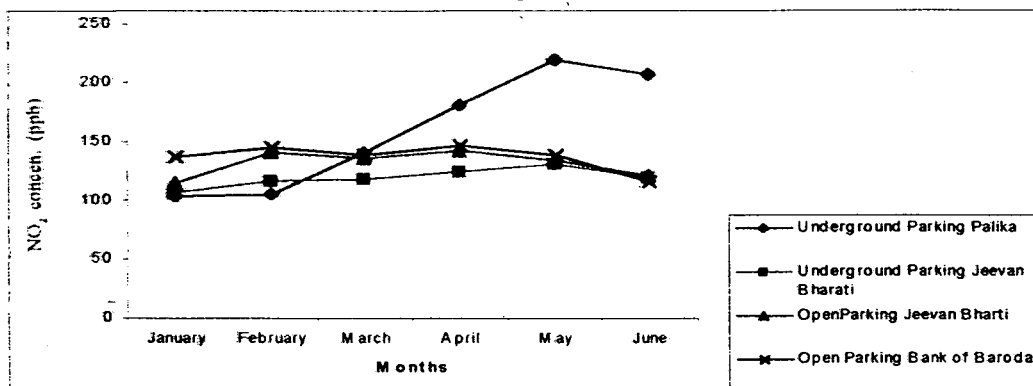

Figure no. 16 : Comparison of Monthly NO$_2$ Variation at Two Underground Parking Site.
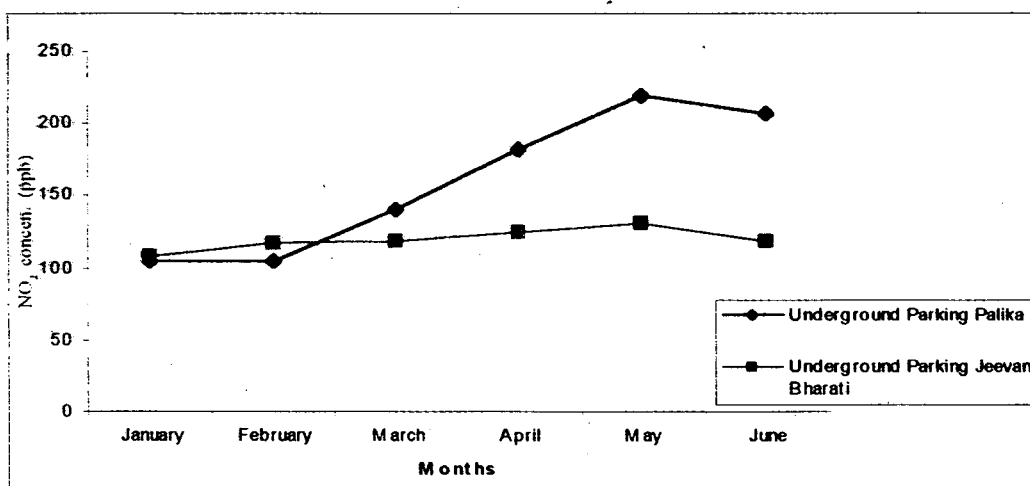
Figure no. 17 : Comparison of Monthly NO$_2$ Variation at Two Open Parking Sites.

Table no. 36 : A Comprehensive List Showing Average Monthly NO$_2$ Concentration at Different Activity Sites.

Month	NO$_2$ concen. at Rural Site (ppb)	NO$_2$ concen. at C.S. (ppb)	NO$_2$ concen. at R.S. (ppb)	C.S./R.S. (ratio)	Rural S./R.S. (ratio)
Dec	100.44	145.70	38.65	3.77	2.60
Jan	57.62	150.10	43.67	3.44	1.32
Feb	61.33	146.30	40.30	3.63	1.52
March	60.06	152.72	43.23	3.53	1.39
April	67.56	144.69	39.34	3.68	2.11
June	56.70	131.47	31.87	4.12	1.78
Average	63.95	145.16	39.51	3.67	1.61

Note :   C.S.   =   Commercial sites
         R.S.   =   Residential sites

83

Table no. 37 : A Comparison of Monthly Average NO_2 Concentration between Urban and Rural Sites.

Months	NO_2 Concen. at Urban Site (ppb)	NO_2 Concen. at Rural Site (ppb)	Urban/Rural (ratio)
Jan	88.39	57.63	1.53
Feb	95.18	61.34	1.55
March	91.46	60.06	1.52
April	96.61	67.56	1.43
June	80.66	56.70	1.42
Average	90.46	60.66	1.49

Table no. 38 : A Comparison of Monthly Average NO_2 concentration between North-West Rural Sites and South-East Rural Sites.

Months	NO_2 Concen. at N-W Rural Sites (ppb)	NO_2 Concen. at S-E Rural Sites (ppb)	S-E Rural/ N-W Rural (ratio)
Dec	83.59	126.28	1.51
Jan	61.51	65.27	1.06
Feb	49.28	84.09	1.70
March	64.72	78.14	1.20
April	62.40	86.71	1.40
June	59.63	66.54	1.12
Average	63.52	84.505	1.33

Note :   N-W   =   North-west
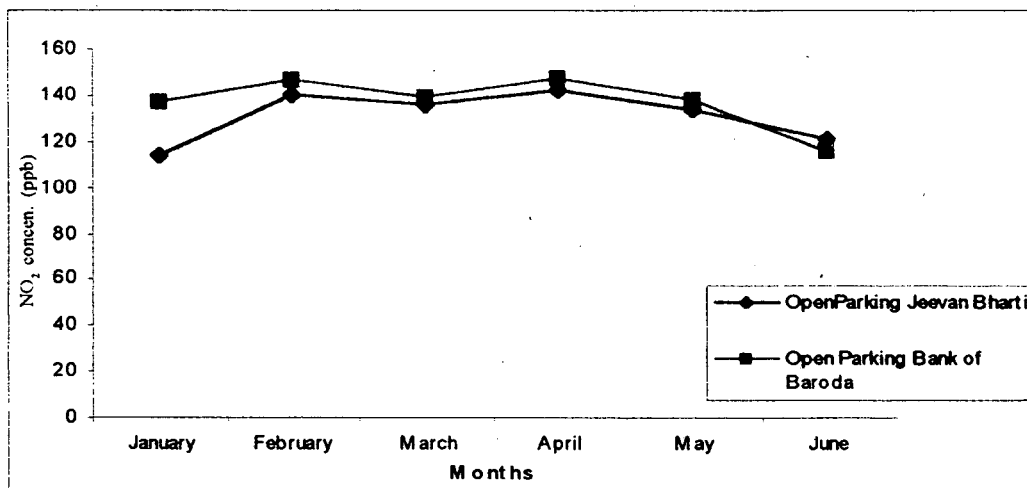   S-E   =   South-east

Table no. 39 a : A Comprehensive List Showing Average Monthly NO_2 Concentration at Different Activity Sites.

Month	NO_2 concen. at P.S. (ppb)	NO_2 concen. at R.S. (ppb)	NO_2 concen. at Road S. (ppb)	P.S./R.S (ratio)	Road S./R.S. (ratio)
Jan	75.8	38.69	93.09	1.95	2.40
Feb	81.81	43.65	105.14	1.87	2.40
March	77.75	40.3	101.49	1.92	2.51
April	83.52	43.23	105.22	1.93	2.43
May	76.36	39.35	100.78	1.94	2.56
June	68.35	31.88	90.00	2.14	2.82
Average	77.18	39.50	96.29	1.95	2.52

Note :   C.S.   =   Commercial sites
         P.S.   =   Parks/Recreation sites
         R.S.   =   Residential sites
         Road S.   =   Road sites

85

Table no. 39 b :   A Comprehensive List Showing Average Monthly NO_2 Concentration at Different Activity Sites.

Month	NO_2 concen. at C.S. (ppb)	NO_2 concen. at P.S. (ppb)	NO_2 concen. at Road S. (ppb)	Road S./P.S. (ratio)	C.S./P.S. (ratio)	C.S./Road S. (ratio)
Jan	145.7	75.8	93.91	1.24	1.92	1.55
Feb	150.1	81.81	105.14	1.28	1.83	1.43
March	146.3	77.75	101.49	1.30	1.88	1.44
April	152.75	83.52	105.22	1.26	1.83	1.45
May	144.69	76.36	100.78	1.32	1.89	1.43
June	131.47	68.35	90.00	1.31	1.92	1.46
Average	145.16	77.18	99.42	1.28	1.88	1.46

Note :   C.S.   =   Commercial sites
           P.S.   =   Park sites
           Road. S.   =   Road sites

Table no.39 c :   A Comprehensive List Showing Average Monthly NO$_2$ Concentration at Different Activity Sites.

Month	NO$_2$ concen. at O.P.S (ppb)	NO$_2$ concen. at C.S. (ppb)	NO$_2$ concen. at R.S. (ppb)	O.P.S./C.S. (ratio)	O.P.S./R.S (ratio)
Jan	135.10	145.70	38.65	0.93	23.49
Feb	142.22	150.10	43.67	0.94	3.25
March	137.54	146.30	40.30	0.94	3.41
April	143.18	152.72	43.23	0.93	3.31
May	135.63	144.69	39.34	0.93	3.44
June	121.74	131.47	31.87	0.92	3.81
Average	135.91	145.16	39.50	0.93	3.45

Note :   C.S.   =   Commercial sites
            O.P.S. =   Open parking sites
            R.S.   =   Residential sites

87

Table no. 40 : A comparison of Average Monthly NO$_2$ Concentration at Different Traffic Density Road Sites.

Month	NO$_2$ concen. H.T.D. sites	NO$_2$ concen. M.T.D. sites	NO$_2$ concen. L.T.D. sites	H.T.D./M.T.D. (ratio)	H.T.D./L.T.D. (ratio)
Jan	122.15	86.55	59.5	1.41	2.05
Feb	132.85	97.13	73.6	1.36	1.81
March	128.76	93.22	70.75	1.38	1.82
April	134.75	96.52	73.45	1.39	1.83
May	129.55	92.36	69.49	1.40	1.86
June	118.18	83.08	54.85	1.42	1.42
Average	127.7	91.47	66.91	1.39	1.795

Note : H.T.D. = High traffic density
M.T.D. = Medium traffic density
L.T.D. = Low traffic density

Table no. 41 : A Comparison of Monthly Average NO$_2$ Concentration betweem Open Parking Sites and Underground Parking Sites.

Month	NO$_2$ concen. at O.P.S (ppb)	NO$_2$ concen. at U.P.S. (ppb)	O.P.S/U.P.S. (ratio)
Jan	135.10	105.33	1.28
Feb	142.27	104.85	1.36
March	137.54	132.83	1.04
AprIL	143.18	144.38	0.99
May	135.63	175.35	0.77
June	121.74	162.6	0.75
Average	135.91	137.56	1.03

Note : O.P.S. = Open parking sites
U.P.S. = Underground parking sites

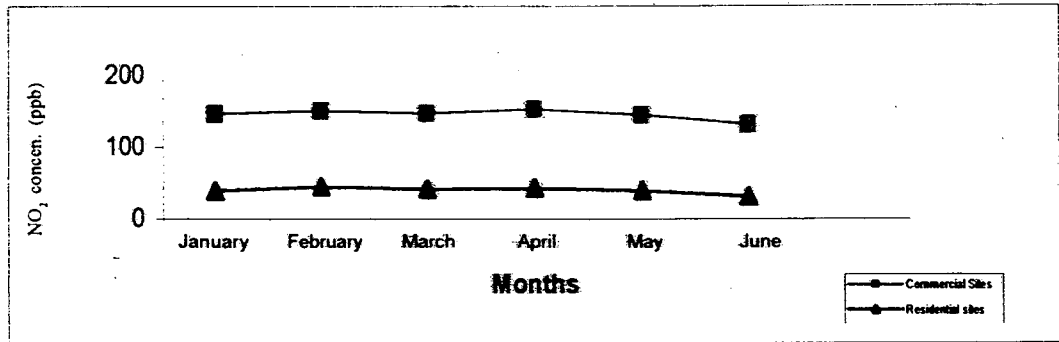**Figure no. 18 : Comparison of Monthly NO$_2$ Variation at Commercial and Residential Site.**

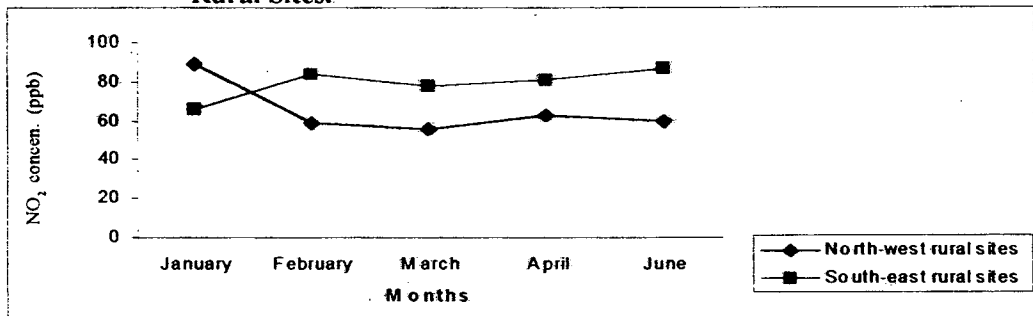**Figure no. 19 : Comparison of Monthly NO$_2$ Variation at North-West and South-East Rural Sites.**

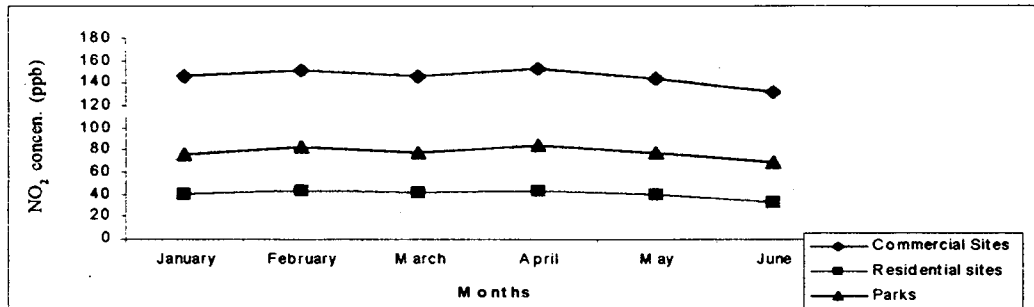**Figure no. 20 : Comparison of Monthly NO$_2$ Variation at Commercial, Park and Residential Site.**

Figure no. 21 : Comparison of Monthly NO$_2$ Variation at Road and Open Parking Sites.
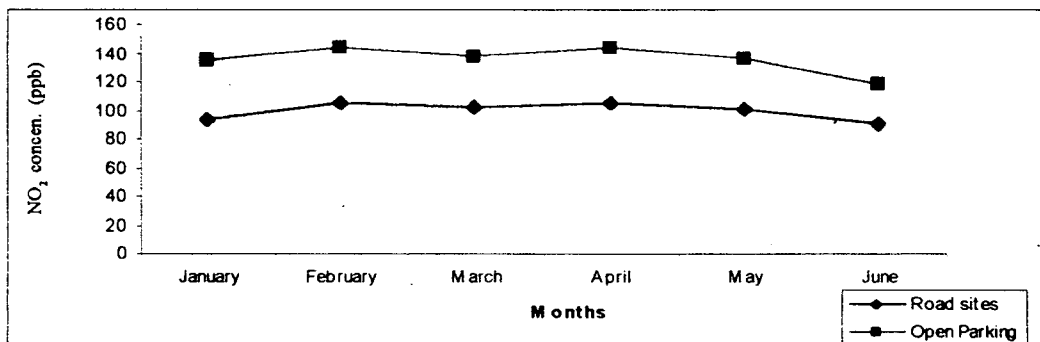
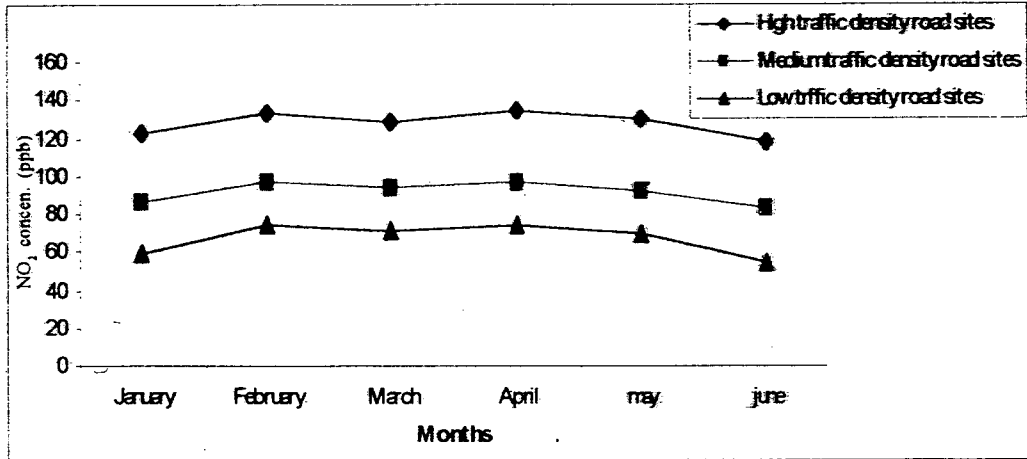**Figure no. 22 : Comparison of Monthly NO$_2$ Variation at Different Traffic Density Road Sites.**

Figure no. 23 : Comparison of Monthly NO$_2$ Variation at South-East, Central and North West Sites.
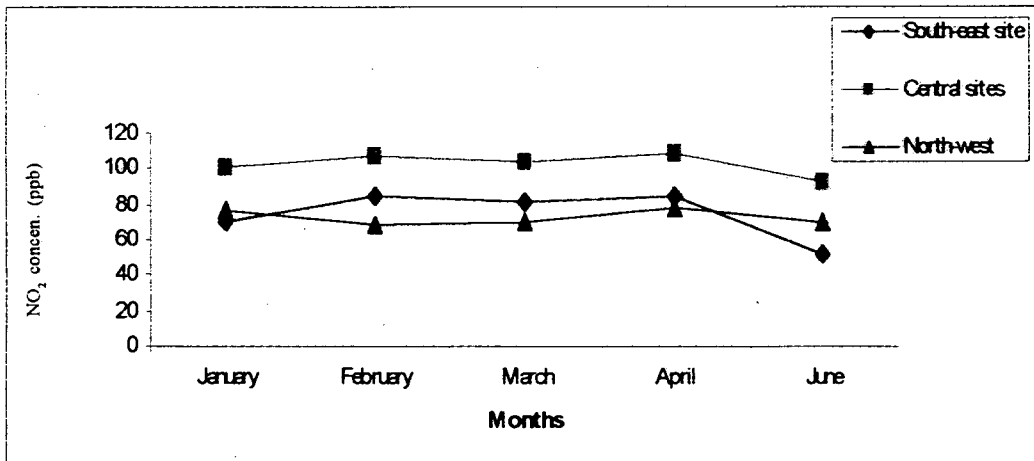

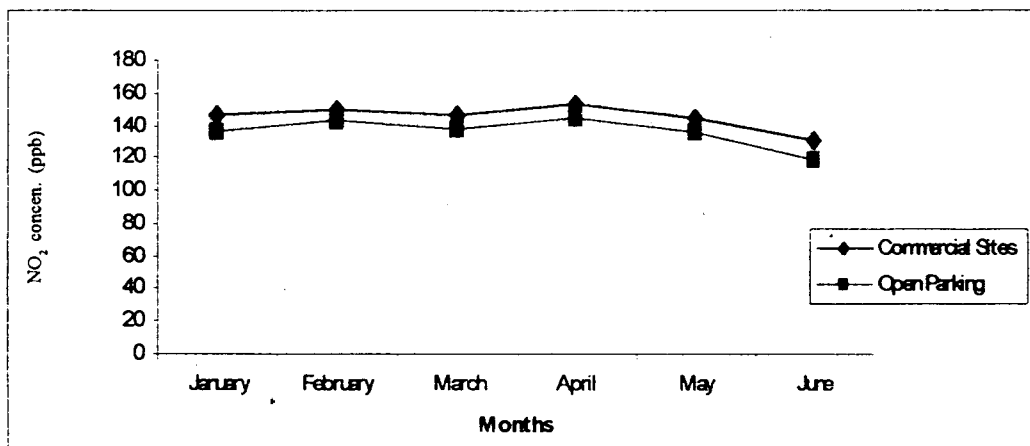**Figure no. 24 : Comparison of Monthly NO$_2$ Variation at Commercial and Open Parking Sites.**

Plate 12 : Badarpur Thermal Power Plant showing plume.

Plate 13 : A scene of Ring Road traffic.

(table no. 35). However, at open parking sites NO_2 concentration (145.40 ppb) varied between 116.97 ppb to 145.40 ppb. The maximum NO_2 concentration observed in the month of April at open parking site, Bank of Baroda and minimum (116.97 ppb) in the month of June at open parking site Jeevan Bharti (table no. 35)

The monthly average NO_2 concentration at commercial sites varied between 115.2 ppb to 168.3 ppb. The maximum concentration (168.3 ppb) was observed in the month of April at Azadpur site and minimum (115.2 ppb) in the month of June at CP site (table no. 33).

At residential site, monthly average concentration varied between 30.4 ppb to 47.15 ppb (table no. 34). The maximum concentration was observed in the month of February at Ashok Vihar site and minimum in the month of June at Poorvanchal Colony site (table no. 34).

Figure no. 8 to 11 show that there was a consistancy in the trend of NO_2 at urban sites (road sites, commercial sites, residential sites and parks sites) where as, large variation observed in the monthly values of NO_2 at rural sites.

At underground parking sites characteristic NO_2 variation was observed, which showed minimum concentration during winter and maximum during summer (figure no. 16).

The monthly average NO_2 concentration varied between 59.8 ppb to 93.0 ppb at parks/recreation sites. The maximum NO_2 concentration (93.0 ppb) observed in the month of February at Deer Park site and minimum concentration (59.8 ppb) in the month of June at Lodhi Garden site. (table no.32)

DISCUSSION

Chapter IV : Discussion

In India NO_2 monitoring studies have been done by using conventional sampling techniques such as high volume sampler, handy sampler and continuous monitor etc., which is bulky, costly and require electricity, high level maintenance, security and other basic infrastructure for monitoring and cannot be used for large scale monitoring. The present study have soon the passive sampler (cheap, light weight, robust, simple technique based on diffusion of air) can be used successfully for large scale NO_2 monitoring. The finding of present study using NO_2 passive sampler are discussed below :

Nitrogen dioxide in the ambient environment of Delhi and Faridabad at 25 sites during December 1998 to June 1999 varied between 24.2 ppb to 186.1 ppb. The maximum NO_2 concentration was observed at Badarpur site (186.1 ppb) and the minimum at Bakoli site (24.2 ppb).

The highest average NO_2 concentration was at Azadpur (160.35 $\pm$ 86.21 ppb) followed by Underground Parking, Palika (155.27 $\pm$ 49.26), Open Parking, Bank of Baroda (137.54 $\pm$ 8.04), Open Parking, Jeevan Bharti (134.26 $\pm$ 7.38), Connaught Place (130.01 $\pm$ 7.77), Ring Road (129.40 $\pm$ 6.86), Janpath (125.91 $\pm$ 5.80), Underground Parking, Jeevan Bharti (119.83 $\pm$ 11.51), Africa Avenue (102.92 $\pm$ 7.13), Badarpur (95.89 $\pm$ 38.26), Libaspur (92.13 $\pm$ 10.6), CRI (90.53 $\pm$ 18.31), AIIMS (90.36 $\pm$ 21.76), Vivekanand Marg (87.02 $\pm$ 8.46), Deer Park (86.88 $\pm$ 5.96), Lodhi Road (86.13 $\pm$ 4.37), Lodhi Garden (67.47 $\pm$ 4.91), Aruna Asaf Ali Marg (66.77 $\pm$ 7.81), Bodhpur-I (61.69 $\pm$ 15.69), IOC (61.22 $\pm$ 16.01), Bodhpur-II (61.69 $\pm$ 15.94), Bakoli (43.05 $\pm$ 13.89), Ashok Vihar (42,31 $\pm$ 4.28), JNU (39.44 $\pm$ 12.67) and Poorvanchal Colony (37.67 $\pm$ 3.70).

At 15 urban sites (commercial, residential, parks, parking and road sites) during Jan'99 to June'99 almost similar NO_2 trends were observed. There was maximum concentration of NO_2 during February and April and minimum NO_2 concentration during June. The reasons for high urban NO_2 concentration at Azadpur site during April may be following :

92

1)   Increased photochemical activity due to high light intensity and insolation. This

      leads to more ozone formation, consequently, NO gets converted into NO_2 as :

$$NO + O_3 \quad = \quad NO_2 + O_2$$

2)   Plants play very important role in NO_2 removal from atmosphere. However, dur-

      ing April month plants have less number of leaves resulting less removal of NO_2

      from the atmosphere.

3)   The removal of NO_2 from atmosphere mainly takes place by reaction of NO_2 with

      OH radical. (Bower et al., 1991). This leads to HNO_3 formation during day time.

      In temperate countries such as UK, high concentration of OH radical during sum-

      mer has been reported. However, in India summer usually has relatively less OH

      radical in the ambient environment except the month of June and sometimes May.

The possible reasons for high urban NO_2 concentration during February (winter month) are fol-

lowing:

      1.   High atmospheric stability

      2.   Reduced mixing depth and consequent poorer dispersive condition.

The possible reason for minimum urban NO_2 concentration during the month of June may be

cloudy condition and rainfall on few occasion (high OH content in atmosphere) resulting less O_3

formation and more depositional loss of NO_2.

At rural sites high NO_2 concentration may be observed during winter months and less during

summer months, following reasons were responsible for high winter and low summer NO_2 con-

centration.

1)   Rural areas have large number of industries and thermal power plant, which have

      greater seasonality in emission. The biomass burning for space heating during win-

      ter in rural areas also contribute significant quantity of NO_2 in the atmosphere.

2)   Increased atmospheric stability, reduced mixing depth and consequent poorer dis-

      persive capacity of the atmosphere during winter.

In India NO_2 monitoring studies carried out by CPCB in Delhi show no trend between winter and summer NO_2 concentrations. The monitoring of NO_2 from Dec.'98 to June'99 at rural sites and Jan'99 to June'99 at urban sites are not sufficient and much longer time series measurements are needed to ascertain the NO_2 in ambient environment, unless long term systematic NO_2 monitoring is undertaken at different activity sites of the city, generation are not possible.

At rural sites, NO_2 concentration varied between 24.2 ppb to 186.1 ppb. Out of 10 selected rural sites, 4 were situated in north-west direction, 4 in south-east direction and 2 in south direction. It was observed that at south-east sites (Badarpur, IOC, CRI and AIIMS) concentration of NO_2 was higher than its concentration at north-west sites. (Bakoli, Bodhpur-I, Bothdpur-II and Libaspur). This is due to the presence of a large number of industries, thermal power plants and high traffic density at south-east rural sites.

At rural sites maximum NO_2 concentration (186.1 ppb) was observed at Badarpur site and minimum (24.2 ppb) at Bakoli. This was probably due to the presence of NTPC (National Thermal Power Corporation) at Badarpur site. Thermal power plant emits considerable quantity of NO_x in plumes above the boundary layers, however, plumes are generally lower in winter due to atmospheric inversion and reduced mixing depth.

However, Bakoli had least NO_2 concentration among selected rural sites. This is due to fact that :

1)   Bakoli is situated about 2 km away from National Highway whilst rest north-west sites were in close vicinity of National Highway.

2)   Bakoli is a rural area with least human interference.

Out of four selected north-west sites, the maximum concentration was observed at Libaspur site. The possible reasons behind it may be following :

1)   It is situated in close vicinity of a National Highway.

2)   Libaspur is about 1.5 km away from outer ring road. Since, its surrounding is open.

94

3)   A large solid waste dumping site is situated in vicinity of Libaspur. The decomposition of organic matters release NO_x in the atmosphere, may acts as another source of NO_2 for Libaspur site.

At 15 urban sites, NO_2 average concentration varied between 42.31 ± 4.28 ppb to 160.32 ± 6.98 ppb. Maximum NO_2 concentration was observed at Azadpur site (160.32 ± 6.98 ppb). The probable reasons for high NO_2 concentration at Azadpur site are following :

1)   Azadpur has very mixed traffic and a high traffic density dominated by diesel trucks. Which carry maximum traffic going out from Delhi to other states and vice versa.

2)   Roads of Azadpur site is narrow, congested.

3)   Frequent traffic jams are also very common.

The NO_2 concentration at parking sites varied between 100.6 ppb to 226.5 ppb. At underground parking sites NO_2 average concentration ranged from 103.5 to 218.45 ppb. However, two open parking sites varied between 116. 97 to 148.2 ppb and similar NO_2 variation (fig. no.___) and less difference in NO_2 concentration were observed. Whilst, at two underground parking sites similar NO_2 trend (fig. no.___) and large difference in monthly NO_2 concentration were observed. During summer in underground parkings high NO_2 concentration in comparison to its concentration in winter were observed. In summer the high NO_2 concentration in underground parking, Palika and comparatively low NO_2 concentration at underground parking, Jeevan Bharti may be due to following reasons :

1)   The underground parking, Jeevan Bharti is only availed by employees of Jeevan Bharti. It's open 5 days in a week between 9 am to 5 pm. It usually houses fixed number of vehicle (200-250) throughout year. However, underground parking, Palika is open 6 days a week between 8 am to 10 pm. It usually have less number (about 200) of vehicle during winter and large number (400) during summer, however, it's capacity is one thousand vehicles.

2)   The exit of the underground parking, Palika directly opens at inner circle road of CP. So, there is a possibility of infiltration of air form road site.

3) In summer, the high rate of photochemical activity leads to more ozone and NO_2 formation. However, in ambient environment the deposition of NO_2 takes place whilst in underground parking, absence of suitable condition for deposition, leads to less removal of NO_2.

It was observed that there is no correlation between open parking and underground parking NO_2 concentration trends. This is due to changes in car park usage and meteorological conditions. The influence of meteorological conditions on dispersion of pollutants can explain much of the week to week variability in ambient NO_2 levels.

The two open parking sites show similar NO_2 variation except for a small difference in concentration. The higher NO_2 concentration was measured at open parking, Bank of Baroda. The reason behind this is that open parking, Bank of Baroda is situated at near a busy road site. So, there may be direct inflow of pollutants from the road.

At six selected road sites NO_2 concentration varied between 49.55 ppb to 140.2 ppb. The maximum concentration was observed at ring road site and minimum at Aruna Asaf Ali Marg because of high traffic density throughout day at ring road and traffic jam during peak hours. Whilst, Aruna Asaf Ali Marg has less traffic density, no congestion, high speed of vehicle and open topography.

The NO_2 monitoring studies carried out by CPCB in Delhi shows that the NO_2 concentration in city exceeds national ambient air quality standard ($60 \ \mu g/m^3$). Whilst in the present study it was found that NO_2 in Delhi urban sites most of the time exceed the national ambient air quality standard. It was also observed that in residential areas also NO_x levels exceeds the national ambient air quality standard.

SUMMARY

Summary

The concentration of oxides of nitrogen in ambient environment is increasing at alarming rate. Most of studies on NO_2 behavior and effect have been done in western countries, particularly, in temperate climate.

In India, most of metropolitan cities facing severe NO_2 pollution problem.

The present study was undertaken from Dec'98 to June'99 at 25 sites in order to determine NO_2 concentration behavior and trend under different activities zone with the help of passive sampler.

The main findings of the study are summarized below :

1. The concentration of NO_2 in ambient rural and urban environment at 25 sites varied between 24.2 ppb to 186.1 ppb. The maximum NO_2 concentration was observed at Azadpur (160.32 ± 6.98 ppb) and minimum at Poorvanchal Colony (37.67 ± 3.70 ppb).

2. The monthly average concentration of NO_2 varied between 30.5 ppb to 169.6 ppb. The maximum monthly average NO_2 concentration (169.6 ppb) was observed at Badarpur site and minimum (30.05 ppb) at JNU site.

3. At rural sites, NO_2 concentration varied between 24.2 ppb to 186.1 ppb. The maximum concentration (186.1 ppb) was at Badarpur site. The rank order of NO_2 at rural sites based on the average observations over six months are as follows:

   Badarpur > Libaspur > CRI > AIIMS > Bodhpur-I > IOC > Bodhpur-II > Bakoli > JNU > Poorvanchal Colony

4. NO_2 concentration at south-east rural sites was 1.33 times over its concentration at north-east rural sites.

5. The NO_2 concentration at rural sites was 1.61 times over to its concentration at residential sites.

6. At urban sites, NO_2 concentration varied between 32.1 ppb to 169.40 ppb. Maximum NO_2 concentration (169.40 ppb) at Azadpur site was observed in the month of April and minimum concentration (32.1 ppb) at Ashok Vihar site in the month of June.

7. The NO_2 concentration at parking sites varied between 100.6 to 226.5 ppb. The rank order of four parking sites based on observation for 6 months are as follows: Underground parking, Palika > Open Parking, Bank of Baroda > Open Parking, Jeevan Bharti > Underground Parking, Jeevan Bharti.

8. The average NO_2 concentration at open parking sites was 1.03 times greater than its concentration at underground parking sites.

9. The NO_2 concentration at road sites varied between 49.55 to 140.20 ppb. The rank order of different road sites based on the observation over six months are follows :

Ring Road > Janpath > Africa Avenue > Lodhi Road > Aruna Asaf Ali Marg

10. The NO_2 concentration at high traffic density road sites were 1.39 and 1.79 times higher that its concentration at medium and low traffic density road sites respectively.

11. At commercial sites, NO_2 concentration varied between 109.8 to 169.4 ppb. The NO_2 concentration at commercial site was 3.67, 1.88 and 1.46 timer over to its concentration at residential, parks and road sites respectively.

12. The NO_2 concentration at residential sites varied between 30.4 ppb 47.15 ppb. The maximum NO_2 concentration observed of Ashok vihar colony and minimum at Poorvanchal Colony.

13. The NO_2 concentration at residential sites was 3.67, 2.52, 3.45, 1.95 and 1.61 times less that its concentration at commercial, road site and open parking, parks and rural sites respectively.

14. At parks/recreation sites, NO_2 concentration varied between 57.66 to 96.6 ppb. The NO_2 concentration at parks sites was 1.95 times over to its concentration at residential and 1.88 times less than its concentration at commercial site.

15. At all urban sites, similar NO_2 trends were observed, whilst, the two rural sites (north-west and south-east) showed large variation.

16. At rural sites, high NO_2 concentration were observed during winter (Dec, Jan, Feb.) & low concentration during summer, however, at urban sites, high concentration during Feb & April & less during June were observed.

17. The present study have shown that the passive sampler can used successfully to monitor NO_2 spatial concentration and its concentration at remote areas, in subtropical countries.

18. In urban environment, automobiles are the main source of NO_2 while in rural environment industries, vehicle, thermal power plant are main source of NO_x.

19. The NO_2 concentration at underground parking sites was 1.03 times less than its concentration at open parking sites.

20. A characteristic NO_2 variation was observed at underground parking sites, which showed low NO_2 concentration during winter and high during summer, except the month of June.

REFERENCES

References

Amaya, K., Suguira, K. (1983). Environ. Prot. *Engineering*, 9, 5-9.

Amundson, R.G. and MaClean, D.C. (1982). Influence of oxides of nitrogen on crop growth and yield. T. Schneider and L. Grant, eds. In : *air pollution by NO₂*. 50, 1-10. Amsterdam, Elsevier Scientific Publishing Company.

Anderson, L.S. and Manasfield, T.A. (1979). The effect of NO pollution on growth of tomato. *Environ. Pollut.*, 20, 113-21.

Aoyama, T., Yashiro, T. (1983). Analytical study of low-concentration gases, IV investigation of the reaction by trapping NO_2 in air using the triethanolamine method. *J. of Chromatography*, 265, 69-78.

Apling, A.J., Stevenson, K.J., Goldstein, B.D., Melia, R.J.W. and Atkins, D.H.F. (1979). Air pollution in homes 2, Validation of diffusion tube measurements of NO_2, W.S.L., **In** : Report LR 311 (AP).

Ashenden, T.W. and Williams, I.A.D. (1980). Growth reduction in Lolium multiflorum and Phellum pratense as a result of SO_2 and NO_2 pollution. *Environ. Pollut.*, 21, 131-39.

Ashenden, T.W. (1979a). Effect of SO_2 and NO_2 pollution on transpiration in Phaseolus vulgaris. *Environ. Pollut.*, 15, 161-66.

Ashenden, T.W. (1979b). Effect of long term exposures to SO_2 and NO_2 pollution on the growth of Dactylus glomerata and Poa pratensis. *Environ. Pollut.*, 18, 249-58.

Ashenden, T.W. and Bell, S.A. (1989). Rural concentration of NO_2 pollution throughout Wales. *Environ. Pollut.*, 58, 179-93.

Ashenden, T.W. and Manasfield, T.A. (1978). Extreme pollution sensitivity of gases when SO_2 and NO_2 presents in atmosphere together, *Nature*, 273, 142-43.

Ashenden, T.W. and Williams, I.A.D. (1980). Growth reduction as a result of SO₂ and NO₂ pollution. *Environ. Pollut.*, 21, 131-39.

Atkins, C.J. Wookey, P.A. and Manasfield, T.A. (1991). Atmospheric pollution and sensitivity of stomata on barely leaves to abscisic acid and carbon dioxide. *New Phytol.*, 117, 535-41.

Atkins, D.H.F. and Lee, D.S. (1995). Spatial and temporal variation of rural nitrogen dioxide concentrations across the United Kingdom. *Atmospheric Environ.*, 29, 223-39

Atkins, D.H.F., Healy, C. and Torrant, J.B. (1978). The use of simple diffusion tubes for measurement of NO₂ levels in homes using gas and electricity for cocking. In : UK Atomic Energy Authority Report R 9184, AERE, Harwell.

Atkins, D.H.F., Sandalls, J., Law, D.W., Hough, A.M. and Stevenson, K.J. (1986). The measurement of NO₂ in the outdoor environment using passive diffusion tube samplers. In : AERE-R 12133, HMSO, London.

Becker, T.W., Foyer, C., Caboche, M. (1992). Light-regulation led expression of the nitrate-reductase and nitrite reductase genes in tomato and in phytochrome-dificient aurea mutant of tomato. *Planta*, 188, 39 - 47.

Beevers, L. (1976). Nitrogen metabolism in plants, London, Arnold (Contemporary biology series).

Bennett, J.H., Hill, A.G., Soleimani, A. and Edwards, W.H. (1975). Acute effect of the combination of SO₂ and NO₂ on plants. *Environ. Pollut.*, 12, 7-16.

Besford, R.T., Hand, D.W. (1989). The effect of CO₂ enrichment and nitrogen oxides on some celvin cycle enzymes and nitrate reductase in glass house lettuce. *J. of Experimental Botany*, 40, 319 - 36.

Boleij, J.S.M., Lebret, E., Hoek, E., Noy, D. and Brunekreff, B. (1986). The use of palmes diffusion tubes for measuring NO₂ in homes. *Atmospheric Environment*, 20 (3), 597-600.

Bottger, A., Ehhalt, D.H. and Gravenhorst, G. (1978). Atmospheriasche kreislaufe von strickoxiden and ammoniak, K.F.A. Julich, **In** : Report no. **1553**, 155.

Bowden, W.B. (1986). Gaseous nitrogen emission from undisturbed terrestrial ecosystem : An assessment of their impacts on local and global nitrogen budgets. *Biogeochemistry*, **2**, 249-79.

Bower, J.S., Broughton, G.F.J, Dando, M.T., Lees, A.J., Stevenson, K.J., Lampert, J.E., Sweeney, B.P., Parker, V.J., Driver, G.S., Waddon, C.J. and wood, A.J. (1991). Urban NO_2 concentration in United Kingdom in 1987. *Atmospheric Environment*, **2513(2)**, 267-85.

Bower, J.S., Lampert, J.E., Stevenson, K.J., Atkins, D.H.F. and Law, D.V. (1991). A diffusion tube survey of NO_2 levels in urban areas of the U.K. *Atmospheric Environment*, **25 A (2)**, 256-65.

Bremner, J.M. and Blackmer, A.M. (1978). Nitrous oxide emission from soils during nitrification of fertiliser nitrogen. *Science*, **199**, 295-96.

Bull, J.N. and Manasfield, T.A. (1974). Photosynthesis in leaves exposed to SO_2 and NO_2. *Nature, Lond.*, **250**, 443-44.

Bull, J.N. and Manasfield, T.A. (1979). Photosynthesis in leaves exposed to SO_2 and NO_2, **250**, 443 - 44.

Cadoff, B.C. and Hodgeson, J. (1983). Passive sampler for ambient levels of nitrogen dioxide. *Analytical Chemistry*, **55**, 2083-85.

Campbell, G.W. (1988). Measurement of nitrogen dioxide concentrations at rural sites in the United Kingdom using diffusion tubes. *Environ. Pollut.*, **55**, 251-70.

Campbell, G.W., Stedman, J.R., and Stevenson, K. (1994). A survey of nitrogen dioxide concentrations in the United Kingdom using diffusion tubes, July - December 1991. *Atmospheric Environment*, **28(3)**, 477-86.

Capron, T.M. and Manasfield, T.A. (1976). *J. of Experimental Botany*, **27**, 1181-86.

Capron, T.M. and Manasfield, T.A. (1977). Inhibition of growth in tomato by air polluted with nitrogen oxides. *J. of Experimental Botany*, **28**, 112-16.

Carlson, R.W. (1983). Interaction between SO_2 and NO_2 and their effects on photosynthetic properties of soybean (Glycine max). *Environ. Pollut.*, (Series A), **32**, 11-38.

Central Pollution Control Board (1996). Pollution Statistics in Delhi (1995-96), Delhi.

Chameides, W.L. (1979). *Nature*, **277**, 123-125.

Chameides, W.L., Stedman, D.H., Dickerson, R.R., Rusch, D.W. and Cicerone, R.J. (1977). *J. of Atmospheric Sciences*, **34**, 143-49.

Coffey, P.E. and Satsuik, W.N. (1979). Evidence of atmospheric transport of ozone into urban areas. *Environ. Sci. Tech.*, **9(1)**, 59-62.

Colbeck, I. (1998). Nitrogen dioxide is the work place environment. *Environ. Monit. Assess.*, **52**, 123-30.

Colls, J.J. (1986). Measurement of nitrogen dioxide profiles by diffusion tubes within a Barley canopy. *Atmospheric Environment*, **20 (1)**, 239-42.

Crutzen, P.J. (1974). Photochemical reactions initiated by and influencing O_3 in unpolluted troposphere air. *Tellus*, **26**, 47-49.

Crutzen, P.J. and Zimmermann, P.H. (1991). The changing photochemistry of the troposphere. *Tellus*, **43AB**, 136-51.

Czeck, M. and Nothdurft, W. (1952). Investigation of the damage to field and horticultural crops by chlorine, nitrous and sulphur dioxide gases. *Landwirt Forsch*, **4**, 1-36.

Darrel, N.M. (1989). The effect of air pollutants on physiological process in plants. *Plant, Cell and Environment*, **5 (12)**, 1-30.

Delaney, C. and Dowding, P. (1998). The relationship between extreme nitrogen oxide (NO_x) concentration in Dublin's atmosphere and meteorological conditions. *Environ. Monitoring and Assessment*, **52**, 159-72.

Delwiche, C.C and Bryan, B.A. (1976). Denitrification. *Annu. Rev. Microbiology*, **30**, 241-262.

Dignon, J. (1992). NO_x and SO_x emission from fossil fuels. *Atmospheric Environment*, **24**, 171 - 176.

Doelman, J., Elshout, A.J., Guicherit, R. and Vanderkooy, J. (1975). De Ingenieur, 45.

Dowson, G.A. (1980). *J. of Atmospheric Science*, **37**, 174-78.

Ehhalt, D.H., Drummond, J.W. (1981). The troposhperic cycle of NO_x, presented at Nato Advanced Study Institute on, *chemistry of the polluted and unpolluted troposphere*, Corfu, 28 Sept.

Fenimore, C.P. (1976). *Combustion and Flame*, **26**, 249-52.

Ferguson, E.E. and Libby, W.F. (1971). Mechanism for fixation of nitrogen by lightning. *Nature*, **329**, 37-38.

Ferm, M. and Svanberg, P.A. (1998). Cost-efficient techniques for urban and background measurements of SO_2 and NO_2. *Atmospheric Environment*, **32(8)**, 1377-81.

Focht, D.D. and Verstraete (1977). Biochemical ecology of nitrification and denitrification. *Adv. Microbial Ecol.*, **1**, 135-214.

Fowler, D. and Cape, J.N. (1982). Air pollution and horticulture. In : Unsworth MH, Ormrod, D.P. eds. *Effect of gases air pollution in agriculture and horticulture*. London : Butter worths, 3-26.

Freer-smith, P.H. (1984). The responses of six-broad leaves trees during long term-exposure to SO$_2$ and NO$_2$. *New Phytol.* **97**, 49-61.

Furokawa, A. and Totsuka, T. (1979). Effect of NO$_2$, SO$_2$ and O$_3$ alone and is combination on net photosynthesis in sunflower. *Environment Control in Bio.*, **17**, 161-66.

Gair, A.J. and Penkett, S.A. (1995). The effects of wind speed and turbulence on the performance of diffusion tube samplers. *Atmospheric Environment*, **20(18)**, 2529-33.

Gair, A.J., Penkett, S.A. and Oyala, P. (1991). Development of simple passive technique for the determination of nitrogen dioxide in remote continental locations. *Atmospheric Environment*, **25 A**, 1927-89.

Georgii, H.W. (1963). *J. of Geophys. Res.*, **68**, 3963-70.

Girman, J.R., Hodgson, A.T., Robinson, B.K. and Traynor, G.W. (1983). Lawrence Berkeley Laboratory Report. **In** : LBL 16302, Berkeley, C.A.

Glasius, M., Carlson, M.F., Hansen, S., Lohse, C. (1999). Measurements of NO$_2$ on Fuenen using diffusion tubes. *Atmospheric Environment*, **33**, 117-85.

Goldsmith, A. (1986). Measurements of NO$_2$ at rural sites using passive samplers. **In** : W.S.L. report no. LR 582 (A.P.), Stevenge, UK.

Hameed, S. and Dignon, J. (1988). Change in geographical distributions of global emissions of NO$_x$ and SO$_x$ from fossil fuel combustion between 1966 and 1980. *Atmospheric Environment*, **22**, 441-49.

Heal, M.R. and Cape, J.N. (1997). A numerical evaluation of chemical interference's in the measurement of ambient, nitrogen dioxide by passive diffusion samplers. *Atmospheric Environment*, **31(13)**, 1911-23.

Heal, M.R., Donoghue, M.A., Cape, J.N. (1999). Overestimation of urban NO_2 by passive diffusion tubes. *Atmospheric Environment,* **33,** 513-24.

Heck, W.W. (1964). Plant injury induced by photochemical reaction products of propylene-nitrogen dioxide mixtures. J. *Air Pollu. Contr. Ass.,* **14,** 255-61.

Heicklen, J. and Cohen, N. (1968). The role of nitric oxide in photochemistry. *Adv. Photo. Chem,* **5,** 157-328.

Hergreaves, K.J., Flower, D., Storeton -V. West, R.L. and Duyzer, J.H. (1992). The exchange of nitric oxide, nitrogen dioxide and ozone between pasture and the atmosphere. *Environ. Pollut.,* **75,** 53-59.

Hewitt, C.N. (1991). Spatial variation in nitrogen dioxide concentration in urban area. *Atmospheric Environment,* **2513(3),** 429-34.

Hill, A.C. and Bennett, J.H. (1970). Inhibition of apparent photosynthesis by NO_2, *Atmospheric Environment,* **4,** 341-48.

Hill, A.C., Hill, S., Lamb, C. and Barrett, T.W. (1974). Sensitivity of native desert vegetation to SO_2 and NO_2 combined. J. *of Air Pollution Control Association,* **24,** 153-57.

Hill, R.D., Rinker, R.G. and Wilson, H.D. (1980). J. *of Atmospheric science,* 179-92.

Hisham, M.W.M. and Grosjean, D. (1990). Sampling of atmospheric NO_2 using TEA interference from PAN. *Atmospheric Environment,* **24 A,** 2523-25.

Hoen, P.J., Leaderer, B.P. and Stolwijk, J.A.J. (1984). Continuos monitoring in occupied residences of air contaminants from unvented combustion sources. *Indoor air,* **4,** 277-83.

Horsman, D.C. and Wellburn, A.R. (1975). Synergistic effect of SO_2 and NO_2 polluted air upon enzyme activity of (Pisum sativum). *Environ. Pollut.,* **8,** 123-33.

Irwin, G. and Williams, M.L. (1988). *Environ. Pollut.*, **50**, 29-59.

Johansson, C. (1987). Pine forest : a negligible sink for atmospheric NO_2 in rural Sweden. *Tellus,* **3913**, 426-38.

Judeikis, H.S. and Siegel, S. (1973). Particle-catalysed oxidation of atmospheric pollutants. *Atmospheric Environment,* **7**, 619-31.

Judeikis, H.S., Seigel, S., Stewart, T. B. and Hedgepeth, H.R. (1977). **In** : EPA Report, EPA 600/3-77 - 028.

Judeikis, H.S., Wren, A.G. (1978). *Atmospheric Environment,* **12**, 2315-12.

Junge, C.E. (1958). The distribution of ammonia and nitrate in rainwater over the united states. *Trans. Am. Geopys. Union,* **39**, 241-48.

Kaji, M., Yoneyama, T., Tosuka, T. and Iwaki, H. (1980). Absorption of atmospheric NO_2 by plants and soils. *Res. Rep. Natl. Inst. Envir. Stud. Japan,* **11**, 51-58.

Kasana, M.S. and Lea, P. (1994). Growth responses of mutants of spring barley to fumigation with SO_2 and NO_2 in combination. *New Phytol.,* **126**, 629-36.

Kress, L.W., Skeely, J.M. and Hinkelmann, K.H. (1982). Growth impact of O_3, NO_2 and/or SO_2 on Pinus species. *Environ. Monit. Assess.,* **1**, 229-39.

Kring, E.V., Lautenberger, W.J., Baker, B.W., Pouglas, J.J., Halfman, R.A. (1981). *Am. Ind. Hyg. Assoc. J.,* **42**, 373-75.

Krochmal, D. and Gorski, L. (1991). Determination of nitrogen dioxide in ambient air by use of a passive sampling technique and triethanolamine as absorbent. *Environ. Sci. Tech.,* **25(3)**, 531-35.

Krochmal, D. and Kalina, A. (1997). A method of nitrogen dioxide and SO_2 determination in ambient air by use of passive samplers and ion chromatography. *Atmospheric Environment*, **31(20)**, 3473-79.

Laxen, D.P.H. and Noordally, E. (1987). Nitrogen dioxide distribution in street canyons. *Atmospheric Environment*, **21(9)**, 1899-03.

Lee, Y. and Schwartz, S.E. (1981). Evaluation of the rate of uptake of NO_2 by atmospheric an surface liquid water. *J. Geophys. Res.*, **86(11)**, 971-83.

Levine, J.S. (1991). Global biomass burning, atmosphere, climatic and biospheric implications. MIT Press, Cambridge, M.A.

Lindqvist, O., Ljungstrom, E. and Svensson, R. (1982). Low temperature thermal oxidation of nitric oxide in polluted air. *Atmospheric Environment*, **16(8)**, 1957-72.

MaClean, D.C., Mcune, D.C., Weinstein, L.H., Mandi, R.H. and Woodruff, G.N. (1968). Effect of acute HF and NO_2 exposures on citrus and ornamental plants of central Florida. *Environ. Sci. Tech.*, **2**, 444-49.

Manasfield, T.A. and Freer-smith, D.H. (1981). Effects of urban air pollution on plants growth. *Biol. Rev.* **56**, 343-68.

Martin, A. and Barber, F.R. (1984). Acid gases and acid in rain monitored for over 5 years in rural-east-central England. *Atmospheric Environment*, **18**, 1715-24.

Matsushima, J. (1972). Influence of SO_2 and NO_2 on assimilation of aminoacids, organic acids and saccharoides in Citrus natsudaidai seedlings. **In** : Bull. Fac. Agri. Mic University, **44**, 131-39.

McConnel, J.C. (1973). Atmospheric ammonia. *J. Geophys. Res.*, **75**, 7812-21.

Melia, R.J.W., Florey, C.V. Darby, S.C., Palmes, E.D. and Goldstien, B.D (1978). Differences in NO_2 levels in kitchen with gas or electric cocking. *Atmospheric Environment*, **12**, 1369-81.

Melzer, J.M, Kleinhofs, A. and Warner, R.L. (1989). Nitrate reductase regulation : effect of light nitrate on nitrate reductase messenger RNA accumulation. *Molecular Genetics*, **217**, 341-46.

Middleton, J.T., Dorly, E.F. and Brewer, R.F. (1958). Damage to vegetation from polluted atmospheres. *J. Air Pollution Contr. Ass.*, **8**, 9-15.

Miller, D.P. (1984). Ionchromatographic analysis of palmes tubes for nitrite. *Atmospheric Environment*, **18(4)**, 891-92.

Miller, D.P. (1988). Low level determination of nitrogen dioxide in ambient air using the palmes tube. *Atmospheric Environment*, **22(5)**, 945-47.

Moschandreas, D.J., Relwani, S.M., Taylor, K.C. and Mullik, J.D. (1990). A laboratory evaluation of NO$_2$ personal sampling device, *Atmospheric Environment*, **24A**, 2807-11.

Mostsumo, M., Mizoguchi, T. (1988). *Chem. Abstr.*, **88(109)**, 98000.

Mullik, J.D., R.G., Levis, and MaClenny, W.A. (1989). Modification of a high efficiency passive sampler to determine nitrogen dioxide or formaldehyde in air. *Analytical Chemistry*, **61**, 187-89.

Murray, F., Wilson, S. and Samarweera, S. (1994). NO$_2$ increases wheat grain yield even in presence of SO$_2$. *Agriculture, Ecosystem and Environment*, **48**, 115-23.

Neighbour, A., Cottam, D.A. and Manasfield, T.A. (1988). Effect of SO$_2$ and NO$_2$ on the control of water loss by birch. *New Phytol.*, **108**, 149-57.

Norby, R.J., Weerasuriya, Y. and Hanson, P.J. (1989). Induction of nitrate reductase activity in red spruce needles by NO$_2$ and HNO$_3$ vapour. *Can J. for Res.*, **19**, 889-96.

Noxon, J.F. (1976). *Geophy Res. Lett.*, **3**, 463-66.

Noy, D., Lebret, E., Boleij, J.S. M. and Brunekreef, B.C. (1984). Integrated NO$_2$ exposure estimates. *Indoor Air*, **4**, 37-42.

Okano, K. and Totsuka, T. (1985). Growth responses of plants to various consentration of NO_2. *Environ. Pollut.* (Series A), **38**, 361-73.

Palmes K.D., Tomaczyk, C. and DiMattio, J. (1977). Average NO_2 concentration in houses with gas or electric stoves. *Atmospheric Environment*, **11**, 869-872.

Palmes, E.D. and Jonson, E.R. (1987). Explanation of pressure effect on NO_2 sampler. *American Industrial Hygeine Association J.*, **37**, 570-77.

Palmes, E.D., Gunnison, A.F., Dimattio, J. and Tomaczyk, C. (1976). Personal sampler for nitrogen dioxide. *Am. Ind. Hyg. Assoc. J.*, **37**, 570-77.

Pandey, P.C. and Manasfield, T.A. (1985 a). Responses of spring barley to SO_2 and NO_2 Pollution. *Environ. Pollut.* (Series A), **38**, 87-97.

Pandey, P.C. and Manasfield, T.A. (1985 b). Responses of winter barley to SO_2 and NO_2 pollution alone and in combination. *Environ. Pollut.* (Series A), **39**, 281-91.

Pearson, J. and Stewart, G.R. (1990). Susceptibility of trees to foliar input of nitrogen In : *abstracts of conference on acidic deposition, Its nature and impact,* P. 80, Glasgow, Edinburgh, Royal society of Edinburgh.

Perkauskas, D. and Mikelinskiene, A. (1998). Evaluation of SO_2 and NO_2 concentration levels in vilnius using passive diffusion samplers. *Environ. Pollut.*, **102**, 249-52.

Ramijn, B., Fischer, P., Brunekreef, B., Lebret, E., Bolij, J.S. and NOy, D. (1984). Indoor air pollution and its effect on pulmonary function of adult non-smoking women-exposure estimates for NO_2 and passive smoking. *Int. J. Epidem.*, **14**, 215-20.

Rasmussen, K.H., Taheri, M. and Kabel, R.L. (1975). Global emission and natural processes for removal of gaseous pollutants. *Water, Air and Soil Pollut.*, **4**, 33-64.

Raven, J.A. (1988). Acquisition of nitrogen by roots of land plants, its occurrence and implications for acid-base regulation. *New phytol.*, **109**, 1-20.

Reinert, R.A. and Gray, T.N. (1981). The response of NO_2, SO_2 and O_3, alone and in combination. *J. Environ. Qual.*, **10**, 240-43.

Robinson, E. and Robbins, R.C. (1968). Sources, abundance and fate of gaseous atmospheric pollutants. Standford Research Institute, Melano, C.A. In : SRI Project Report No. 6755.

Robinson, E. and Robbins, R.C. (1970). *J. of Air pollution Contro Association*, **20**, 303-06.

Rodes, C.E. and Holland, D.M. (1981). Variational NO, NO_2 and O_3 concentrations down wind of Los Angeles freeway. *Atmospheric Environment*, **15**, 243-50.

Rogers, H. H. and Campbell, J.C. (1979). Nitrogen-15 dioxide uptake and incorporation by Phaseolus vulgaris. *Science*, **206(33)**, 3-5.

Rondon, A., Johansson, C. and Granat, L. (1993). Dry deposition of NO_2 and O_3 to coniferous forests. *J. Geophys. Res.*, **98**, 5159-72.

Rowland, A.J., Drew, M.C. and Wellburn, A.R. (1987). Foliar entry and incorporation of atmospheric NO_2 into barley plant of different nitrogen status. *New Phytol.*, **107**, 357-71.

Rubino, R.A., Bruckman, L. and Magyariw, J. (1976). Ozone transport. *J. Air Pollut. Control Association*, **26(10)**, 972-73.

Sandhu, R. and Gupta, G. (1989). Effects of NO_2 on growth and yield of black turtles, bean. *Environ. Pollut.*, **59**, 337-44.

Saxe, H. (1986 a). Effect of NO, NO_2 and CO_2 on net photosynthesis, dark respiration and transpiration of pots plant. *New Phytol.*, **103**, 185-97.

Saxe, H. (1986 b). Stomatal-dependent and stomatal independent uptake of NO_2. *New Phytol.*, **103**, 199-05.

Saxe, H. (1994). Relative sensitivity of green house pot plants to long term exposure of NO and NO_2 containing air. *Environ. Pollut.*, **85**, 283-90.

Schmeltekopf, A.L., Albritton, D.L., Crutzen, P.J., Golden, P.D., Harrop, W.J., Henderson, W.R., McForland, N., Schiff, H.I., Thompson, T.L., Hofmann, D.J. and Kojome, N.T. (1977). *J. of Atmospheric Science*, **34**, 3963-70.

Shinn, M.B. (1941). Colourimetric method for determination of nitrite. *Ind. Eng. Chem Anal. Ed.*, **13**, 33-35.

Skiba, U., Hargreaves, K., Flower, D. and Smith, K.A.C. (1992). Flux of nitric and nitrous oxides from agricultural soils in a cool temperate climate. *Atmospheric Environment*, **26 A**, 2477-88.

Soderlund, R. and Svensson, B.H. (1976). The global nitrogen cycle. **In** : Scope Report no. 7, *Ecological Bulletin no. 22*, 23-73 Royal Swedish Academy of Sciences, Stockhalm.

Spierings, F.H.F.G. (1971). Influence of fumigation with NO_2 on growth and yield of tomato plants. *J. Plant Pathology*, **77**, 194-200.

Srivastava, H.S., Ormrod, D.P. and Murray, B.H. (1990). Photosynthesis photon flux effects on bean response to NO_2. *Environ. Exp. Bot.*, **30**, 463-70.

Srivastava, H.S., Wolfenden, J., Lea, P.J. and Wellburn, A.R. (1994). Differential responses of growth and nitrate reductate activity in wild type and NO_2 tolerant barley mutant to atmospheric NO_2 and nutrient nitrate. *J. of Plant Physiology*, **143**, 738-743.

Srivastava, H.S., Wolfenden, J., Lea, P.J., Wellburn, A.R. (1984). Differential Reponses of growth and nitrate reductase activity in wild type and NO_2 tolerant barley mutants. *J. of Plant Physiology*, **143**, 738-43.

112

Taylor, O.C. and Eaton, F.M. (1966). Suppression of plant growth by NO_2. *Plant Physiology*, **41**, 132-135.

Thoene, B., Schroder, P., Papen, H., Egger, A. and Rennenberg, H. (1991). Absorption of atmospheric NO_2 by spruce (<u>Picea abies L.</u>) tree, NO_2 influx and its correlation with nitrate reduction. *New phytol.*, **117**, 575-85.

Thompson, C.R., Hensel, E.G., Kats, G. and Taylor, O.C. (1970). Effect of continuos exposure of naval orange to NO_2. *Atmospheric Environment*, **4**, 344-55.

Tingey, D.T., Reinert, R.A., Dunning, J.A. and Heck, W.W. (1971). Vegetation injury from the interaction of NO_2 and SO_2. *Phytopathology*, **61**, 1506-11.

Transport Research Division (1995), Transport Statistics in India (1995), Ministry of Surface Transport.

Troiano, J.J. and Leone, I.A. (1977). Changes in growth rate and nitrogen content of tomato plants after exposure to NO_2. *Plant Pathalogy*, **67**, 1130-33.

Tsunogai, S. (1971). *J. of Geochem.*, **5**, 57-68.

Weber, P. and Rennenberg, H. (1996). Dependency of NO_2 fluxes to wheat leaves from NO_2 concentration, light intensity, temperature and relative humidity determination from controlled dynamic chamber experiments. *Atmospheric Environment*, **30(17)**, 3001-09.

Wellburn, A.R. (1990). Why are atmospheric oxides of nitrogen usually phytotoxic and not alternative fertiliser. *New Phytol.*, **115**, 395-429.

Wellburn, A.R., Higginson, C., Robinson, D. and Wamsley, C. (1981). Biochemical explanation of more than additive inhibitory effect of low level atmospheric SO_2 and NO_2 upon plants. *New phytol.*, **88**, 223-37.

Wellburn, A.R., Majernik, O. and Wellburn, F.A.M. (1972). Effect of SO_2 and NO_2 polluted air upon the ultrastructure of chloroplasts. *Environ. Pollut.*, **3**, 37-49.

Wellburn, A.R., Wilson, J. and Aldridge, D.H. (1980). Biochemical responses of plants to NO polluted atmosphere. *Environ. Pollut.*, **22**, 219-28.

Wesely, M.L., Eastman, J.A., Stedman, D.H. and Yalvac, E.D. (1982). An eddy correlation measurement of NO_2 flux to vegetation and comparison to O_3 flux. *Atmospheric Environment*, **16**, 815-20.

White, K.L., Hill, A.C and Bennett, J.H. (1974). Synergistic inhibition of apparent photosynthesis rate of alfalfa by combination of SO_2 and NO_2. *Environ. Sci. Tech.*, **8**, 574-76.

Whitemore, M.E. (1985). Relationship between dose of SO_2 and NO_2 mixtures and growth of Poa pratensis, *New Phytol.*, **99**, 545-53.

Whitemore, M.E. and Freer-smith, P.H. (1982). Growth effect of SO_2 and/or NO_2 on woody plants and grasses during spring and summer. *Nature*, **300**, 55-70.

Whitemore, M.E. and Manasfield, T.A. (1983). Effect of long term exposure to SO_2 and NO_2 on Poa pratensis and other grasses. *Environ. Pollut.* (Series A), **31**, 217-35.

Williams, M.L., Broughton, G.F.J., Bower, J.S.,Durry, V.J., Lilley, K., Powel, K., Rogers, F.S.M. and Stevenson, K.J. (1988). Ambient NO_x concentrations in the UK 1976 - 1984 - a summary. *Atmospheric Environment*, **22**, 2819-40.

Willson, A.L.(1987). Comparison of passive and chemiluminescence monitor for determining one week average NO_2 concentrations. **In** : *Proc. Indoor Air Conp.*, **4**, Berlin.

Wollum, A.G. and Davey, C.B. (1975). Nitrogen accumulation, transformation, transport, **In** : B. Bernier, Band, C.H. Winget eds. *Forest Soil and Forest Land Management, Proc. Fourth North America Forest Soil Conference*, 67-106, Level Univ. Quebec, Lees presses de university level, Quebec, Canada.

Yoneyama, T. and Sasakawa, H. (1979). Transformation of atmospheric NO_2 absorbed in spinach leaves. *Plant Cell Physiol.*, **20**, 263-66.

Zeevaart, A.J. (1974). Induction of nitrate reductase NO_2. *Acta Botanica Indica*, **23**, 345-46.

Zeevaart, A.J. (1976). Some effects of fumigating plants for short periods with NO_2. *Environ. Pollut.*, **11**, 97-108.

Zeldovich, B.Y. (1946). *Acta Physico Chemia URSS*, **21**, Nv. 4.