

## Measurement of ambient concentration of NO<sub>2</sub> in Delhi using passive diffusion tube sampler

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**NO<sub>2</sub> is an important gaseous air pollutant that plays a critical role in atmospheric chemistry. In spite of its critical importance for atmospheric chemistry and human health, information on ambient levels of NO<sub>x</sub> from urban, peri-urban, rural and remote areas is limited in the country, because of the limited availability of expensive, heavy, electricity-based NO<sub>2</sub> monitoring equipments. Passive samplers provide a convenient alternative for measuring ambient NO<sub>2</sub> in a highly cost-effective manner. The passive sampler is a simple, cheap device, which is independent of power supply. The present study deals with fortnightly measurements of NO<sub>2</sub> concentration at nine sites along northwest and southeast transact passing through the capital city of Delhi, using passive diffusion tube samplers, from November 1998 to June 1999. At 45% of the sites, NO<sub>2</sub> levels were found to violate the National Ambient Air Quality Standard of 80 µg/m<sup>3</sup>. A large inter-site variation ranging from 13 to 200 µg/m<sup>3</sup> was observed. In addition, a marked seasonal variation was also noticed. Winter values were higher compared to the summer values.**

NITROGEN oxide is an important gaseous air pollutant that plays a critical role in atmospheric chemistry. It is one of the key reactants contributing to environmental acidification, formation of ozone, peroxyacyl nitrate (PAN), nitrate aerosols and other photochemical oxidants. NO<sub>2</sub> is an important constituent of oxides of nitrogen (NO<sub>x</sub> = NO + NO<sub>2</sub>), formed as a by-product of the combustion process. Nitric oxide (NO) predominates in the emission mixture. In fact, most of the NO<sub>2</sub> in the atmosphere is formed from the oxidation of NO by ozone.

In recent years, interest in NO<sub>2</sub> as an air pollutant is growing not only because of its phytotoxic nature<sup>1,2</sup> and adverse effect on crops yield<sup>3</sup>, but also on account of growing evidence of its adverse effect on human health<sup>4,5</sup>. Moreover, NO<sub>2</sub> is also an important precursor of ozone formation. Significantly high ozone levels, violating World Health Organization (WHO) standard 8 h guideline of 120 µg/m<sup>3</sup>, have been reported from Delhi and its environs<sup>6</sup>. Accordingly, wide spatial comprehensive monitoring of NO<sub>2</sub> is becoming increasingly important for air quality assessment and management. In India, a network of 298 air-quality monitoring stations has been

established across the length and breadth of the country by the Central Pollution Control Board (CPCB). It may be pointed out that majority of air-quality monitoring stations are located in urban areas. Accordingly, information on air quality status of peri-urban and rural areas is scanty. Even in urban areas, the number of air-quality monitoring stations is rather limited. For example, Delhi, which has an area of 1486 km<sup>2</sup>, has only nine air-quality monitoring stations, i.e. for every 165 km<sup>2</sup> area there is only one monitoring station. In such a situation it is difficult to expect a good resolution of spatial variation of air pollution levels from such a sparsely spread network of air-quality monitoring stations. In order to determine spatial variation of NO<sub>2</sub> levels, a more elaborate monitoring network would be necessary. However, establishment of an elaborate air-quality monitoring network is difficult, in want of resources required for expensive imported equipment and access to dependable power supply, apart from the need for technical manpower. In view of these constraints, passive samplers offer an attractive alternative on account of their simplicity, low cost and are not dependent on electricity. Thus, by deploying passive samplers it is possible to develop a wide spatial NO<sub>2</sub> monitoring network in a highly cost-effective manner. In this study an attempt has been made to measure ambient levels of NO<sub>2</sub> in Delhi along northwest and southeast transact using passive diffusion tube samplers.

Delhi, the capital city of India, is located between 76°50'E–77°23'E and 28°12'N–28°53'N, on the west bank of river Yamuna. It lies within the subtropical belt, and experiences a maximum temperature of 46°C in summer and a minimum of 2°C in winter. It has a monsoon climate with an average yearly rainfall of 73 cm, 80% of which is received during June–August. The predominant wind direction is northwesterly, except during the monsoon season (July to mid-September). Wind speed exhibits seasonal fluctuations, being maximum during summer and monsoon months. Delhi is a cosmopolitan city spread over an area of 1486 km<sup>2</sup>, with a population of over 13 million. It is a major centre both for industry and commerce, and is also highly polluted.

Nine sites were selected along northwest and southeast transact in Delhi for NO<sub>2</sub> monitoring using a passive sampler. The criteria for selecting these sites differ in the magnitude of anthropogenic activity, traffic density and wind direction (Figure 1). Different sites were grouped into two categories: (1) Sites close to National Highways (S2, S4, S6, S8 and S9) and (2) Sites away from National Highways/busy traffic corridors (S1, S3, S5 and S7).

S1 (MGIIPD): An academic complex, surrounded by agricultural fields, situated northwest of Delhi, approximately 2 km from the National Highway-I.

S2 (SSC): An academic institution, approximately 200 m away from National Highway-I, northwest of Delhi.

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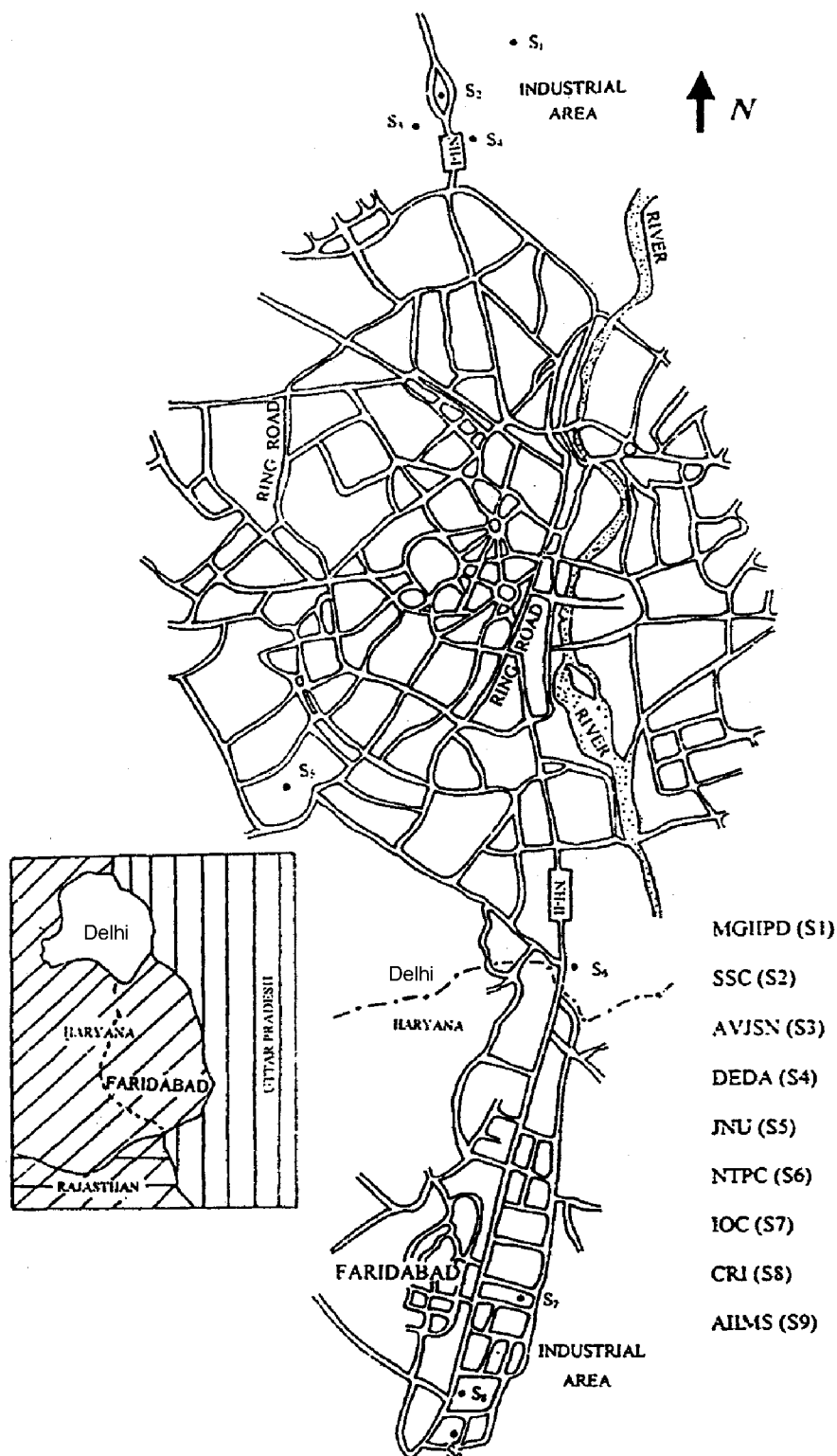


Figure 1. Map of Delhi and Haryana showing approximate sampling site locations.

S3 (AVJSSN): A temple complex situated approximately 1 km away from National Highway-I, northwest of Delhi, in the neighbourhood of farm houses.

S4 (DEDA): Delhi Energy Development Agency located northwest of Delhi, approximately 50 m east of National Highway-I. It is a fast-moving traffic corridor.

S5 (JNU): Located inside a vast tract of natural vegetation approximately 1 km away from Aruna Asaf Ali Marg, south of Delhi and fairly insulated from heavy vehicular traffic.

S6 (NTPC): National Thermal Power Corporation Limited is the largest thermal power-generating company in India. NTPC operates a 720 MW coal-based power station which lies along National Highway-II (approx. 100 m away), southeast of Delhi at a distance of about 25 km from the city centre.

S7 (IOC): A large research and development complex of Indian Oil Corporation, situated about 2.5 km east of the National Highway-II, southeast of Delhi.

S8 (CRI): A research institute, situated southeast of Delhi along National Highway-II on which traffic is heavy, mixed and slow.

S9 (AIIMS): A hospital complex situated about 200 m east of National Highway-II, southeast of Delhi.

The passive sampler is based on the principle of air diffusion. It consists of an acrylic tube of 7.1 cm length and 1.1 cm diameter, having two stainless-steel wire meshes with 0.2 mm mesh size and 0.1 mm wire diameter, and sealed with a coloured plastic cap at one end and a colourless cap at the other end. The sampler preparation involves, placing of the two meshes into the coloured cap and injecting 50  $\mu$ l of 20% v/v triethanolamine (TEA)/aqueous solution (in deionized water) directly on the meshes. Triethanolamine ( $N(CH_2CH_2OH)_3$ ) acts as an absorbent for  $NO_2$ . To aid the coating on the meshes, 0.5 ml of Brij-35 (a wetting agent) was added to 20 ml of the TEA aqueous solution. One end of the tube was closed immediately with a coloured cap, while the other end of the tube was closed with a colourless cap.

At each site, three freshly prepared passive samplers were positioned at a height of 1.5 m above the ground, out of which two samplers were exposed by removing their colourless caps, while the third one was maintained as such without removing the colourless cap to serve as a field blank. The atmospheric  $NO_2$  diffuses up the tube where it gets absorbed on the TEA-coated mesh. This establishes a  $NO_2$  concentration gradient along the length of tube. Consequently  $NO_2$  diffuses up the tube where it is absorbed on TEA-coated meshes. After two weeks of continuous exposure, the open ends of the passive samplers were closed by the colourless caps. Exposed samplers along with the field blanks were collected and were immediately replaced by a new set of samplers. Air sampling was carried out twice during each month at nine sites during November 1998–June 1999.

Passive diffusion tube samplers were analysed according to modified Saltzman reaction<sup>7</sup>. The colourless caps from the samplers were removed and to each sampler, 0.6 ml of water was added followed by 0.6 ml of a 2% (w/v) solution of sulphanilamide in 5% (v/v) orthophosphoric acid, and finally 0.1 ml of a 0.14% w/w N-1, naphthyl ethylene diamine dihydrochloride (NEDA) solu-

tion. The nitrite in the solution reacted with sulphanilamide to form diazonium compound, which on coupling with NEDA forms purple azo-dye. Optical absorbance of the coloured solution was measured at 540 nm on a Japanese dual port UV/VIS spectrophotometer (JASCO, Model 7800). The absorbance reading of the blank sampler was subtracted from the reading of exposed samplers. The amount of nitrite ions in the sample was determined with the help of a calibration plot derived from standard nitrite solutions. The nitrite concentration was then used to calculate average ambient  $NO_2$  concentration for the particular period of exposure.

The results of this study show that minimum and maximum two-weekly values of  $NO_2$  along northwest and southeast transect in Delhi varied between 13 and 200  $\mu$ g/m<sup>3</sup>. The maximum  $NO_2$  concentration was observed at site S6 and minimum at site S5 during winter and summer seasons respectively. The average value for each site along with winter and summer mean values for individual sites are given in Table 1. The seven-month average values of  $NO_2$  for individual sites varied between 20 and 119  $\mu$ g/m<sup>3</sup>, and were recorded at sites S5 and S6 respectively. The proximity of site S6 to a 720 MW coal-based thermal power plant and to a busy National Highway-II, experiencing frequent traffic congestion could be a possible reason for high  $NO_2$  values there. The minimum value was observed at site S5, which lies in an area surrounded by natural vegetation and was free from heavy traffic. At sites S4, S6, S8 and S9,  $NO_2$  levels were found to violate the National Ambient Air Quality Standard of 80  $\mu$ g/m<sup>3</sup>.

Table 1 shows significant variation in ambient  $NO_2$  levels during the study period, which may mainly be on account of variation in meteorological conditions and fluctuations in traffic density. Maximum variation (CV 37%) was observed at site S6, which was largely under the influence of the thermal power plant and minimum variation (CV 10%) was at site S4, situated along a busy National Highway-I, which was consistently under the influence of highway traffic emission. Coefficient of variation of duplicate samplers was low, ranging between 1.3 to 3.5%, indicating that the passive diffusion tube samplers provided reliable measure of  $NO_2$  concentration.

A large inter-site variation from 13 to 200  $\mu$ g/m<sup>3</sup> was observed. Such variation appears to be on account of inter-site differences in the intensity of anthropogenic activity. A distinct seasonal variation in the ambient  $NO_2$  level was observed at each site. During winter,  $NO_2$  values were higher compared to summer values by a factor of about 1.17. Relatively higher  $NO_2$  values during winter can be attributed to a combination of the following possible factors:

(1) Meteorological conditions, which exert a strong influence on atmospheric dispersal of pollutants; for example, during winter pollutants tend to accumulate close to the ground because of high atmospheric stability,

**Table 1.** Ambient NO<sub>2</sub> concentration (µg/m<sup>3</sup>) in Delhi during November 1998–June 1999

Site	Concentration	CV (%)	Minimum	Maximum	Winter (concentration)	Summer (concentration)	W/S
S1	30	25	15	78	36	28	1.3
S2	61	25	26	117	63	61	1.03
S3	40	22	14	90	46	35	1.3
S4	110	10	80	145	114	112	1.0
S5	20	28	13	51	24	19	1.30
S6	119	37	62	200	140	105	1.33
S7	43	25	36	114	49	40	1.24
S8	104	18	80	182	109	105	1.04
S9	103	22	70	176	106	105	1.01

**Table 2.** Comparison between NO<sub>2</sub> values observed at study sites and those reported by CPCB (1997) for comparative sites in Delhi

Present study site <sup>1</sup>	NO <sub>2</sub> (µg/m <sup>3</sup> )	CPCB (RM site) <sup>a</sup>	NO <sub>2</sub> (µg/m <sup>3</sup> )	Present study site <sup>2</sup>	NO <sub>2</sub> (µg/m <sup>3</sup> )	CPCB (TI site) <sup>b</sup>	NO <sub>2</sub> (µg/m <sup>3</sup> )
MG IIPD (S1)	30	Shahadara	29.3	SSC (S2)	61	Azadpur	66
AVJSSN (S3)	40	Janakpuri	34.8	DEDA (S4)	110	Azad market	111
JNU (S5)	20	Ashok Vihar	23	NTPC (S6)	119	Shymlal C	100
IOC (S7)	43	Shahzada Bagh	44.8	CRI (S8)	104	Punjabi Bagh	84
				AIIMS (S9)	103		
	33.2		32.9		99.4		90.2

<sup>a</sup>Regular monitoring site; <sup>b</sup>Traffic intersection sites.

<sup>1</sup>Study sites are comparable with CPCB (RM sites)<sup>a</sup>, being in low traffic-density area; <sup>2</sup>Study sites are comparable with CPCB (TI sites)<sup>b</sup> on account of proximity to busy traffic corridors, supporting high traffic density.

lower mixing depth leading to poor dispersive capacity of the atmosphere. (2) Burning of biomass, as a prime source of energy, increases during winter for heating purposes, especially in peri-urban and rural areas. According to an estimate, in Delhi about 313.3 thousand tonnes biomass is burnt annually<sup>8</sup>. (3) A relatively low rate of chemical removal of ambient NO<sub>2</sub>, in the form of HNO<sub>3</sub>, from atmospheric reaction with OH radical whose concentration is relatively less during winter. Formation of OH radicals is light-dependent, hence their concentration remains relatively high during the summer months.

Winter/summer NO<sub>2</sub> concentration (W/S) ratios are given in Table 1. W/S ratios were less at sites S2, S4, S8 and S9, except for site S6, they were all close to National Highways. The emission from a coal-based 720 MW thermal power plant was likely to be responsible for high W/S concentration ratio at site S6. W/S ratios were relatively high at sites S1, S3, S5 and S7, which were away from National Highways/busy traffic corridors. Increased distance between monitoring site and major polluting sources provided enhanced opportunity for NO → NO<sub>2</sub> oxidation. Consequently, relatively high W/S ratio was observed at sites situated away from National Highways. However, strong seasonal fluctuations were absent from those sites which were close to the National Highways, because such sites were under direct influence of highway traffic emissions.

In northwest and southeast industrial zones, NO<sub>2</sub> levels were significantly high at sites (S2, S4, S6, S8 and S9)

close to National Highways and relatively low at sites (S1, S3, S5 and S7) lying away from National Highways or busy roads. These observations strongly suggest that automobile traffic is a dominant source of NO<sub>2</sub> pollution, even in industrial areas. Small-scale miscellaneous industries operating in the area, and biomass burning by migrant labour population working in such industries represent other minor sources of NO<sub>2</sub> emission.

An attempt has also been made to compare NO<sub>2</sub> values observed at study sites with values reported by CPCB for comparative sites in Delhi, although the location of monitoring sites was different. In 1997, CPCB measured NO<sub>2</sub> concentrations at some traffic intersections in Delhi for the first time, which were different from the nine regular air pollution-monitoring sites maintained by CPCB. Subsequently, observations on traffic intersections were not made. Most of the regular CPCB monitoring sites in Delhi fall in low anthropogenic-activity zones. Sites S1, S3, S5 and S7 were comparable with the regular air-quality monitoring sites of CPCB, being in low traffic-density area; and CPCB traffic intersection sites were comparable with sites S2, S4, S6, S8 and S9 on account of proximity to busy traffic corridors supporting high traffic density. A comparison of NO<sub>2</sub> values obtained during this study with values reported by CPCB for regular monitoring sites<sup>9</sup> as well as with the traffic intersection sites<sup>10</sup> is given in Table 2. Data in Table 2 show relatively high NO<sub>2</sub> values (1.1 times) at sites S2, S4, S6, S8 and S9 compared to the values reported at traffic

intersection sites of Delhi. Higher NO<sub>2</sub> values observed in the present study appear to be on account of rapid growth in the number of automobiles in Delhi during the intervening period between 1997 and 1999. NO<sub>2</sub> values at CPCB regular monitoring sites were close to the NO<sub>2</sub> values observed at sites in the present study, S1, S3, S5, and S7, which were away from the direct impact of any busy traffic corridor.

High levels of NO<sub>2</sub> observed in the present study suggest that there is a need for comprehensive NO<sub>2</sub> monitoring network, including urban, peri-urban, rural and remote areas in order to determine the effect of NO<sub>2</sub> on crop plants, human beings and to also design pollution control strategies. Results of this study have demonstrated the convenience of passive samplers for the measurement of NO<sub>2</sub> in ambient environment in a highly cost-effective manner. Passive samplers are simple, cheap and efficient devices, which operate without any power source and do not need elaborate calibration and maintenance. They are found to be ideally suited for developing wide spatial monitoring network of NO<sub>2</sub> in a highly cost-effective manner covering urban, peri-urban, rural and remote areas.

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## Development of a rapid ‘mollusc foot adherence bioassay’ for detecting potent antifouling bioactive compounds

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**Developing potent antifouling compounds from marine organisms has several R&D applications. The ‘foot stimulating bioassay’ for assessing the antifouling activity suffers interference with the reflex system of test organisms. The assay was modified with a new, rapid ‘mollusc foot adherence technique’ in order to measure the activities of potent marine natural products (MNPs). The common limpet, *Patella vulgata* was used as the test organism to detect the foot adherence. In the experiments with methanol extract of holothuria, *Holothuria scabra*, the foot adherence of *P. vulgata* was completely prevented at a concentration of 4.2 mg/ml. For detecting the potent activity, the assay plates require minimum quantity of test compound and the assay can be completed within one hour. In addition, after the evaluation of activity, the relative toxicity can also be estimated based on the per cent regaining ability of test organism in fresh seawater. This will lead to a rapid and sensitive evaluation of the MNPs when compared to the conventional ‘foot stimulating bioassay’ system.**

IN view of serious fouling problems in the cooling systems of power stations, and culture systems of oysters, seaweed and fish, constant efforts are being made to screen efficient antifouling substances. Although formulations of copper and organotin have been used effectively against these foulers, there is a concern over the impact of such chemicals on the environment. Alternate less toxic but more potent compounds have to be screened that the fouling organisms do not colonize on the surfaces of sponges, echinoderms and corals, as they may produce potent secondary metabolites including specific deterrents<sup>1–5</sup>.

In addition to screening potent products, it is also required to develop reliable and rapid *in vitro* assay systems for the bioassay-guided purification and fractionation processes. Of the known bioassay procedures, the common one is the conventional ‘submerged method’. This method is advantageous, but requires a month or even more to obtain reliable results. In order to reduce the test period and to detect antifouling properties, a rapid ‘mollusc foot adherence assay’ was developed using the common limpet, *Patella vulgata*. The limpet

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