5. DISCUSSION

1. Automobile traffic density.

2. Concentration of SPN, TPAH and individual PAH compounds.

3. Statistical analysis.

4. Correlations.

5. Meteorological factors affecting the PAH concentration.

6. Photo oxidation of PAH.
Delhi has the maximum number of vehicles plying on its roads when compared to other metropolitan cities of India. Delhi has 14.65 lakhs of vehicles at present and they are going up at a rate of 14,000 vehicles every month (Ministry of Surface Transport, 1989 personal communication). (Table 1.5)

The present study was carried out to assess the atmospheric PAH concentration in the ambient air of Delhi, particularly near busy traffic intersections and big bus depots, so that an assessment can be made about possible contribution of automobile exhaust vis-a-vis different types of areas and traffic density.

Four sampling sites were selected in South Delhi, on the basis of particular characteristics of their locations. The sampling was carried out for a period of one year from Nov. 1988 to Oct. 1989. The sampling stations chosen were -

1. Jawaharlal Nehru University (Control Point).
2. Vasant Vihar (adjacent to a big bus depot).
3. Dhaula Kuan (busy traffic intersection).
4. Defence Colony (busy traffic intersection and proximity to a bus depot)

The importance of choosing traffic intersections as sampling sites lies in the fact that deceleration normally occurs at a traffic intersection, when the vehicle is forced to stop due to the traffic lights. The composition of pollutants increases during the deceleration. This is the reason why
traffic intersections are selected for such studies

Central Board for the prevention and control of water pollution
(82 & 86).

The diesel engine has a substantial emissions problem
which is quite different from that of the petrol engines. It
is relatively clean with respect to unburnt hydrocarbons and
carbon monoxide but it produces large amounts of particulates
comprising of soot and adsorbed organics. The particulate
matter is a complex mixture of pure carbon plus hundreds of
organic compounds. The amount of particulate matter emitted
by a diesel vehicle is generally related to the vehicle
weight with heavy vehicles producing greater amounts. It is
60-100 times greater than comparable gasoline powered vehicles
(Howitt and Montierth, 1981). The chemical and biological
tests have shown that certain compounds associated with diesel
particles are potentially carcinogenic (Behymer & Hites, 1984).

Air fuel ratio, ignition timing, density of air fuel mixture,
combustion chamber geometry and engine temperature are important
parameters which affects the combustion process. These parameters
behave differently in petrol and diesel engine (Tamakwala, 1983).

The automobile traffic density at a number of traffic
intersection has been assessed (CRAI, 1980).

(1) At Defence Colony it was (266 h.v.) 6312 vehicle hr.
(2) Our assessment and as assessed by CRAI the number of
vehicles was 1139/hour, which included 143 heavy
vehicles/hour, at Vasant Vihar.
(3) At Dhaul Kuan it was 377 (h.v) 2813 vehicles/hour and
Our assessment of automobile traffic density at Jawaharlal Nehru University, School of Life Science bus stop is (20 h.v.) 101 vehicles/hr. These vehicles comprise of heavy vehicles, light diesel driven vehicles, petrol driven four, three and two wheelers. In Dhaula Kuan, there is more of heavy vehicular traffic consisting of buses (single, double deckers and mini buses), trucks, passenger and goods vans plying. Thus the density of diesel driven vehicles plying here is more. In Defence Colony the light motor vehicles are more in number, (cars, scooters, motor cycles, mopeds and auto rickshaws). Thus it is observed that light motor vehicles are more due to the areas being commercial and residential in nature. In case of Vasant Vihar also a similar pattern of automobile profile is observed. Jawaharlal Nehru University being an institutional and residential area, there is low traffic, so this sampling station is considered as the control point.

The various PAH compounds, which have been estimated during this study are, Benzo (a) pyrene, Benzo (e) pyrene, Fluoranthene, Benze (b) fluoranthene, Benz (a) anthracene, Chrysene, Phenanthrene and Benzo (ghi) perylene. These are some of the PAH compounds present in the automobile exhaust. Benzo (a) pyrene and Benzo (b) fluoranthene are potent carcinogens. Benzo (a) anthracene, Benzo (e) pyrene and Benzo(ghi) perylene are moderate carcinogens. Phenanthrene is a possible carcinogen, and fluoranthene is non carcinogen. These compounds have been estimated separately by fluorometric methods.
The concentration of SPM and total individual PAH compounds

The concentrations of SPM, TFAH and individual PAH compounds on different sampling days is summarised in the table (IV, 1, 2, 3, 4).

In general it was observed that the SPM is the highest at Dhaula Kaun. Monthly average of SPM was generally high in the month of May, the highest concentration being recorded in Dhaula Kaun which was 759.7 ug/m$^3$ (Table IV-11). The monthly average concentration SPM at all sites are shown in Table - IV.9.

The annual average concentration of SPM in various stations varies from a minimum 199/ug/m$^3$ in JNU, to a maximum of 361.33/ug/m$^3$ in Dhaula Kaun. The annual average concentration in Vasant Vihar and Defence Colony were 262.84/ug/m$^3$ and 326.087/ug/m$^3$ respectively (Table IV-13). The annual average of SPM in Dhaula Kaun (highest), was roughly double the value obtained in JNU (lowest). The values at Vasant Vihar and Defence Colony ranged between these two values.

There is a significant variation in the pattern of SPM throughout the year. The concentration of SPM
is more in summer months. The calm conditions are reduced considerably during the summer months. The wind speeds prevailed between 5 km to 30 km. The high values of SPM can be attributed to frequent dust storms and the transportation of high load of dust from the nearby Rajasthan desert areas, while the low values of SPM was observed from July to September. This is because of the washout by rain in the monsoon season. (Refer Appendix - 3). (Figs. 1-12)

The annual average concentration of SPM worked out to be 292.29/ug/m³. This value is much higher than the value specified for residential area by two national bodies, viz. NEERI (150/ug/m³ and the Central Pollution Control Board, 200/ug/m³.

However, the value has still not reached half the specified standard of 500/ug/m³ for industrial cum mixed area prescribed by Central Pollution Control Board.

**Total PAH**: The annual average concentration of TPAH ranges from 406 ng/m³ in JNU to a maximum of 1056.12 ng/m³ in Dhaula Kuan. The concentration of TPAH in Vasant Vihar and Defence Colony were 955.83 ng/m³ and 978.26 ng/m³ respectively. The annual average of TPAH concentration in Dhaula Kuan (highest) was roughly 2.5 times the value at JNU (lowest). The values of TPAH at Vasant Vihar and
It was observed that the concentrations of TPAH varied with the seasons. The TPAH concentrations were low during the summer months. Higher values were recorded during the winter months. During summer seasons, calm conditions are reduced considerably. The day temperatures are quite high. This is the reason for low concentration of TPAH during summer (thermal degradation). The wind speeds ranged between 6 km to 39 km.) These conditions were observed during the months March, April, May and June. In winter season, November, December, January and February, there is more "calm" conditions. During "calm" conditions there is no apparent movement of winds. This is responsible for the high concentration of TPAH (Viras, et al, 1957). The other meteorological conditions which enhances the concentration of "TPAH" are the low temperatures and low wind speed (0-5 km). The pre and post monsoon months July and October has recorded high concentration of TPAH. During August and September there were occasional rains which affected in lowering the concentration of TPAH. This is because of the scavenging.
The concentrations of TPAH in all the four stations were due to the various factors. The concentration of TPAH at JNU can be attributed to the carried over load and exhaust from air crafts, which fly directly over JNU at very low heights, Shabald, et al (1971) reported that jet air crafts exhaust is a major source of PAH compounds (B(a)P). JNU falls directly below the landing path of the air craft and is in a very close proximity to Palam Airport (at a distance of 5 Kms). These are some of the other factors affecting the PAH concentration in addition to automobiles. In Vasant Vihar, the bus depot is adjacent to the sampling point. This bus depot is the biggest bus depot in South Delhi. The high concentrations of PAH is due to operational and maintenance works of diesel run buses in Vasant Vihar bus depot. In case of Dhaul Kaun and Defence Colony it is more due to the flowing traffic density.

The concentrations of individual PAH compounds:

The concentration of individual PAH compounds followed a typical pattern. There was a seasonal variation observed in the case of individual PAH compounds. (Table IV-1a, 2a, 3a, 4a). The winter months recorded higher PAH concentrations than in summer months. The annual average concentration of PAH compounds are given in detail in Table IV-13.

The annual average BaP concentrations at Bombay and Ahmedabad both industrial sites with heavy vehicular traffic were reported to be 21 ng/m$^3$ (Mohan Rao, Vohra, 1975) and
31 ng/m$^3$ (Aggarwal, et al, 1982) respectively. The annual average BaP concentration in Delhi, at Vasant Vihar (adjacent to a bus depot) and Dhaula Kuan (a busy traffic intersection) presently recorded were 34.76 ng/m$^3$, 33.23 ng/m$^3$ respectively. This is more than Bombay and Ahmedabad. However in Calcutta the winter concentrations of BaP is reported to be very high, 120.2 ng/m$^3$ (Shyam Bazaar area - Calcutta) (Chakraborti, et al, 1988). The BaP winter concentration in Calcutta is about four times higher than that of Delhi viz. 36.42 ng/m$^3$ (DK-winter).

JNU and Vasant Vihar recorded maximum BaP concentration in the month of July (26.33 ng/m$^3$ and 107.61 ng/m$^3$ respectively) whereas Defence colony and Dhaula Kuan recorded this in the month of October (124.77 ng/m$^3$ and 73.71 ng/m$^3$ BaP respectively. The wind direction in July was South East and South West whereas in October, it was North East and North West. The minimum concentrations of BaP was recorded in summer months at all the four stations. The maximum and minimum concentrations of all the other PAH compounds are given in the Table IV-11.

The maximum concentrations (annual average) was observed at Dhaula Kuan in the case of the remaining compounds. The lowest concentrations were always recorded at the JNU sampling point. The average concentration during winter season was less when compared to Calcutta, as cited above.
Statistical analysis:

The values have been analysed statistically and annual arithmetic mean, standard deviation and co-efficient of variation of SPM, TPAH and various individual compounds at different sites have been calculated. The results are shown in Table IV-14.

The variation in the values of SPM, TPAH and various PAH compounds followed multimodal distribution (Fig. IV - 1 to 10) because of various factors such as wind dispersion pattern, temperature and relative humidity etc. In view of the above meteorological factors the standard deviation and co-efficient of variation has varied largely, the maximum CV being ± 1.51 at Dhaula Kuan for fluoranthene. The correlation between SPM and TPAH was not significant. In case of individual PAH compounds their correlation with reference to TPAH was significant. (Table IV-18).

The correlation between BaP & B(ghi)P, BaP & CH, BaP & BbF and BaP & BaA showed a linear correlation. We may conclude that automobile exhaust in metropolitan areas is a dominant source of pollution, except in the case of areas close to industrial plants. In the case of TPAH and the respective PAH compounds showed a positive correlation (Handa, et al, 1980).

There is a positive correlation between the individual PAH compounds and the total PAH. There is no significant correlation between SPM and TPAH. (Table IV-18). This implies
that the portion of aerosol particulate associated with PAH differs markedly from the remainder. The difference is due to the particle size, whereas SPM covers a wide range of particle sizes, PAH are associated with submicron soot particles. In the latter case the meteorological factor and the topography influence the aerosol dilution and dispersion (Butler, et al., 1982).

Correlation of PAH concentration in direct diesel exhaust and the immediate vicinity at Okhla and Vasant Vihar bus depots:

Diesel exhaust samples were collected directly from the buses at Vasant Vihar and Okhla bus depots and analyzed for PAH concentrations. The period of collection was approximately a minute per bus, when the vehicle was in the idling condition. The collection method has been described earlier in detail in Chapter III.

Ambient air samples in the immediate vicinity of buses were also collected simultaneously at the bus depots at a site located 4 feet away from the bus.

The detail of PAH concentrations are given in the Table IV-17.

The concentration of PAH in direct exhaust samples and PAH in ambient air samples showed that there is an obvious dilution in the concentrations of PAH. This dilution is about
five time, that is the value of PAH concentration in the vicinity is approximately one fifth of the diesel exhaust values.

As shown in Table IV-17 the concentration of TPAH in direct exhaust at Vasant Vihar was 21.3975 ng/m$^3$ whereas the concentration of TPAH at 4 feet away was 4.814 ng/m$^3$, that means, the dilution was 4.56 times. The corresponding figures for Okhla depot were 50.346 ng/m$^3$ and 10.512 ng/m$^3$ respectively. (dilution : 4.789 times).

**Correlation of PAH concentration with Automobile Traffic Density (ATD) and Meteorological factors at all points:**

A typical pattern of variation has been observed in the case of total ambient PAH concentrations. TPAH concentration varied with seasons, at all four sampling points. The concentrations were high during the winter seasons (November, December, January and February), as compared to the concentration in Summer (March, April, May & June) Table IV-1a, 2a, 3a, & 4a. The high concentrations in winter months are due to the calm conditions and low wind speed (0-5 km), this helps in building up high concentrations. In summer months the day temperature is quite high, so there is every possibility of thermal degradations. The high wind speeds during these months helps in the dispersion of pollutants. The 'calm condition' is also reduced during the summer months. The pre and post monsoon months (July and October) recorded higher concentration, than the winter months.
This can be attributed to the less relative humidity. In winter months the relative humidity varied between 90-100% during the sampling period, whereas in the pre and post monsoon period the relative humidity was around 70% - 80%. Relative humidity is one of the meteorological factors which affects the TPAH concentration. High percentage of relative humidity decreases the concentrations of TPAH (Kamens, et al, 1986; Kamens, et al, 1988). This is the reason why the concentration of PAH is more in the post monsoon month. In monsoon months there is a general washout of the pollutants taking place (scavenging). The monsoon months, are generally July, August and September. These are the general conditions which have been observed during sampling period, in all the four stations.

Jawaharlal Nehru University (control) sampling point is situated in an open area, so this sampling point receives winds from all directions. The TPAH concentration at JNU can be attributed to the active "wind carry" component and the exhaust from the air crafts which fly directly over the area. The sampling point is 5 km away from the run away of Palam airport. The automobile traffic density is very low, which is 101 vehs/hour. In JNU, sampling point the maximum TPAH concentration was recorded in July 89. The prevailing wind direction during the month is south east and south west.

In case of Vasant Vihar, the maximum TPAH concentration was recorded in July 89. This sampling point receives winds
from south east and south west. The automobile traffic density here is 1139 vehs/hr. The 'TPAH' concentration at Vasant Vihar is enhanced due to the busy bus depot, which is adjacent to the sampling point. This is the biggest bus depot in South Delhi. In this depot a lot of operational and maintenance works are carried out for diesel buses, which results in a lot of idling time. This may contribute to the ambient TPAH concentration to some extent in addition to the automobile exhausts.

The sampling points, Dhaula Kuan and Defence Colony are busy traffic intersections. The automobile traffic density is 2813 vehicles/hour, in the case of Dhaula Kuan and there are number of heavy vehicles. In the latter case, the automobile traffic density 6,312 vehicles/hour, with more number of light motor vehicles.

Dhaula Kuan is affected by winds from North East, East and West; whereas Defence colony is affected by winds from North East and South East. The maximum concentrations were recorded in the month of October. (Appendix-3, Figs 1-12).

The low concentrations of TPAH was observed during the summer months in all the four stations. The details have already been discussed earlier.

**Correlation between ambient PAH concentration and automobile traffic density (Diesel vehicles)**

Vehicular exhaust sampling from diesel driven buses was
carried out at Vasant Vihar and Okhla bus depots. Diesel exhaust particulate matter was collected using a "Kimoto" portable sampler from a number of diesel operated buses at the rate of one minute per bus. The PAH concentration was assessed for each vehicle. This worked out to be, on an average 0.22 ng/m\(^3\) in Vasant Vihar and 0.5 ng/m\(^3\) in Okhla bus depot. Ambient sampling which was carried out at the vicinity of the bus depot showed a 4 to 5 fold dilution; these concentrations are given in Table IV-17.

Based on these average figures, an estimate could be made of the sum total emissions of PAH from these depots taking into account the total number of operating vehicles at these depots. This number is 3376/day at Vasant Vihar and 7740/day at Okhla. The contribution of PAH by these vehicles works out to be approximately 742.72 ng/m\(^3\) in Vasant Vihar and 3870 ng/m\(^3\) in Okhla respectively.

In addition to the emission from the diesel vehicles, PAH is also contributed by other vehicles such as petrol driven, two, three and four wheeler at each sampling point. In case of Vasant Vihar automobile traffic density is 18,944/day and in Defence Colony 1,00,990/day respectively. Thus diesel driven vehicles constitute a low percentage of the total number. Topography and meteorological conditions also play a role in ambient PAH concentration at sampling points.

At a traffic intersection vehicles decelerate and
accelerate due to traffic lights and conditions on the road. The values obtained at the bus depots is for the vehicles under idling conditions only. Therefore, the dilution factor quoted above from exhaust to ambient PAH concentrations can be taken as notional, but the dilution at the ambient level will be much more, which has not been assessed.

Meteorological factors affecting the PAH concentration

There is a seasonal variation in the ambient concentration of PAH compounds. That can be clearly observed from the Tables IV - 1a, 2a, 3a, 4a and corresponding figures IV - 1 to 10. High concentrations are observed during the winter season and low concentrations in summer seasons. Even in rainy season there is a slight decrease in concentration of PAH due to the rainfall and resulting washout.

The high temperature during summer season affects the PAH concentration due to thermal degradation. The wind speed and wind direction also affects the dispersion pattern of PAH compounds. The relative humidity varied from 75% to 100% in winter and 50-70% in the summer months. This has also affected the concentration of PAH. All these aspects have been discussed in detail in the earlier paras.

The mechanisms by which light, humidity and temperature affect photoinduced PAH decay on atmospheric soot particles are not well understood. Direct PAH photolysis, \( \Delta \) molecular oxygen
oxidation, and hydroxyl radical (OH) attack are pathways that need to be investigated. (Kamens, et al, 1988).

Kamens, et al, 1988, assume that atmospheric soot particles are surrounded by a film of water, then the depth of this condensed water layer is most probably related to the water vapor concentration or humidity of surrounding air. Particle size, curvature, and chemical composition will be of importance. The ability of this water layer to accept reactive species like OH from the surrounding atmosphere will be related to the volume and temperature of the water layer, the OH accommodation coefficient, the equilibrium distribution, the gas-phase to particle mass transfer coefficients, and possibly the particle pH among the other factors.

**Photo oxidation of PAH compounds**

The photo oxidation studies on PAH was carried out in liquid media. A standard mixture was prepared from pure PAH standards by mixing them together. The standard mixture was prepared in double distilled benzene using pure PAH compounds. Eight ml of this standard solution prepared, contain 0.13 µg of Benzo (a) pyrene, Benzo (e) pyrene, fluoranthene, Benzo (b) fluoranthene, 0.013 µg of chrysene, Benz (a) anthracene, Benzo (ghi) perylene, and Phenanthrene per ml of the standard mixture. The standard mixtures was exposed to sunlight for a period of 20 hours. Percentage recovery of each constituent in the
Standard mixture was recorded spectro fluorometrically after ~ry hour. The details of methodology are given in Chapter-III. e results are shown in Table IV-16, Fig.IV-27 to 34. was observed that all the 8 PAH compounds in the standard xture subjected to photo oxidation were degraded upto 60-80% ring the exposure of first ten hours, while 90-95% of each H compound was photo oxidised during 15 hrs exposure except the case of fluoranthene, which degraded to 70%. After at there was no noticeable change in PAH degradation.