CHAPTER IV

RESULTS AND DISCUSSION

4.1 Identification of PNA in Airborne Particulates

Figures 4-1 and 4-2 show chromatograms of representative samples from roadside and off-road, respectively. Table 4-1 indicates the detection limits of the PNA through the analytical procedure. PNA identifications are presented in Table 4-2.

It was difficult to analyse lower molecular weight (MW)PNA than 202(fluoranthene) in the particulate samples as they are mainly presented in the gas phase under ambient atmospheric conditions. For example, acenaphthylene and acenaphthene were not detected in any samples. Dibenzo[a,h]anthracene was not found in glass fiber filter but may be found in other filter types.

Of he total of 13 selected PNA, Two-ring PNA (naphthalene) to six-ring PNA (benzo[ghi]perylene), were identified in these samples. Three PNAs, phenanthrene, fluoranthene and pyrene, were quantified but the concentrations of others were less than the detection limit of GC/MS analysis.

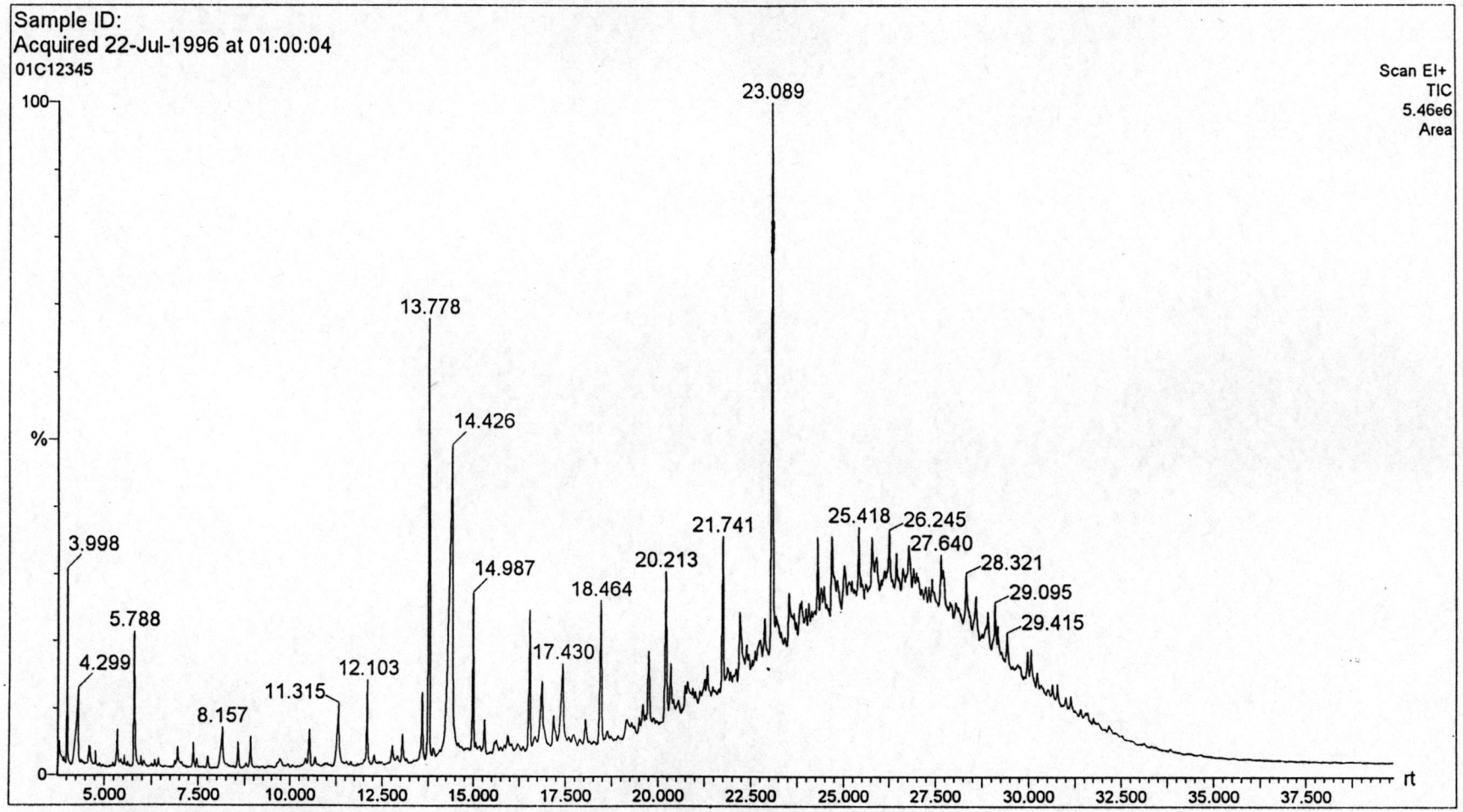


Figure 4-1 Chromatogram of Roadside(Yaowaraj) Area

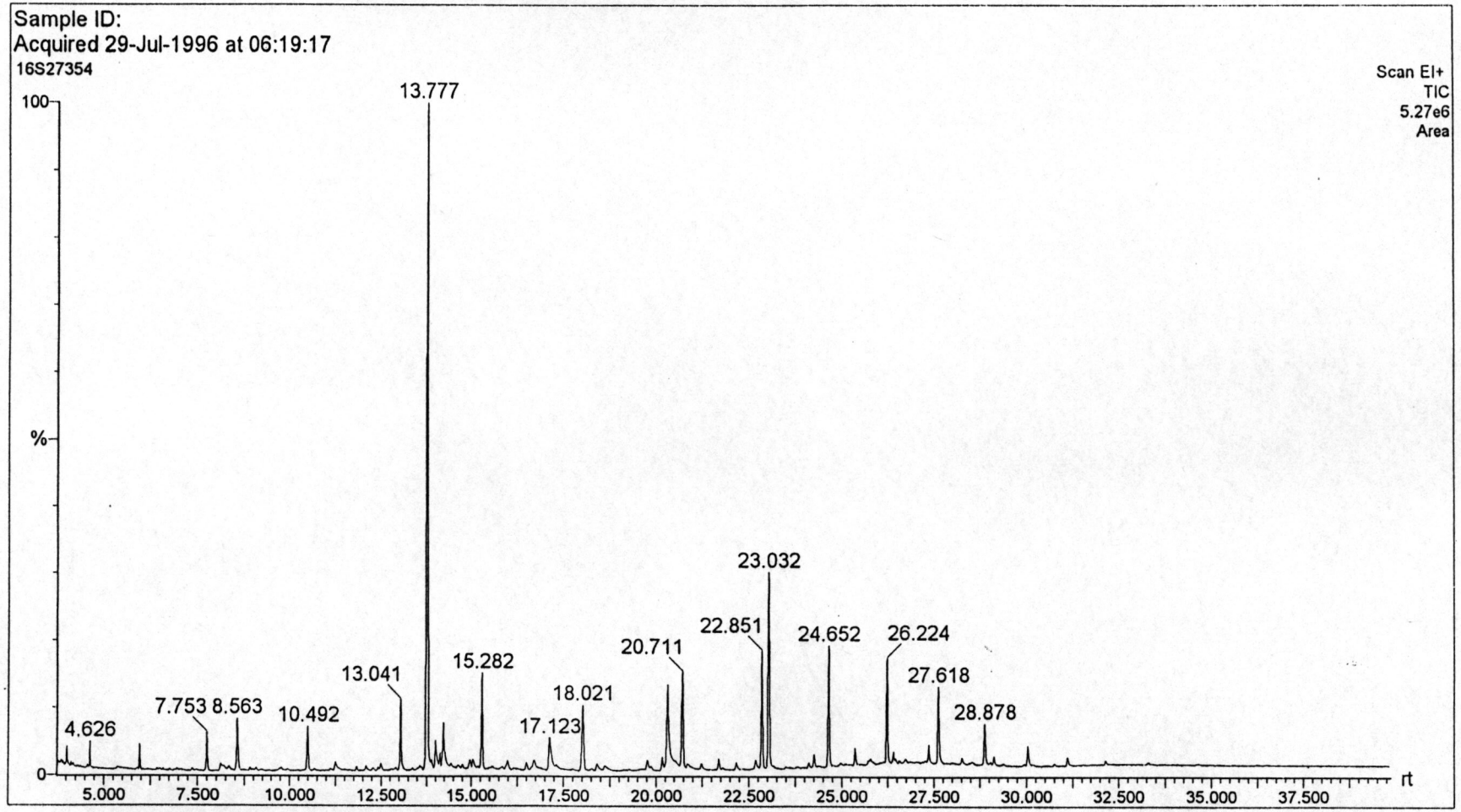


Figure 4-2 Chromatogram of Off-road(Bansomdej) Area

Table 4-1 PNA Identified in Sampling Sites Samples during the Study Period (Feb-April,1996).

PNA	MW.	Concentration with particulates(ng/m^3)				
		BangYeeKhan	Pratunam	Yaowaraj	Nat.Stat.Off.	Bansomdej
1. Naphthalene	128	identified	identified	identified	identified	identified
2. Acenaphthylene	152	nd	nd	nd	nd	nd
3. Acenaphthene	154	nd	nd	nd	nd	nd
4. Fluorene	165	nd	nd	nd	nd	identified
5. Phenanthrene	178	2.44	7.07	3.40	2.84	2.59
6 Anthracene	178	nd	identified	identified	identified	identified
7. Fluoranthene	202	4.00	8.85	5.15	3.00	2.72
8. Pyrene	202	11.55	25.95	15.16	7.66	5.28
9. Benzo[a]anthracene	228	identified	identified	identified	identified	identified
10. Chrysene	228	identified	identified	identified	identified	identified
11.Benzo[b]Fluoranthene	252	identified	identified	identified	identified	identified
12. Benzo[k]Fluoranthene	252	identified	identified	identified	identified	nd
13. Benzo[a]pyrene	252	identified	identified	identified	identified	identified
14. Indeno[1,2,3-cd]pyrene	276	identified	identified	nd	nd	identified
15. Dibenzo[a,h]anthracene	278	nd	nd	nd	nd	nd
16. Benzo[ghi]perrylene	276	identified	identified	identified	nd	identified
Total PNA		17.99	41.87	23.71	13.50	10.59

nd = non detected

Table 4-2 Detection Limits of PNA by GC-MS

PNAs	MW.	Retention time (min)	Detection limits (ppm)
Naphthalene	128	4.611	0.25
Acenaphthylene	152	6.689	0.25
Acenaphthene	154	7.026	0.25
Fluorene	166	8.158	0.25
Phenanthrene	178	10.994	0.25
Anthracene	178	11.155	0.25
Fluoranthene	202	14.898	0.25
Pyrene	202	15.546	0.25
Benz[a]anthracene	228	21.117	0.50
Chrysene	228	21.210	1.00
Benzo[b]fluoranthene	252	25.063	nd
Benzo[k]fluoranthene	252	25.143	nd
Benzo[a]pyrene	252	26.091	1.00
Indeno[1,2,3-cd]pyrene	276	29.189	2.00
Dibenzo[a,h]anthracene	278	29.309	2.00
Benzo[ghi]perylene	276	29.569	1.00

nd = non detected

The detection limits in this table 4-2 are produced by SIR mode of GC-MS which peak to noise ratio are 5:1.

Westerholm *et al* . (1988) found that essentially all of naphthalene to trimethylnaphthalene (including their biphenyl, biphenylene and alkyl derivatives) are in the gas phase, i.e., < 1 % is found on the particles, at a dilution temperature of 30 °C, althrough their boiling points all exceed 200 °C , approximately 50% of pyrene (bp. 398 °C) is gaseous to at 30 °C, and benzo[a] anthracene(BaA) (bp. 438 °C) is found in the gas phase (approximately 30%).

Therefore, the actual PNA concentration in ambient should be more than found here because of the PNA concentration in the gas phase not sampling. High tremperature and 24 hour sampling time may induce PNA to volatile.

4.2 Characteristics of PNA in Airborne Particulates

Figures 4-1 and 4-2 show gas chromatograms of the isolated PNA fraction from aerosols collected from the heavily trafficed street and off-road area. For PNA in those aerosols samples, unsubstituted ring systems (i.e.,parent PNA) ranging from naphthalene (two aromatic rings) to benzo[ghi]perylene (six aromatic rings) were the primary components. Of special interest is that the concentrations of phenanthrene, fluoranthene and pyrene although varying from sample to sample, are the highest in almost all samples. They may be used as indicators of PNA pollution (Yang and Bauman,1995) and Gardner *et al.*(1995) found that phenanthrene, fluoranthene and pyrene occured highest in summer samples.

It has also been found that the fraction of PNA in the gas phase increases with temperature (Yamasaki *et al.*, 1982, McVeety and Hites, 1988 quoted in Allen *et al.*, 1996). Previous studies have shown that diesel exhaust is enriched

in phenanthrene, fluoranthene, chrysene and pyrene (low MW PNA) (Westerholm *et al.*,1988, Masclet *et al.*, 1986, quoted in Venkatanaman *et al.*, 1994), while gasoline exhaust has a high benzo[ghi]perylene concentration (Daisey *et al.*, 1986 quoted in Venkatanaman *et al.*, 1994) and coronene (Greenberge *et al.*,1984 quoted in Harrison, R.M.,1996.

Mean concentrations of PNA in samples collected at roadside and off-road areas in Feb-April, 1996, are shown in Table 4-3. PNA contents in the aerosols in both heavily traffic road and background sites are in the range of nanograms per cubic metre of air volume. It was shown that the mean PNA concentration at Pratunam area exhibited the highest (41.87 ng/m^3). Mean PNA concentration at Bang Yee Khan and that at Yaowaraj areas are slightly different (18.00, 23.71 ng/m^3, respectively), with Nat.Stat.Off. and Bansomdej areas having considerably lower levels(13.50 and 10.59 ng/m^3). These illustrated that the mean of total PNA in Pratunam area was 3.95 fold more than that in Bansomdej area.

This indicates that the selected PNA concentrations may vary significantly according to the influence of traffic density (traffic volume) at each site. For example, the PNA concentrations in Pratunam are extremely high levels, but depleted in at the Nat.Stat.Off. and Bansomdej areas. This is because the Pratunam area is more heavily affected by vehicular emissions than other areas. Pratunam is a commercial area and a shopping center of Bangkok. Moreover, it has high traffic intensity all times. In contrast, the Nat.Stat.Off. and Bansomdej station have less traffic intensity than Pratunam. This demonstrated the significant of direct motor vehicular emissions of PNA, and indicates that they are the major sources of PNA in urban areas.

However, the observed differences in partitioning at roadside and off-road areas is consistent with the hypothesis that PNA concentration in roadside areas are much more than in off-road area.

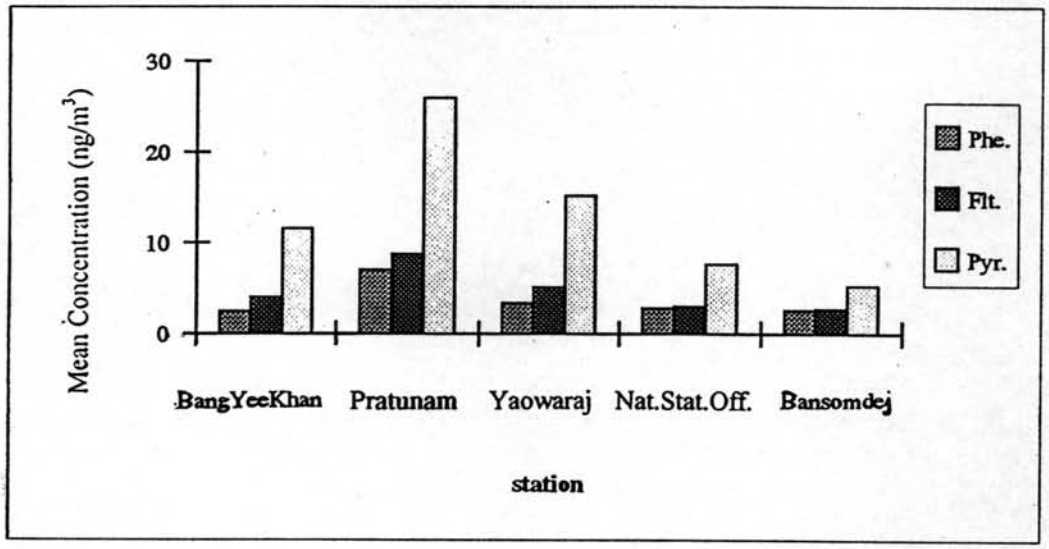


Figure 4-3 Histogram of Mean Concentrations of Selected PNA measured at All Sampling Sites during Study Periods (Feb- April, 1996).

Source commonality is supported by similarities in average PNA profiles measured at each site ,as shown in Figure 4-3. It has already been mentioned that the concentrations of pyrene, fluoranthene and phenanthrene are much higher than those of all PNA in all the investigated airborne particulate samples. As expected, the lowest concentrations were found in a Bansomdej area.

An obvious observation about variations of PNA concentrations can be made. It was found that the concentrations reveal a trend : concentrations appear to be distinctly higher in roadside than those in off-road areas, which could be explained by increasing intensity of traffic.

Pyrene accounted for about 61.1% of total PNA in roadside areas and 49.8% at off-road area., fluoranthene was about 22.6% of total PNA in both locations and phenenthrene was about 16.5% of total PNA in roadside area and 24.4% at off-road area. It should be noted that pyrene was the predominant species in all samples because it is usually adsorbed on particulate matters more than phenenthrene and fluoranthene. These latters are semi-volatile PNA and are present in both gas and particulate phases.

The relative abundance of four to six ring PNA was lower at areas with a low intensity of traffic, such as Nat.Stat.Off. and Bansomdej areas, and the ratio of phenanthrene :fluoranthene was depleted because total PNA concentrations at both locations were low.

4.3 Effect of Traffic Intensity

From the study of total PNA concentration in the same periods between roadside and off-road areas, it was found that PNA levels in roadside area have more than those in off-road area, obviously. For example, Figure 4-4 illustrates the comparison of total PNA concentrations of intersites between the sampling areas; the null hypothesis of matual independence was accepted at a level of significance $\rho = 0.05$, it was found that Bang Yee Khan, Pratunam, Yaowaraj had selected PNA concentrations more than Bansomdej areas and highly significant ($p = 0.000, 0.029, 0.008$, respectively, Table 4-5). In contrast, the Nat.Stat.Off. was not significant because it has low traffic volume in this areas, like the off-road (Bansomdej) areas.

Septhum (1996) studied PNAs emitted from diesel engines and he found that the amount of PNAs in diesel exhaust was higher at no load than at 50%

load.(Fig.4- 5). In the case of traffic jams, high traffic intensity, motor vehicles are operated at no load and low speed, therefore they emitted a high concentration of PNAs.He suggested that optimum driving conditions should be a moderated speed and load.

Also, Table 4-4 showed that in Pratunam Yaowaraj areas have low traffic volume than in BAngYeeKhan but have high PNAs levels because in those areas have high building standing on both sides of the roads. It may have been ventilation of the wind was difficult to diluted PNAs concentration.

As shown in Figure 4-4(B), it was found that daily concentrations of PNA in the Pratunam area were higher on Sunday, Friday and Saturday. This may result from an increasing intensity of traffic at the weekend because of several shopping centers and a high density of population.

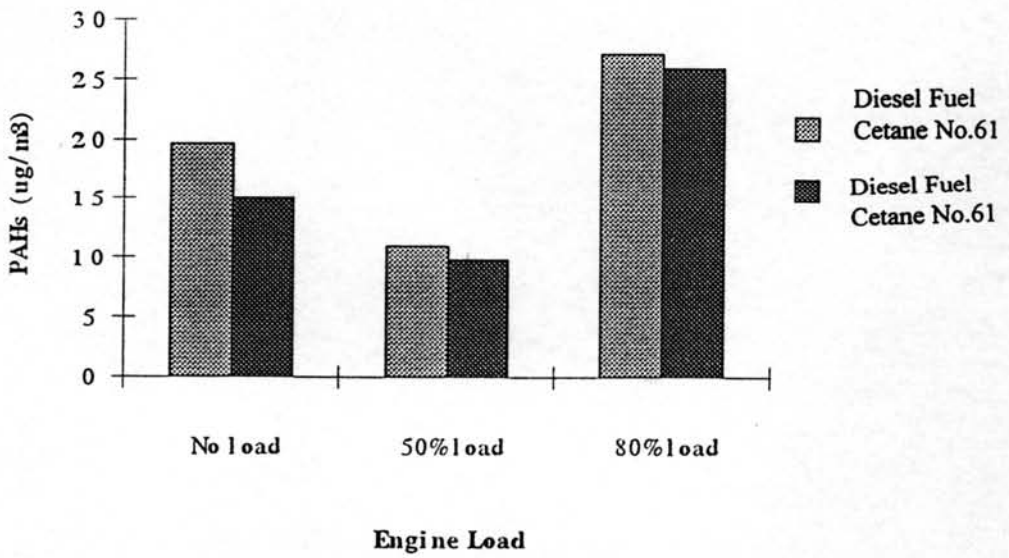
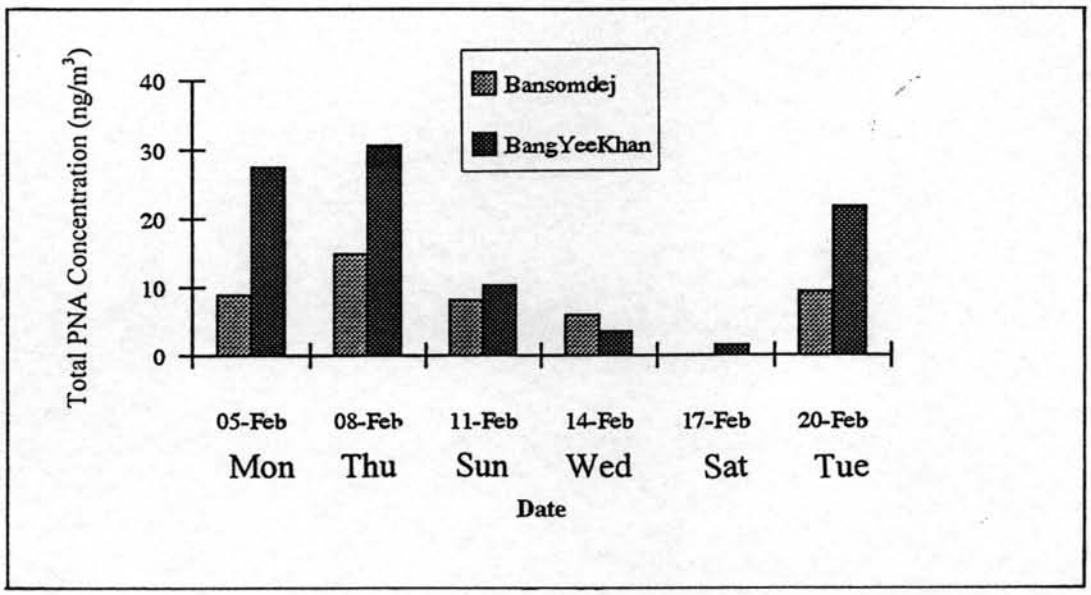


Figure 4- 5 The Effect of Engine Load on PNAs in Diesel Exhaust.

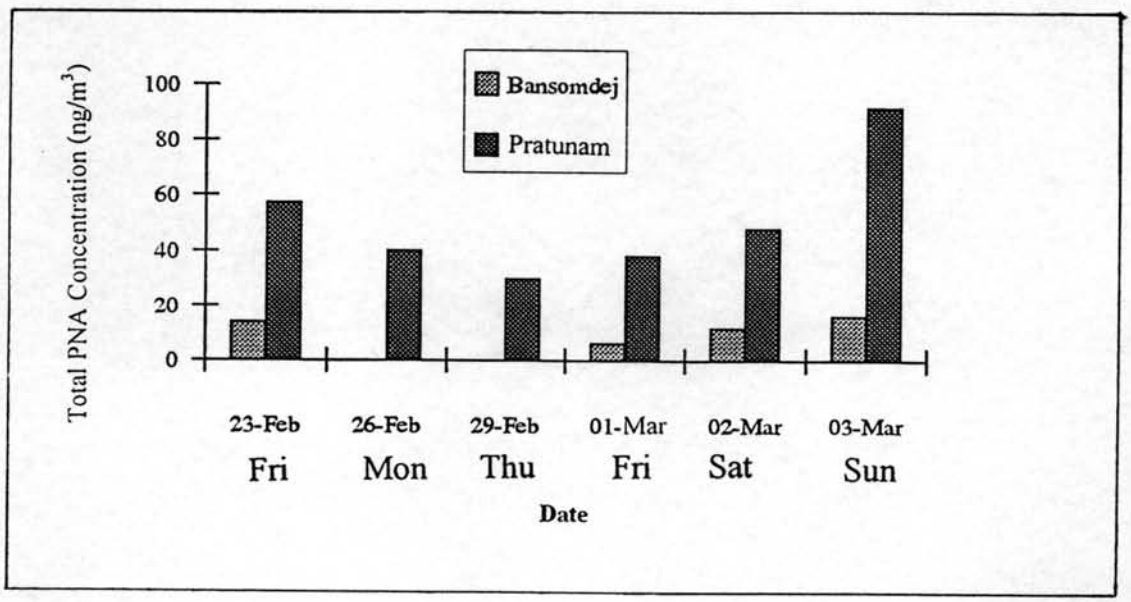
Table 4-3 Mean and Range of Individual PNA, ΣPNA (ng/m^3) and TSP (mg/m^3) Concentration Measured at Sampling Sites during the Study Periods (Feb-April,1996)

PAHs/Station	BangYeeKhan		Pratunam		Yaowaraj		Nat.Stat.Off.		Bansomdej	
	mean	range	mean	range	mean	range	mean	range	mean	range
Phenanthrene.	2.44(15)	0.37 - 4.88	7.07(17)	3.54 - 10.78	3.40(18)	0.95 - 5.91	2.84(7)	1.66 - 3.95	2.59(9)	1.38 - 4.47
Fluoranthene	4.00(15)	0.47 - 8.76	8.85(17)	4.69 - 18.89	5.15(16)	1.21 - 10.04	3.01(13)	1.92 - 4.17	2.72(9)	1.54 - 4.18
Pyrene.	11.55(14)	0.48 - 27.86	25.95(17)	13.03 - 62.34	15.16(16)	1.25 - 35.81	7.66(13)	4.19 - 12.46	5.28(9)	2.69 - 8.25
Total PAHs	17.22	1.14 - 41.24	41.87	22.08 - 91.78	22.58	3.34 - 51.76	12.20	6.21 - 20.54	10.60	5.95 - 16.15
TSP	0.34	0.12 - 0.93	0.56	0.26 - 0.89	0.54	0.45 - 0.77	0.22	0.16 - 0.46	2.44	0.13 - 0.36

(n) = Number of Samples

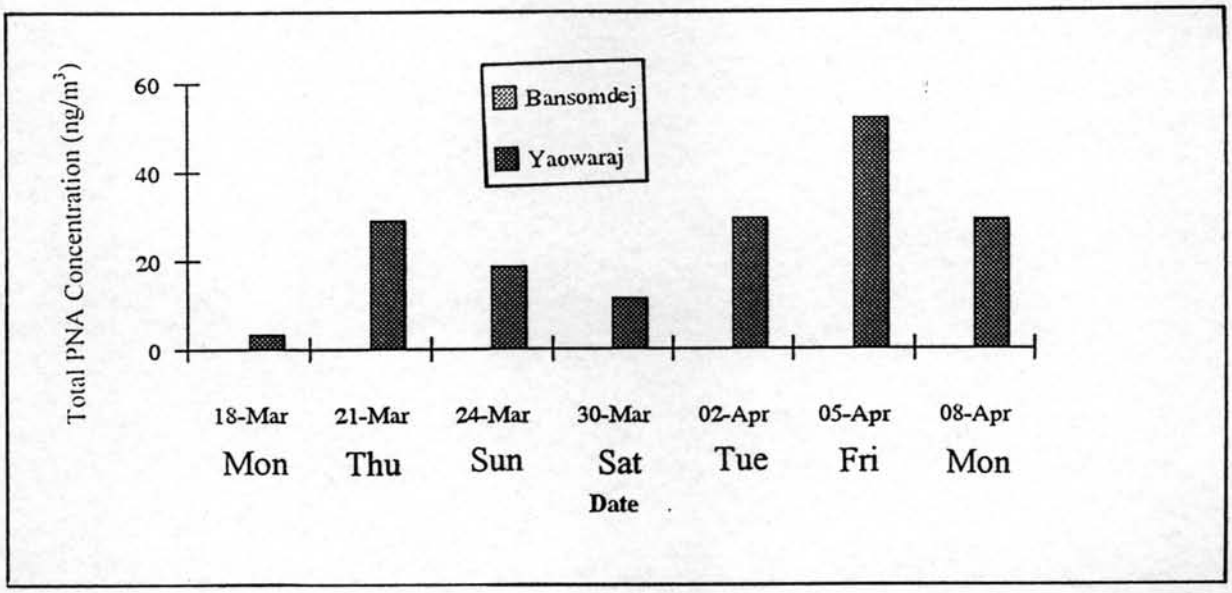


(A) BangYeeKhan / Bansomdej

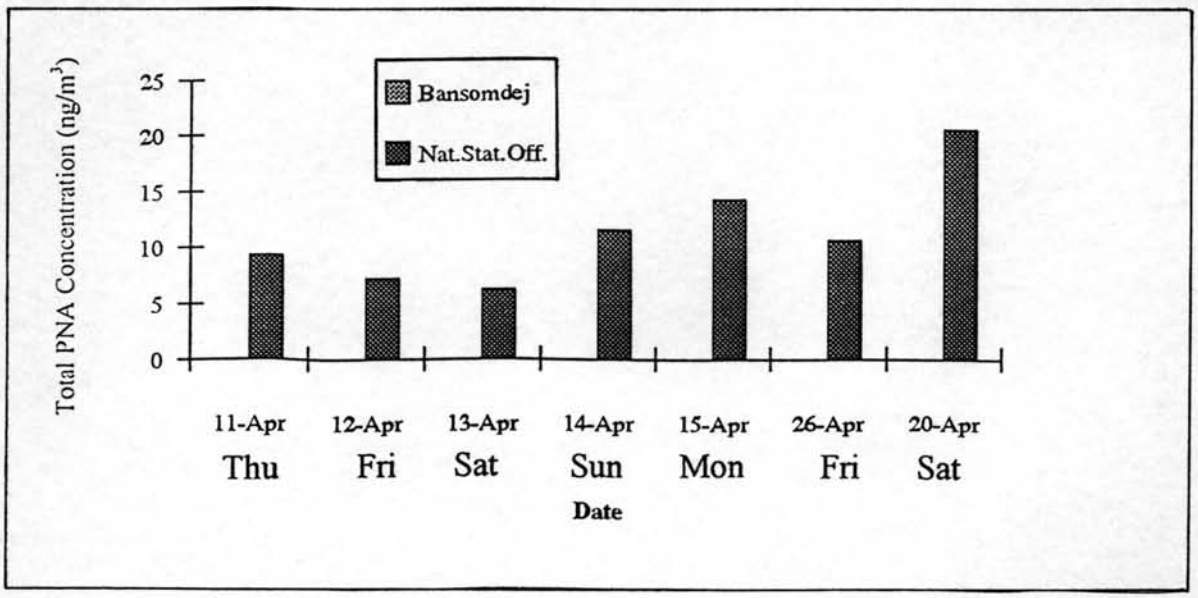


(B) Pratunam / Bansomdej

Figure 4-4 Total PNA Concentration Compared between Roadside/Off-road Areas



(C) Yaowaraj / Bansomdej



(D) Nat.Stat.Off./ Bansomdej

Figure 4-4 Total PNA Concentration Compared between Roadside/Off-road Areas (continue)

Table 4-4 Traffic Volume (vehicles/day) and Total PNA Concentration (ng/m^3) at Study Areas

AREAS	TRAFFIC VOLUME (VEHICLES / DAY)	TOTAL PNA CONCENTRATION (ng/m^3)
Bang Yee Khan	97,390	17.22
Pratunam	92,693	41.87
Yaowaraj	48,037	22.58
Nat.Stat.Off.	62,340	12.20
Bansondej (Off-road)		10.60

Table 4-5 p-Value for t-test(independent) of total PNA Concentration between Station

Station	Bansomdej	BangYeeKhan	Pratunam	Yaowaraj
BangYeeKhan	0.000			
Pratunam	0.029	0.780		
Yaowaraj	0.008	0.620	0.524	
Nat.Stat.Off.	0.584	0.000	0.014	0.004

4.4 Effect of TSP Concentration

Compared to all of the areas as shown in Figure 4-6, the Bansomdej area showed lower PNA and TSP concentrations.

In order to fully characterize the difference of TSP concentration between roadside and off-road samples in densely populated areas and high intensity of traffic, it was necessary for supplementary PNA concentration data.

It was found that TSP was distributed differently in roadside and off-road areas. For roadside samples, a maximum was found in the Pratunam and Yaowaraj areas because of higher traffic intensity. In the Bansomdej and Nat.Stat.Off. areas , the distribution tended to be flattened.

Table 4-6 shows that experimentally measured PNA concentrations in roadside samples have a moderate correlation with TSP concentrations (Υ > 0.65, $P < 0.05$, respectively). This indicates that traffic intensity dose influence TSP concentrations.

The TSP concentrations of roadside areas were in the range of 0.221 to 0.564 mg/m^3 that was considerably higher than Thai regulations (0.33 mg/m^3,24 hr), especially average TSP concentrations in Pratunam and Yaowaraj areas were 0.564 and 0.542,respectively, higher than the EPA and EEC recommendation upper limit of TSP = 0.150 mg/m^3(quoted in Aceves and Grimalt,1993).

It was found that Bangkok has higher TSP concentration than permitted by regulations of other countries. It is a problem for urban areas and harmful to health. In the off-road area, Bansomdej, TSP concentration was found to be very low (0.244 mg/m^3) because Bansomdej was about 50 m faraway from roadside and has low traffic intensity, and Nat.Stat.Off. has low traffic volume and also has low TSP concentration.

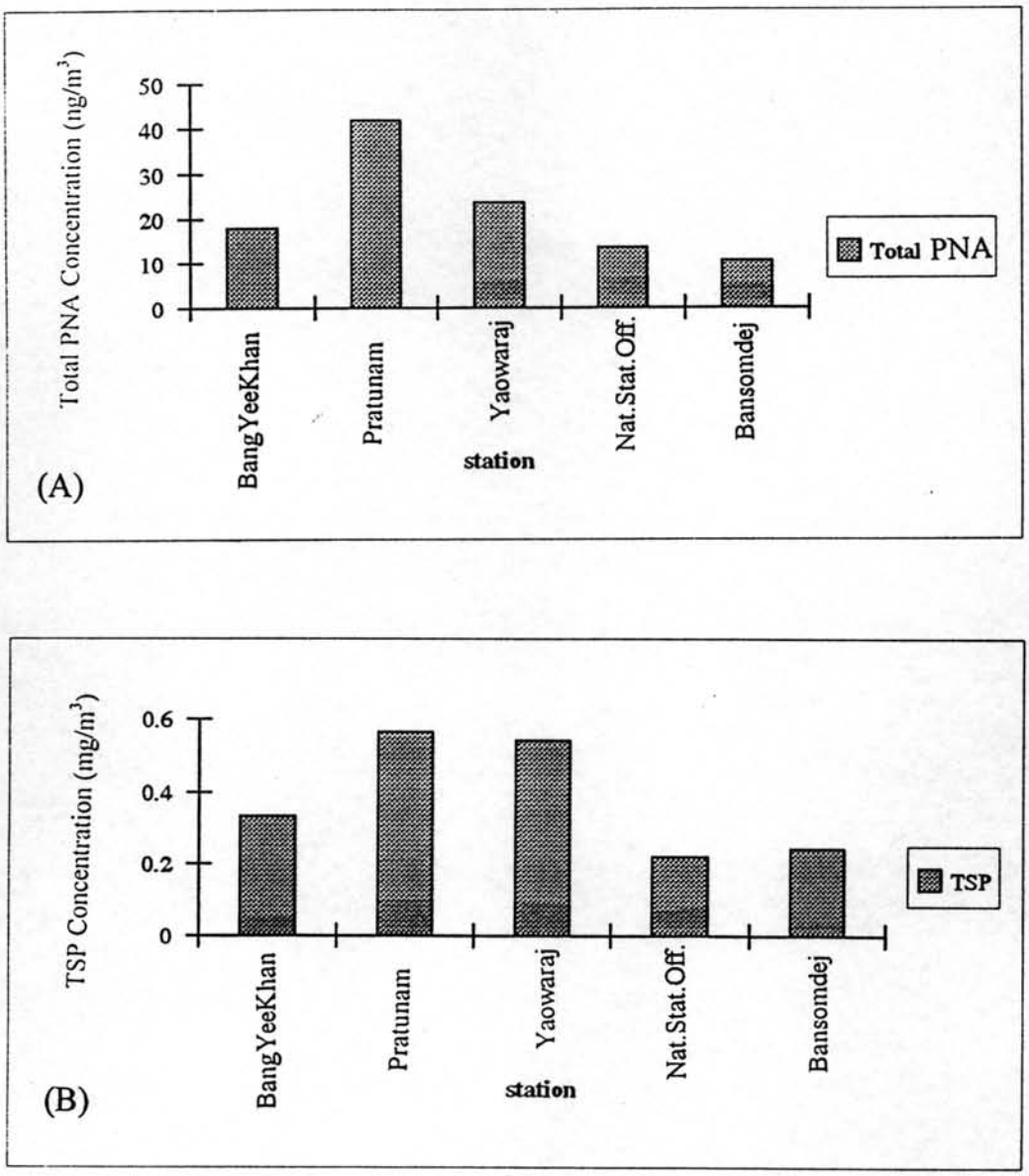


Figure 4-6 Variation of (A) Total PNA Concentration and (B) TSP Concentration in Sampling Sites during Study Periods (Feb-April,1996).

Table 4-6 Correlation Coefficient between Total PNA and TSP Concentrations.

Total PNA/TSP	p-Value	Coefficient (γ)
All Station	0.000	0.6814
BangYeeKhan	0.005	0.6871
Pratunam	0.037	0.5093
Yaowaraj	0.008	0.6047
Roadside	0.000	0.6586

Coefficient 0.70-1.00 - high correlation,
0.30-0.70 - moderate correlation,
0.00-0.30 - low correlation,
p-value < 0.05 = significant difference

4.5 Effect of Meteorological Parameters

The meteorological parameters such as temperature, relative humidity, and solar radiation, have a poor correlation to total PNA concentrations. It should be noted, however, that whereas these ambient conditions vary over only a narrow range. The results from statistical analysis are shown in Table 4-7. Meteorological parameters did not influence the change of PNA concentration due to the short period of this study.

Table 4-7 Correlation of Total PNA Concentration / Meteorological Factors

Total PNA / Meteorological Factors	Bang Yee Khan (15)		Pratumwan (17)		Yaowaraj (18)		Nat.Stat. Off. (13)		Bansomdej (9)		All Station (72)	
	P-Value	Coefficient	P-Value	Coefficient	P-Value	Coefficient	P-Value	Coefficient	P-Value	Coefficient	P-Value	Coefficient
Rain	0.7540	-0.0883	0.7410	0.8650	-	-	0.8330	-0.6500	0.7810	0.1087	0.5510	0.7150
RH	0.1290	-0.4101	0.3120	-0.2607	0.7660	-0.7560	0.0710	0.5164	0.2280	-0.4470	0.7300	-0.0414
Sun	0.8780	-0.4350	0.5880	-0.1416	0.3090	-0.2541	0.6600	-0.1350	0.5400	0.2364	0.7990	0.0305
Temperature	0.1090	-0.4304	0.9420	0.0190	0.9420	0.0183	0.5050	-0.2037	0.9560	0.0216	0.4520	-0.0901
VP.	0.0620	-0.4939	0.3260	-0.2535	0.3990	0.2119	0.2700	0.3307	0.2550	-0.4239	0.3590	-0.1097

(n) = Number of Samples

$P < 0.05$ = significant

Rain = Maximum rainfall for each period , mm.

RH = Relative Humidity , %

Sun = Solar Radiation (sun + sky) , T , MJ/m*m

Temp. = Daily Mean Temperature (max. + min/2) , Celcius

VP = Vapor Pressure, at msl, Hectapascal