CHAPTER IV

RESULTS AND DISCUSSION

4.1 Ambient TSP concentrations in Bangkok

Ambient TSP concentrations are observed at the four sampling sites namely: 1.Chulalongkorn Hospital (CH) the central business and commercial area, 2. Huay-Khwang Community Housing (HCH) the residential area, 3. Ministry of Science and Technology (MST) the government offices' area with heavily traffic and 4. Ratburana Post Office (RPO) the industrial area. The sampling period including for a whole year started from March 2006 to March 2007. The 24 Hours average TSP concentrations ($\mu g/m^3$) of four sites are shown in Table 4.1, and Figure 4.1.

Table 4.1 Summary of 24-hour TSP concentration in sampling sites.

Parameter	**24 Hours average TSP concentrations ($\mu g/m^3$)**			
	CH	HCH	MST	RPO
Mean	114.96	110.93	111.11	144.47
Median	107.69	106.84	95.24	124.37
SD	35.99	43.53	49.66	71.70
Max	231.01	251.10	253.31	361.93
Min	75.43	61.04	50.51	57.61
Number of samples	29	31	28	28
NAAQS[a] 24 hr-average Annual-average	 330 100			
Number of samples exceed NAAQS (24hr-average)	0	0	0	1
WHO guideline for TSP	120			
Number of samples exceed the WHO guideline	5	11	8	15

[a] NAAQS = Thai National Ambient Air Quality Standards

From Table 4.1, the average concentrations of TSP at CH, HCH, MST, and RPO are 114.96 μg/m^3, 110.93 μg/m^3, 111.11 μg/m^3 and 144.47 μg/m^3, respectively. It is found that the average concentration of TSP at RPO sampling site, which located in industrial area, is the highest while the lowest is found at the residential sampling site, HCH. This result gets along with the previous study which reported about the average concentrations of TSP in the industrial areas is higher than in the residential areas (Fang *et al.*, 2004). From the sampling period, it is found that the 24-h ambient concentrations of TSP at all sites varied in the wide ranges from 50.51 to 361.93 μg/m^3. The highest concentration of TSP found in the RPO sampling site is 361.93, while the lowest concentration of TSP found in the MST sampling site is 50.51 μg/m^3. Meanwhile, the highest and lowest concentrations of TSP found are 231.01 and 75.43 μg/m^3 for CH, 251.10 and 61.04 μg/m^3 for HCH, 253.31 and 50.51 μg/m^3 for MST, and 361.93 and 57.61 μg/m^3 for RPO, respectively. The peak TSP 24-h ambient concentration is at 361.93 μg/m^3 for RPO site and this number is the only value which exceeded the Thai ambient air standard of that 330 μg/m^3. By the way, the clean air guideline recommended by World Health Organization (WHO, 1979) states the level of the 24-h average TSP of that 120 μg/m^3. Considering WHO criteria, it is found that all sampling sites has the levels of 24-h average TSP exceeded the guideline. Number of samples exceed the WHO guide line for CH, HCH, MST, RPO are 5, 11, 8, 15 respectively. By these results, it may imply that the particle pollution on human or health concern issue in the Bangkok atmosphere area is still serious in terms of TSP pollution.

According to Figure 4.1, the increasing trend of TSP level in winter time which is dry season, is observed at all four sites from November 2006 to February 2007. The similar pattern is also found in the previous study at Taiwan study (Fang *et al.*, 2004).

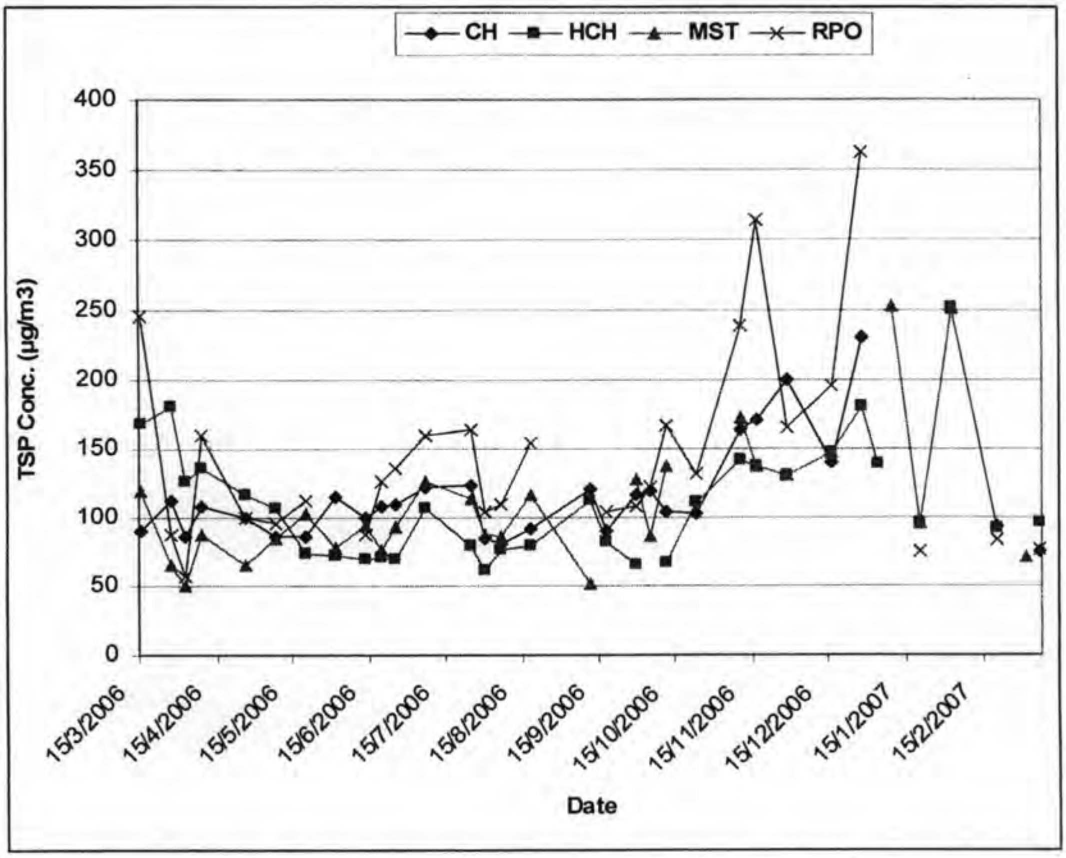


Figure 4.1 Time series of 24-hour TSP concentrations in Bangkok ambient air at all sampling sites.

4.2 Morphology of Particulate Matters

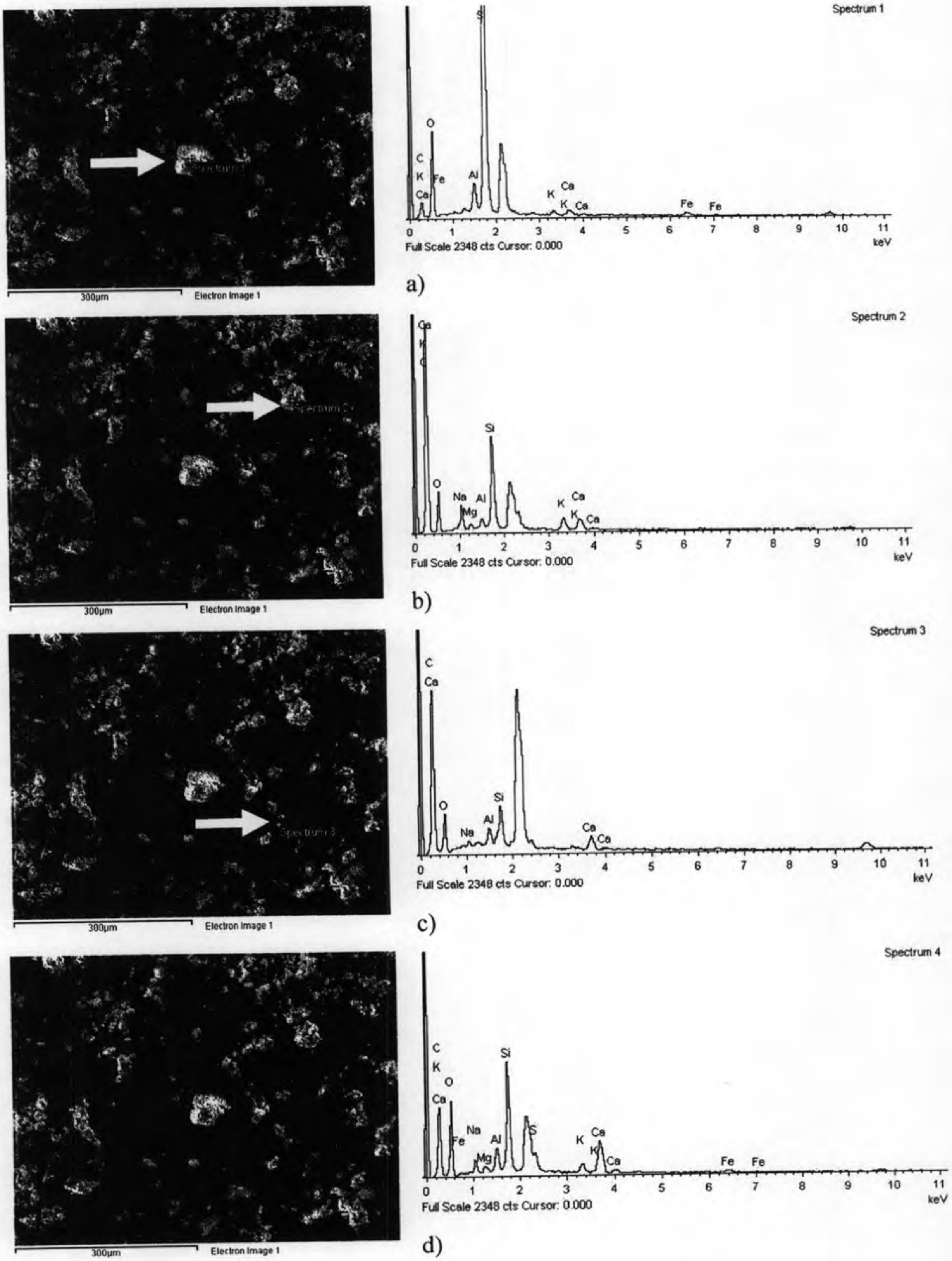
Sample in the study was analyzed on the assumption that the particulates samples were collected in a good distribution on the collecting filters. Sample of TSP filter from Chulalongkorn University station (CH) was brought and then analyzed with a Scanning Electron Microscopy (SEM) equipped with an energy dispersive detector. The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Elements in the filter surface were identified by the energy dispersive X-ray spectrum (EDX) which was obtained for each particle. The preparation of sample would be conducted before taking a picture. Sample must also be prepared in an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. They are therefore usually coated with an ultra-thin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Coating prevents the accumulation of static electric charge on the specimen during electron irradiation. Filter paper sample in the study was covered with a layer of gold to identify elements, and micrographs with the morphological details were obtained with the secondary electron detector. For chemical analysis by EDX, the EDX analysis is performed in two modes. One was a random scan overall the sample surface area, to detect broad chemical differences among dust populations. Another mode is selective analysis on an individual particle. At least three points were analyzed from each sample. The quantitative analysis was calculated by ZAF automated program. The compositional groups were identified according to the relative abundance of key elements compared to the total value of each analysis. A simple formula of ZAF program was shown in equation as

$$\text{Element }\% = \text{ZAF }[I_{\text{sample}} / I_{\text{std}}] \times \%\text{ weight of element standard}$$

Z = Atomic Number
A = Absorption Energy from source
F = Fluorescence emission energy from element
I = Intensity (peak area in X-ray spectra)

From this automated program, analyses can be characterized according to their dominant elements and their fingerprint data.

Characterization of the particles was performed using scanning electron microscopy. The Micrographs and X-ray spectra of individual particle sampling from CH site are shown in Figure 4.2. Particulate matters collected at CH site have several shapes of appearance. There are from fluffy like soft and loose structure, porous and sponge-like, rigid crust as square shape, to hard and dense shape. The elemental composition of airborne particles was identified by the EDX. The results are found that the particle no.1 as shown in Figure 4.2 (a) contains numerous Silicon (Si) which are abundant element composition of sand and soil. Figure 4.2 (b) and (c) shows the elemental composition of particle no.2 and 3 respectively. Both of them contain high calcium (Ca) which represents soil source. The overall quantitative results presented in Figure 4.2 (d) and Figure 4.3 show that carbon (C) oxygen (O), Si, and Ca are major elements found in the air particulates. It can be implied that major source of particle is soil/dust.



a)

b)

c)

d)

Figure 4.2 Micrographs and X-ray spectrum of particles on filter from CH site.

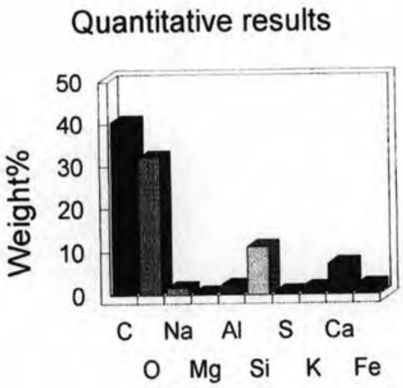


Figure 4.3 Quantitative results of particles on filter from CH site.

4.3 Analysis of metals

The accuracy of the determinations was previously checked by analysis of a certified reference material namely BCR, which is provided by Institute for Reference Materials and Measurements (IRMM). BCR is a registered trademark of the European Commission (EC), for which production was supported by research funding of the European Commission. A reference material BCR-038 Fly ash from pulverised coal (mg/kg) was used in the study. Table 4.2 shows the results of the certified reference materials analyses. These data show that the recovery range was from 80.5 % to 121.1 %, which proved the validity of the methodology used, but only for the elements measured in the reference materials. Acceptable recovery is a function of the concentration and the purpose of the analysis. Acceptable recovery limit requirements for individual assays for concentration of ppm (10 μg/g) and ppb (1 μg/kg) are 80-115% and 70-125%, respectively (AOAC, 2008).

Table 4.2 Measured and certified element concentrations (mg/Kg) in reference materials

Element	Certified value (mg/kg)	Experimental value (mg/kg)	Recovery (%)
Al	-	-	-
Cd	4.6 ± 0.3	3.7 ± 0.4	81.1
Cr	192 ± 10	199.8 ± 48.7	104.1
Cu	176 ± 9	162.4 ± 20.3	92.3
Fe	33800 ± 700	34264.0 ± 1481.5	101.4
K	-	-	-
Mn	479 ± 16	579.9 ± 65.4	121.1
Na	3740 ± 150	3372.8 ± 717.2	90.2
Ni	(194)	172.9 ± 19.6	89.1
Pb	262 ± 11	210.8 ± 18.4	80.5
Zn	581 ± 29	493.7 ± 35.0	85.0

Value in bracket is not certified

4.4 Elemental compositions

Table 4.3 and Figure 4.4 presents the results of a whole year study of the trace elemental composition of total suspended particulate (TSP) and their statistical analysis at all site. Results show the conspicuously high levels of Al, Fe, K, Na and Zn and the trend of elemental levels are in the following order: Na (34939.8) > K (4219.1) > Al (3463.6) > Zn (2463.9) > Fe (1527.8) > Ni (929.4) > Cu (227.5) > Pb (53.5) > Mn (49.0) > Cr (9.5) > Cd (1.6), Na (39911.9) > Fe (5578.6) > K (4452.7) > Al (3510.3) > Zn (2186.7) > Ni (461.9) > Cu (263.1) > Pb(197.4) > Mn (81.7) > Cr (12.0) > Cd (2.7), Na (30357.5) > K (4251.7) > Al (3512.4) > Zn (2933.8) > Fe (2061.0) > Cu (704.0) > Ni (92.8) > Mn (53.8) > Pb (51.1) > Cr (12.6) > Cd (1.6) and Na (22762.7) > K (2613.9) > Al (2171.5) > Fe (1824.9) > Zn (1310.2) > Cu (147.1) > Ni (88.1) > Pb(67.3) > Mn (49.3) > Cr (10.7) > Cd (1.8) in ng/m^3, for the HCH, RPO, CH and the MST respectively.

Table 4.3 Average concentrations (ng/m^3) of metallic element compositions of TSP at four sampling site.

Metal	CH	HCH	MST	RPO	Overall
	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.
Al	3512.4 ± 2915.1	3463.6 ± 2734.5	2171.5 ± 943.4	3510.3 ± 2385.3	3175.2 ± 2426.5
Cd	1.6 ± 1.7	1.6 ± 1.9	1.8 ± 1.5	2.7 ± 2.7	1.9 ± 2.0
Cr	12.6 ± 3.1	9.5 ± 2.2	10.7 ± 3.6	12.0 ± 4.8	11.1 ± 3.7
Cu	704.0 ± 213.1	227.5 ± 71.4	147.1 ± 62.7	263.1 ± 98.6	331.8 ± 249.0
Fe	2061.0 ± 668.5	1527.8 ± 625.7	1824.9 ± 970.1	5578.6 ± 3093.0	2710.6 ± 2314.1
K	4251.7 ± 4657.2	4219.1 ± 3540.7	2613.9 ± 1508.1	4452.7 ± 3178.1	3896.2 ± 3463.0
Mn	53.8 ± 20.1	49.0 ± 28.5	49.3 ± 33.0	81.7 ± 43.6	58.2 ± 34.6
Na	30357.5 ± 7495.3	34939.8 ± 6945.6	22762.7 ± 6147.6	39911.9 ± 13681.6	32055.1 ± 10867.8
Ni	92.8 ± 228.9	929.4 ± 3719.7	88.1 ± 293.4	461.9 ± 1355.9	400.0 ± 2028.0
Pb	51.1 ± 25.0	53.5 ± 50.0	67.3 ± 119.4	197.4 ± 290.4	91.4 ± 167.0
Zn	2933.8 ± 5186.2	2463.9 ± 4918.1	1310.2 ± 2197.0	2186.7 ± 4055.7	2236.0 ± 4266.1
TSP ($\mu g/m^3$)	114.96 ± 35.99	110.93 ± 43.53	111.11 ± 49.65	144.47 ± 71.70	120.71 ± 53.04
n	29	31	28	28	31

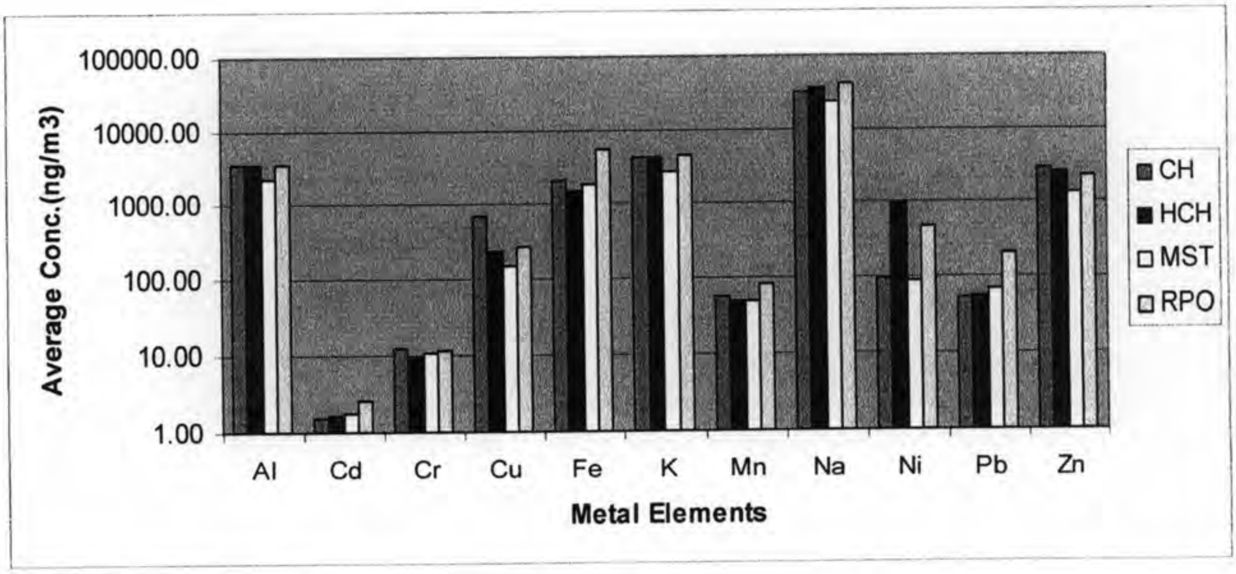


Figure 4.4 Comparison of each metallic element in TSP at four sampling site.

4.4.1 Major elements

The total mean concentrations of individual metals detected in the study are shown in Table 4.3. The results indicated that, concentrations of major elements found in the study namely Na, K, Al, Fe and Zn are quite high in the particulate in all areas. Comparing with all sites, the elemental compositions at RPO site are quite higher than others. The concentrations of Na, K, and Fe at RPO are 39911.9 ng/m^3, 4452.7 ng/m^3 and 5578.6 ng/m^3, respectively. While the highest concentrations of Al and Zn are found at CH with values of 3512.4 ng/m^3 and 2933.8 ng/m^3, respectively.

The lowest value of Fe concentrations is observed at HCH sampling site (1527.8 ng/m^3). Al, K, Na and Zn concentrations are found in the lowest concentration at MST with values of 2171.5 ng/m^3, 2613.9 ng/m^3, 22762.7 ng/m^3 and 1310.2 ng/m^3, respectively.

The high concentration of Na is attributed to the sea salt, road dust and soil's re-suspension (Begum *et al.*, 2004). High concentration of K implies that emissions from anthropogenic sources like biomass burning. Al and Fe are contributed to soil and road dust. Zn is from combustion processes (Samara *et al.*, 2003). The high Zn and Fe characterize signature of lubricating oil used in two-stroke engine where engine oil is mixed with fuel. The combustion process in a two-stroke engine is such that significant quantity of unburned fuel is released along with lube oil (Begum *et al.*, 2004). Zn is normally used as additive in this kind of lube oil. Zn could also be contributed from galvanized materials, tire wear and the use of zinc compounds in rubber production (Fergusson and Kim, 1991). The Na and Mn suggest that the source factor may be attributed to refuse burning (Begum *et al.*, 2004).

4.4.2 Toxic trace elements

The total average concentrations of individual toxic trace elements detected in the study are also shown in Table 4.3 and Figure 4.4. The results indicated that, concentrations of toxic trace elements found in the study namely Cd, Cr, Cu, Mn, Ni and Pb are quite low in the particles in all areas. Comparing with all sites, the elemental compositions at RPO site are quite higher than others. The concentrations of Cd, Mn, and Pb at RPO are 2.7 ng/m^3, 81.7 ng/m^3 and 197.4 ng/m^3, respectively. While the highest concentrations of Cr and Cu are found at CH with values of 12.6

ng/m^3 and 704.0 ng/m^3, respectively. The highest concentration of Ni is found at HCH with values of 929.4 ng/m^3. The lowest concentrations of Cd and Pb are found at CH with values of 1.6 ng/m^3 and 51.1 ng/m^3, respectively. Cr and Mn concentrations are found in the lowest level at HCH with values of 9.5 ng/m^3 and 49.0 ng/m^3, respectively. The lowest values of Cu and Ni concentrations are observed at MST sampling site with levels of 147.1 ng/m^3 and 88.1 ng/m^3, respectively.

Figure 4.5 illustrates that mass contributions of Cu are dominant in CH and MST sites. The mass percentages of Cu at CH and MST are 77% and 40%, respectively. Therefore, the accounts of Cu are found in the second place for HCH and RPO sites. The CH site is the area of downtown which surrounded by many office buildings and shopping arcades. On the working day, this area is crowded with people and vehicles for their working purposes. On the weekend, people and vehicles gather around the area for shopping purposes. It can be said that it has a lot of people and vehicles all the times. Several reports revealed that vehicular emission is key dominant of Cu in the previous studies (Fang *et al.*, 2006; Samara *et al.*, 2003; Begum *et al.*, 2004, Wang *et al.*, 2005). At both sites, Ni is the highest toxic metal found and takes account into 73% and 46% for HCH and RPO respectively. It is quite surprised to find the highest level of Ni in HCH which is not an industrial site instead of RPO which represented the industrial area. The previous report revealed that Ni can be a component of specialty steels (Kumar *et al.*, 2001), oil combustion (Fang *et al.*, 2006), tailpipe emission from diesel engine (Lim *et al.*, 2007). The explanations of this phenomenon may it be the sampling area at HCH are dense community area and close to the big open air market. The area is crowded with all size vehicles from pick-up trucks to 10-wheel buses in the morning and evening. The area is also crowded with mass transportation buses all the day. All these vehicles are diesel engine. This might be the reason of finding high Ni in the area. However, mass contributions of Cd and Cr in the four sampling areas are fairly low, which is attributed to their relatively low concentrations present in particles in all area. Mass percentages of Cr in all the four sampling sites are similar. Cr takes amount of 1–3% in each site. Also, interestingly, there is no significant difference in mass percentage for Cd and Cr among various sampling site. The trend of toxic trace metal in mass percentage are in the following order: Cu (77%) > Ni (10%) > Mn and Pb (6%) > Cr (1%), Ni (73%) > Cu (18%) > Mn and Pb (4%) > Cr (1%), Cu (40%) > Ni (24%) > Pb (18%) > Mn

(14%) > Cr (3%) > Cd (1%) and Ni (46%) > Cu (26%) > Pb (19%) > Cr (1%) for the CH, HCH MST, and the RPO, respectively.

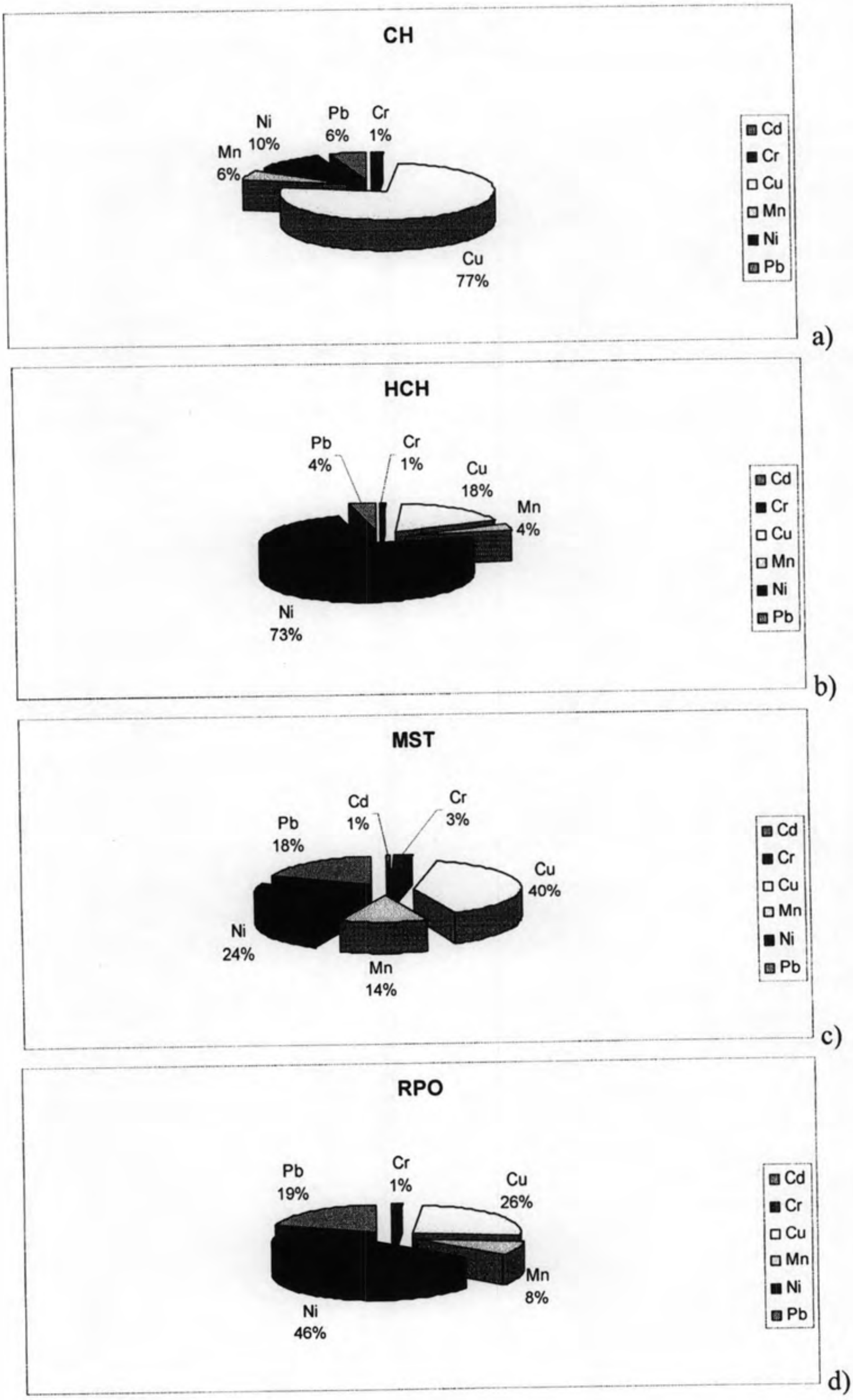


Figure 4.5 Mass percentages distribution of individual toxic trace metal in TSP at all four sites; a) CH, b) HCH, c) MST, d) RPO

4.5 Temporal variations of particulates and elements

The particulate and meteorological conditions data (temperature, relative humidity, wind speed and atmospheric pressure) at the four sampling sites are shown in Table 4.4. The test of homogeneity and normality of TSP concentration data set as shown in Table 4.5 (a) and (b) points that non-parametric analysis of variance (ANOVA) should be used to determine the significant difference of TSP levels in four sites. There is a significant difference in the TSP concentrations found in four different sites according to Table 4.5 (c). The concentrations of TSP at the RPO sampling site, located in industrial area, are higher than those of other sampling sites. The annual average concentrations of TSP at four different monitoring sites were 114.96, 110.93, 111.11 and 144.47 $\mu g/m^3$ for the CH, the HCH, the MST and the RPO, respectively. The temporal variations of TSP and elements would be studied and discussed in the following texts. Not only the annual average concentrations of 4 sites are different but also it has the variations in the numbers of particles as shown in Table 4.4. This might be the effects of meteorological parameters and human activities on the sampling period and sampling locations.

The average temperature, relative humidity, wind speed and atmospheric pressure are also demonstrated in Table 4.4. The variation of TSP concentrations would be observed by the range of maximum and minimum values. The highest difference between maximum and minimum values is found at the RPO site. Meanwhile, the high standard deviation (SD) is also observed at the RPO site. All these finding show that there is higher variation of TSP in the RPO sites than others and this may be caused by different activities in the site on the elapsed times. Otherwise, the difference of maximum and minimum of TSP concentration and SD value observed at the CH site is dramatically low comparing with the RPO site. This may imply that the pattern of activities that emitted the TSP for the CH site is more consistent. While, the inconsistency of activities that emitted the TSP is found for the RPO site.

Because the limitation of meteorological equipment, meteorological data are available only at the HCH and the RPO in the study. The average temperature, relative humidity, wind speed and atmospheric pressure are 28.2 °C, 0.69 m/s, 67.8 %, and 758.3 mmHg for the HCH and 28.4°C, 1.26 m/s, 70.5 %, 756.7 mmHg for the RPO, respectively.

Table 4.4 TSP and meteorological conditions at the CH, HCH, MST and the RPO (Meteorology data are available only at HCH and RPO)

Parameter		CH	HCH	MST	RPO
TSP ($\mu g/m^3$)	Mean	114.96	110.93	111.11	144.47
	SD	35.99	43.53	49.66	71.70
	Max	231.01	251.10	253.31	361.93
	Min	75.43	61.04	50.51	57.61
Temperature (°C)	Mean		28.2		28.4
	SD		1.6		1.9
	Max		31.2		33.9
	Min		23.4		23.7
Wind speed (m/s)	Mean		0.69		1.26
	SD		0.44		0.61
	Max		2.12		2.19
	Min		0.04		0.28
Relative Humidity (%)	Mean		67.8		70.6
	SD		10.3		7.2
	Max		86.0		84.4
	Min		47.8		54.1
Atmospheric Pressure (mmHg)	Mean		758.3		756.7
	SD		2.2		1.7
	Max		764.1		759.9
	Min		754.9		753.6

Table 4.5 Analysis of Variance (ANOVA) by Non-parametric method of the concentrations of TSP at the CH, HCH, MST and the RPO sites.

(a) Tests of Normality

		Kolmogorov-Smirnov(a)			Shapiro-Wilk		
	Site	Statistic	df	Sig.	Statistic	df	Sig.
TSP	1	.235	29	.000	.808	29	.000
	2	.132	31	.179	.886	31	.003
	3	.156	28	.080	.838	28	.001
	4	.199	28	.006	.846	28	.001

a Lilliefors Significance Correction

(b) Test of Homogeneity of Variance

		Levene Statistic	df1	df2	Sig.
TSP	Based on Mean	3.231	3	112	.025
	Based on Median	2.250	3	112	.086
	Based on Median and with adjusted df	2.250	3	81.888	.089
	Based on trimmed mean	2.833	3	112	.042

(c) Test Statistics[a,b]

	TSP
Chi-Square	5.904
df	3
Asymp. Sig.	.116

a Kruskal Wallis Test
b Grouping Variable: Site

According to Table 4.6, the average concentrations of TSP at three different seasons of the CH are 104.9, 157.3, and 94.1 $\mu g/m^3$ for rainy, winter, and summer season, respectively, while the concentrations of TSP at three different seasons of the HCH are 77.6, 142.4 and 132.7 $\mu g/m^3$, respectively. In the meantime, the TSP concentrations at the MST and RPO sites are 98.5, 173.5, 77.7 $\mu g/m^3$ and 127.3, 195.8, 117.6 $\mu g/m^3$ for rainy, winter, and summer season, respectively.

Generally, the sources of metal elements found in the urban atmosphere can be classified into two types according to their origins: anthropogenic and natural sources. The highest concentrations found in this study are the crust elements such as Fe, K, Al and Na. Cadmium is found to be the lowest of the 11 investigated metal element mass concentrations. The seasonal variation of each element observed at all the sites is given in Table 4.6 and Figure 4.6. The ratio of element per TSP in percentage of each element in different seasons is also illustrated in Table 4.7. This percentage ratio helps to make more understanding about the temporal and spatial variation of element according to TSP.

The concentration at all sites followed a similar pattern. For example, the metal concentrations are very low during rainy season and increase through dry season (winter). The results shown in Table 4.7 point that most of the elements found in different seasons are consistent. Na is mostly found in rainy season, while Ni is mostly found in winter. Al, K and Zn are abundant in summer. The explanation of high K and Zn found in summer should be people tend to burn the organic garbage like branches, dried grass even household garbage at the summer period. One of the most important sources of K and Zn found in the atmosphere is biomass burning, oil burning and incinerator (Hedberg *et al.*, 2005; Begum *et al.*, 2004; Hien *et al.*, 2001; Fang *et al.*, 2006).

Waste combustion is also the important source of Zn in particulate matter (Wang *et al.*, 2006). Even though Bangkok Metropolitan Administration has municipal waste disposal system including garbage and waste collection, the system especially waste collection is not fully function. The lack of waste collecting labors and transport vehicles comparing with a huge number of garbage and municipal waste in household makes the waste collecting truck can not load all waste burdens to the waste treatment site in one work cycle. Sometimes this household waste is put on the sidewalk, street even in the front of people house for many days before moving by the waste collecting truck. Normally, the load of waste that can be transported by waste collecting truck is anticipated by normal household waste quantity. Even the normal quantity of household waste is expected but the waste transporting ability is sometimes insufficient. In addition, when the people have extra waste like big broken tree branches, dried leaves collected from the roof and others, these wastes must be waited for many days before being collected and transported. This is why people tend to manage their own extra waste. The cheapest and fastest way to discard their waste is burning. Summer is a good time for burning waste because there is low moisture content and easily to set fire.

Zn is the characteristic signature of lubricating oil used in two-stroke engine where engine oil is mixed with fuel. The combustion process in a two-stroke engine is such that significant quantity of unburned fuel is released along with lube oil. Zn is normally used as additive in this kind of lube oil (Begum *et al.*, 2004). Particulate Zn in ambient air could also be contributed from automobile sources, for example, wear and tear of vulcanized rubber tires, and corrosion of galvanized vehicular parts (Banerjee, 2003; Karar *et al.*, 2006; Begum *et al.*, 2004).

Al and K can also have their origins from soil factor like soil and road dust (Watson and Chow, 2001; Begum *et al.*, 2004). Al is also found its origin from construction sites (Fang *et al.*, 2006). It can be said that the high loading of Al, K and Zn found is a combination emission sources of biomass burning, vehicle emission, construction and road/soil dust. The dry season especially summer in Bangkok is a good period of time for construction works because there is no interference while construction from rain. In addition, the low moisture contents in the atmosphere and dry environment increase the rate of soil re-suspension by wind. This can be the factor attributed to high amounts of Al found in the study. All of these sources might be the reason of the increasing of both airborne particulate and metal concentrations in summer.

Na is mostly found in rainy season. It may be from the monsoon which takes Na from the sea. Rainy or southwest monsoon season starts from mid-May to mid-October. The southwest monsoon prevails over Thailand and abundant rain occurs over the country. The wettest period of the year is August to September (Thai Meteorological Department, 2008).

Table 4.6 Average values for TSP (µg/m^3) and eleven elements (ng/m^3) atmospheric concentrations for three seasons and each sampling site.

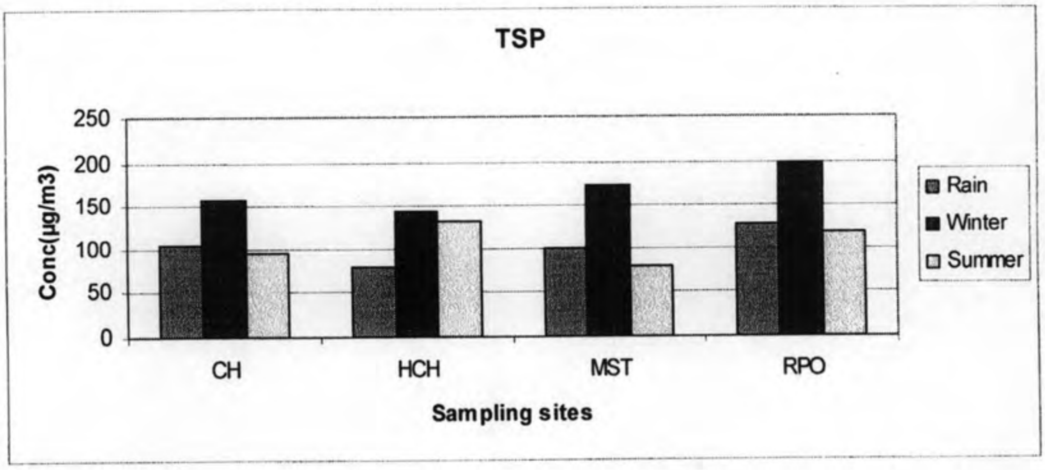
CH site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	104.9	157.3	94.1	115.0
	Al	2265.8	2723.9	6972.0	3512.4
	Cd	1.0	3.5	1.2	1.6
	Cr	12.7	14.6	10.5	12.6
	Cu	702.1	722.3	691.9	704.0
	Fe	1869.5	2781.5	1750.7	2061.0
	K	2290.3	2694.7	10011.8	4251.7
	Mn	46.3	79.0	44.5	53.8
	Na	28920.7	30667.8	33126.1	30357.5
	Ni	10.1	266.2	109.6	92.8
	Pb	52.0	65.0	37.3	51.1
	Zn	968.5	387.4	9691.8	2933.8
HCH site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	77.6	142.4	132.7	110.9
	Al	1978.3	2870.8	7281.0	3463.6
	Cd	0.6	4.1	0.9	1.6
	Cr	8.2	10.2	10.9	9.5
	Cu	193.2	256.9	253.2	227.5
	Fe	1019.2	1980.6	1898.1	1527.8
	K	2232.4	3360.4	9419.3	4219.1
	Mn	29.2	67.9	61.7	49.0
	Na	34710.5	35300.8	34882.5	34939.8
	Ni	7.4	2913.0	91.2	929.4
	Pb	51.6	63.9	43.6	53.5
	Zn	242.0	352.5	9923.8	2463.9
MST site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	98.5	173.5	77.7	111.1
	Al	1637.6	2638.0	2772.7	2171.5
	Cd	1.4	3.4	1.0	1.8
	Cr	10.3	14.1	8.0	10.7
	Cu	139.7	195.3	113.6	147.1
	Fe	1522.9	3032.8	1221.2	1825.0
	K	1689.3	2708.2	4369.0	2613.9
	Mn	35.9	89.2	36.4	49.3
	Na	24889.0	25154.2	16118.5	22762.7
	Ni	8.9	288.9	45.9	88.1
	Pb	85.8	71.0	26.8	67.3
	Zn	269.7	339.8	4361.8	1310.2
RPO site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	127.3	195.8	117.6	144.5
	Al	3662.0	3710.1	3000.3	3510.3
	Cd	1.8	6.7	1.0	2.7
	Cr	13.3	13.6	7.8	12.0
	Cu	207.4	356.2	273.6	263.1
	Fe	5027.2	5932.8	6197.9	5578.6
	K	4164.8	4388.0	5061.2	4452.7
	Mn	71.3	106.8	72.3	81.7
	Na	44662.1	47775.0	22103.9	39911.9
	Ni	12.6	1625.9	132.2	461.9
	Pb	286.1	101.6	128.3	197.4
	Zn	2010.6	536.0	4400.2	2186.7

Table 4.7 The percentage ratio of each element per TSP (% Element / TSP) in each site at different seasons.

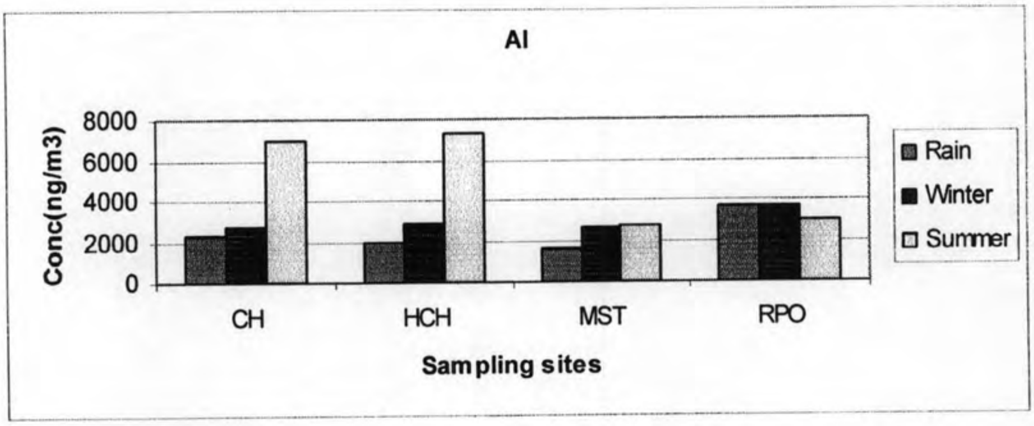
CH site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	100	100	100	100
	Al	2.160	1.732	7.409	3.054
	Cd	0.001	0.002	0.001	0.001
	Cr	0.012	0.009	0.011	0.011
	Cu	0.669	0.459	0.735	0.612
	Fe	1.782	1.768	1.860	1.792
	K	2.183	1.713	10.640	3.697
	Mn	0.044	0.050	0.047	0.047
	Na	27.570	19.496	35.203	26.398
	Ni	0.010	0.169	0.116	0.081
	Pb	0.050	0.041	0.040	0.044
	Zn	0.923	0.246	10.299	2.551
HCH site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	100	100	100	100
	Al	2.549	2.016	5.487	3.123
	Cd	0.001	0.003	0.001	0.001
	Cr	0.011	0.007	0.008	0.009
	Cu	0.249	0.180	0.191	0.205
	Fe	1.313	1.391	1.430	1.378
	K	2.877	2.360	7.098	3.804
	Mn	0.038	0.048	0.046	0.044
	Na	44.730	24.790	26.287	31.506
	Ni	0.010	2.046	0.069	0.838
	Pb	0.066	0.045	0.033	0.048
	Zn	0.312	0.248	7.478	2.222
MST site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	100	100	100	100
	Al	1.663	1.520	3.568	1.955
	Cd	0.001	0.002	0.001	0.002
	Cr	0.010	0.008	0.010	0.010
	Cu	0.142	0.113	0.146	0.132
	Fe	1.546	1.748	1.572	1.643
	K	1.715	1.561	5.623	2.353
	Mn	0.036	0.051	0.047	0.044
	Na	25.268	14.498	20.745	20.488
	Ni	0.009	0.167	0.059	0.079
	Pb	0.087	0.041	0.034	0.061
	Zn	0.274	0.196	5.614	1.179
RPO site	**Parameter**	**Rain**	**Winter**	**Summer**	**Annual**
	TSP	100	100	100	100
	Al	2.877	1.895	2.551	2.429
	Cd	0.001	0.003	0.001	0.002
	Cr	0.010	0.007	0.007	0.008
	Cu	0.163	0.182	0.233	0.182
	Fe	3.949	3.030	5.270	3.861
	K	3.272	2.241	4.304	3.081
	Mn	0.056	0.055	0.061	0.057
	Na	35.084	24.400	18.796	27.621
	Ni	0.010	0.830	0.112	0.320
	Pb	0.225	0.052	0.109	0.137
	Zn	1.579	0.274	3.742	1.513

The measured concentrations are arranged to evaluate the variation of the concentrations of trace elements in the three different seasons. The temporal variation is illustrated as bar graph shown in Figure 4.6. Generally, the average trace metal concentrations in dry season are higher than those of wet season. The average concentrations of TSP, Cd, and Ni show higher values for winter season than other seasons. Meanwhile, the average concentrations of Al, K and Zn show higher values for summer season than others. The similar pattern for elevated values of Cd and Ni is former reported (Khillare *et al.*, 2004). The highest concentration of Cd is observed during the winter at the RPO which is the industrial site having various types of industries such as plastic, paints, smelters and foundries. At all other sites, Cd is found in the highest rank in winter also. Cd is dispersed into the environment from various sources. The possible sources of Cd are coal and oil combustion, pyrometallurgical non-ferrous metal production, mining and other manufacturing (Khillare *et al.*, 2004). Chronic exposures to Cd can result in respiratory system, prostate, kidney and blood (NIOSH, 1994). Ni in the atmosphere originates from the combustion of fossil fuels (particularly from oil) smelting, crustal sources and volcanoes (Khillare *et al.*, 2004). Atmospheric Ni concentration from the remote areas that are considered to be relatively free from man made Ni emissions is in the range of 0.1–1 ng/m^3 (marine) and 1–3 ng/m^3 (Continental). It is also found that combustion of oil and incineration of waste contributes more than 70% of total Ni to the atmosphere from man made sources followed by refining process with 17%. Continuous and prolonged exposure to Ni can produce dermatitis and disorders in the respiratory system and it is also a possible carcinogen (Khillare *et al.*, 2004).

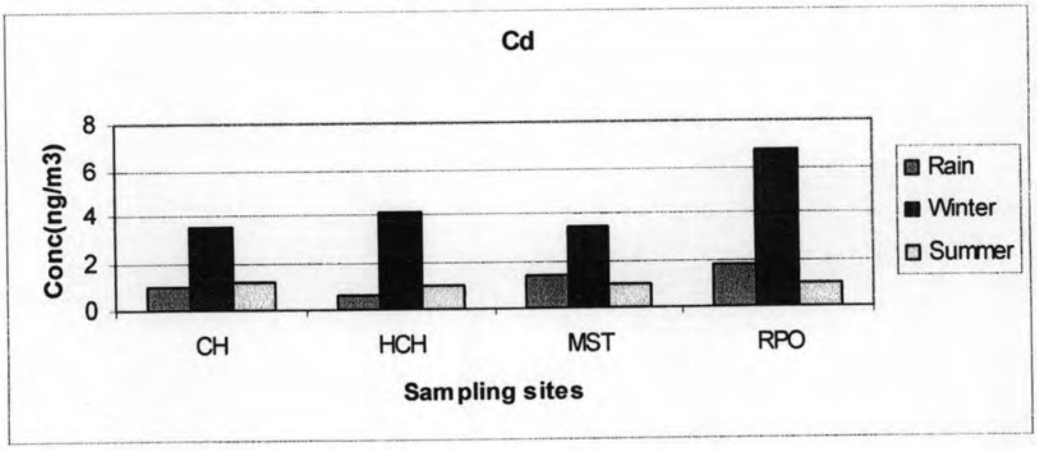
The difference between seasonal concentrations could be attributed to the precipitation levels. Cu is only observed the element which has similar pattern in all different seasons. The concentration levels were probably reasonable because the contaminant sources and turbulence originated from motor vehicles in the sampling point. It is known that Cu is emitted at a large proportion from the brake linings and is a major contributor to the element in coarse particles (Weckwerth, 2001; Harrison *et al.*, 2003,). Vehicular emission is also known as the important source of Cu (Fang *et al.*, 2006). The characteristic of Bangkok is dense and traffic congested area. The area is crowded with all types of vehicle in everyday for all seasons. This might be the reason of that why it has no difference on Cu concentration in different seasons.



a)

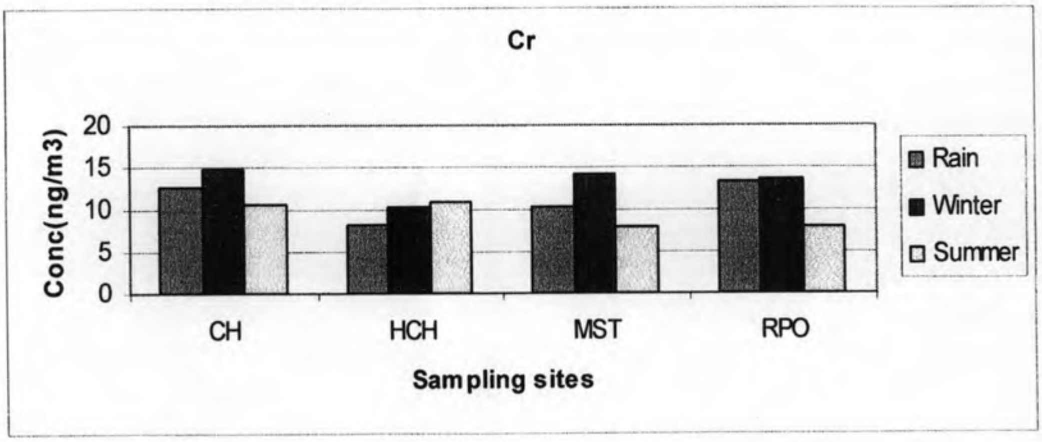


b)



c)

Figure 4.6 Seasonal variations of a)TSP, b)Al, c)Cd, d)Cr, e)Cu, f)Fe, g)K, h)Mn, i)Na, j)Ni, k)Pb, l)Zn at four sampling sites.



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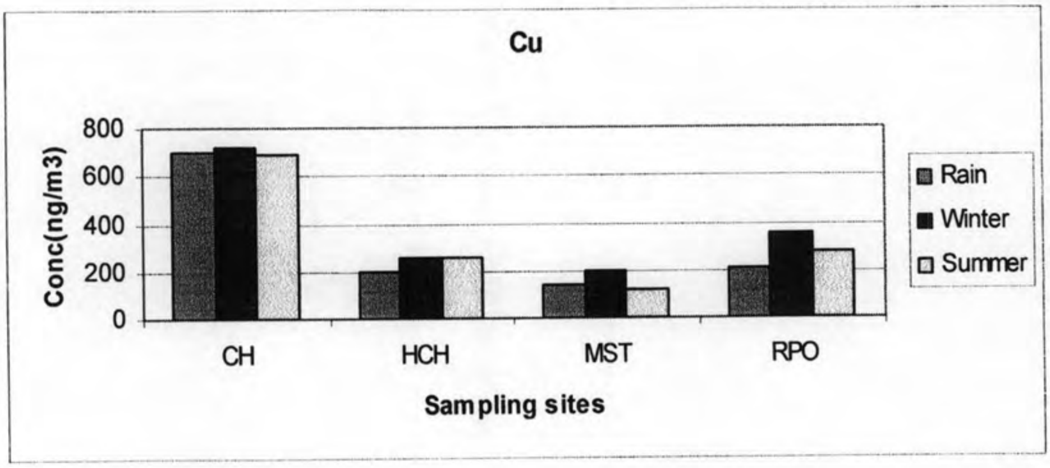

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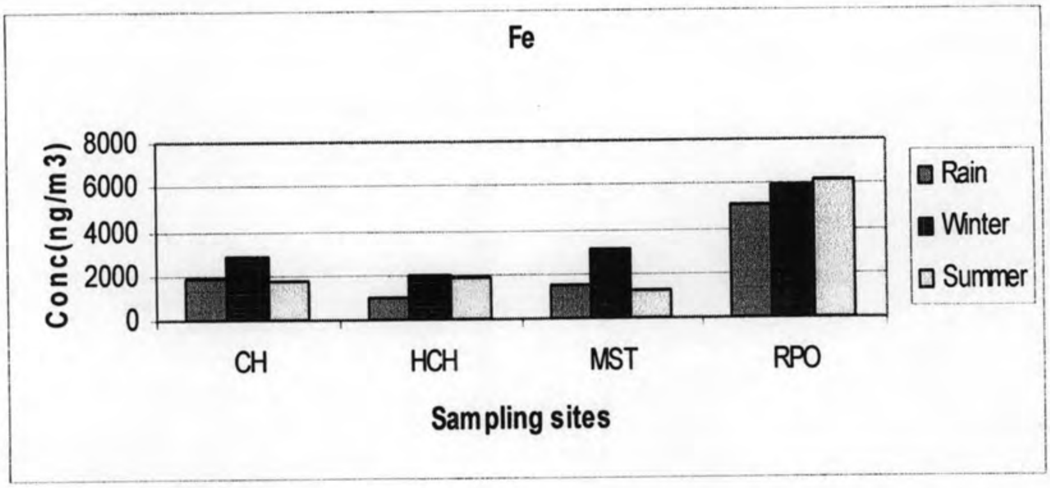


f)

Figure 4.6 Seasonal variations of a)TSP, b)Al, c)Cd, d)Cr, e)Cu, f)Fe, g)K, h)Mn, i)Na, j)Ni, k)Pb, l)Zn at four sampling sites **(continued).**

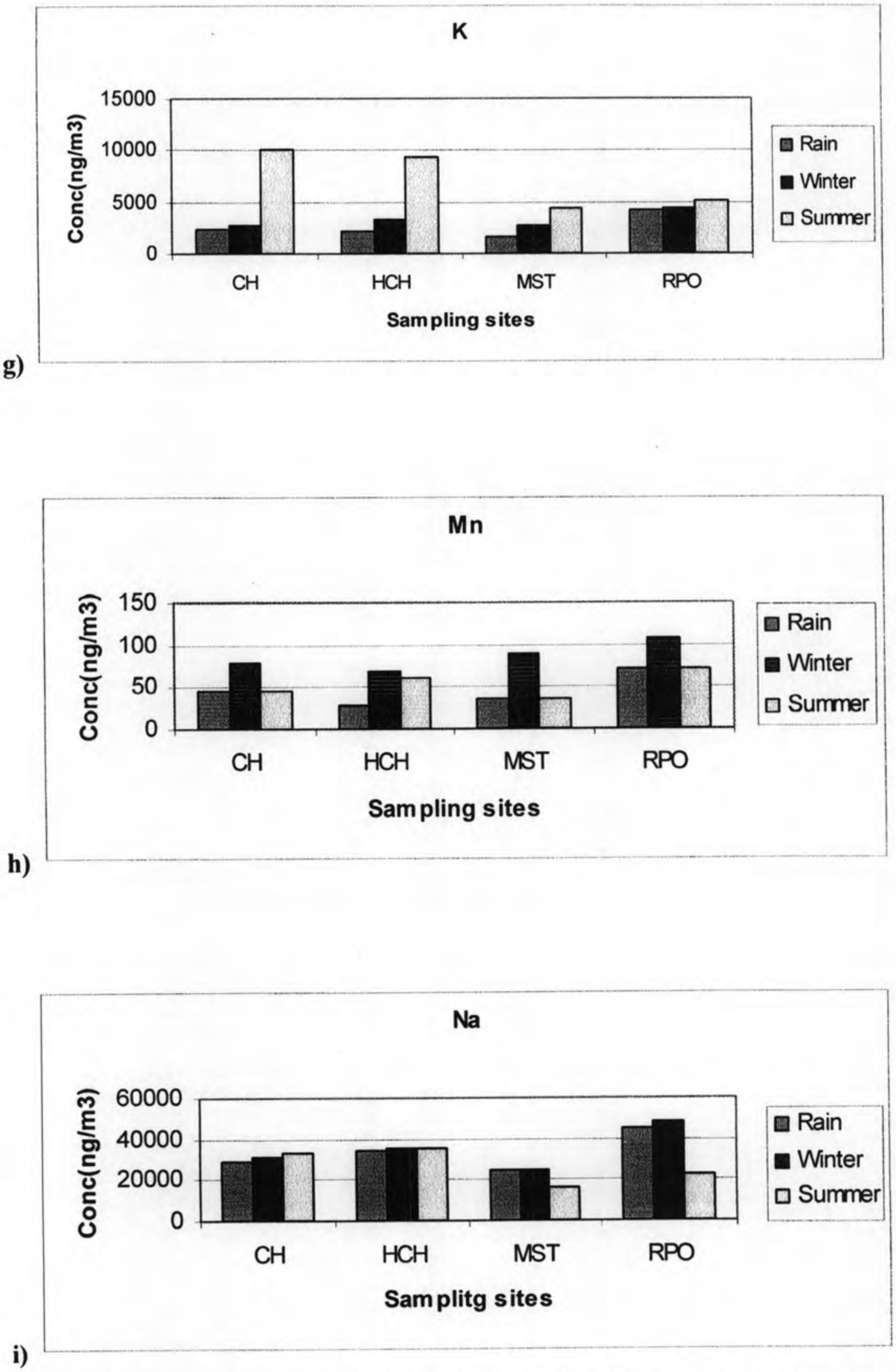
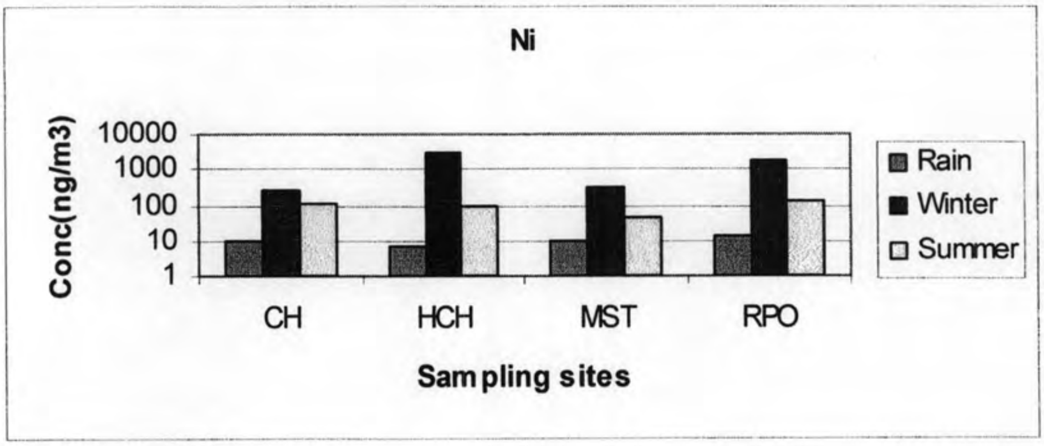


Figure 4.6 Seasonal variations of a)TSP, b)Al, c)Cd, d)Cr, e)Cu, f)Fe, g)K, h)Mn, i)Na, j)Ni, k)Pb, l)Zn at four sampling sites **(continued).**



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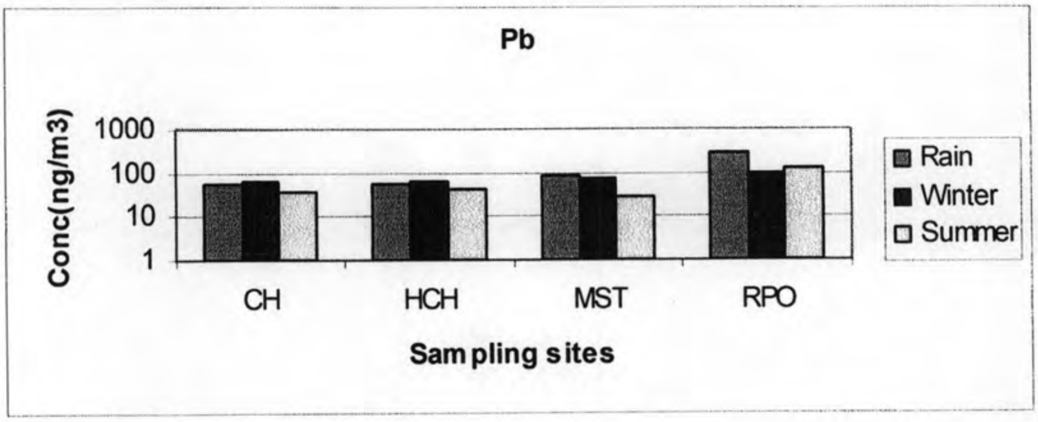

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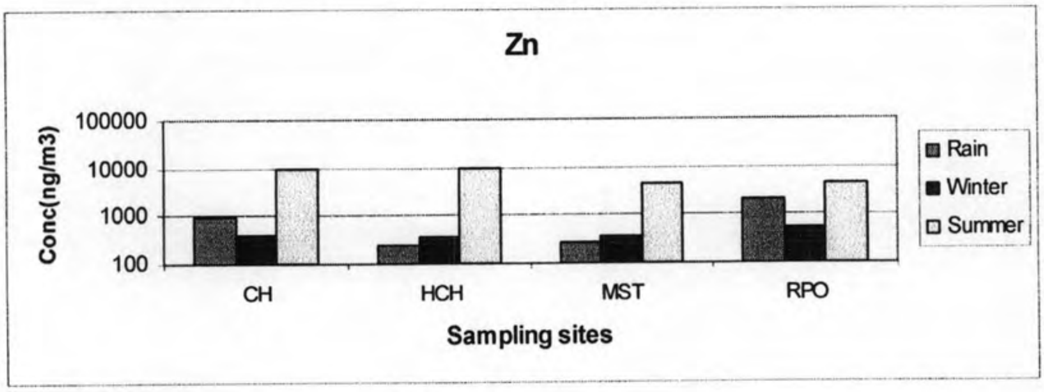


l)

Figure 4.6 Seasonal variations of a)TSP, b)Al, c)Cd, d)Cr, e)Cu, f)Fe, g)K, h)Mn, i)Na, j)Ni, k)Pb, l)Zn at four sampling sites **(continued).**

Figure 4.7 shows time series of monthly variations of TSP and 11 elements. It is found that the highest concentration of TSP is observed in November. Meanwhile, the high concentrations of Al, K and Zn are found in April, while Cd is found in September. The high concentration of Mn and Ni is found in December. The concentrations of Cr, Cu, Fe, Na and Pb tend to be similar in amount for a year.

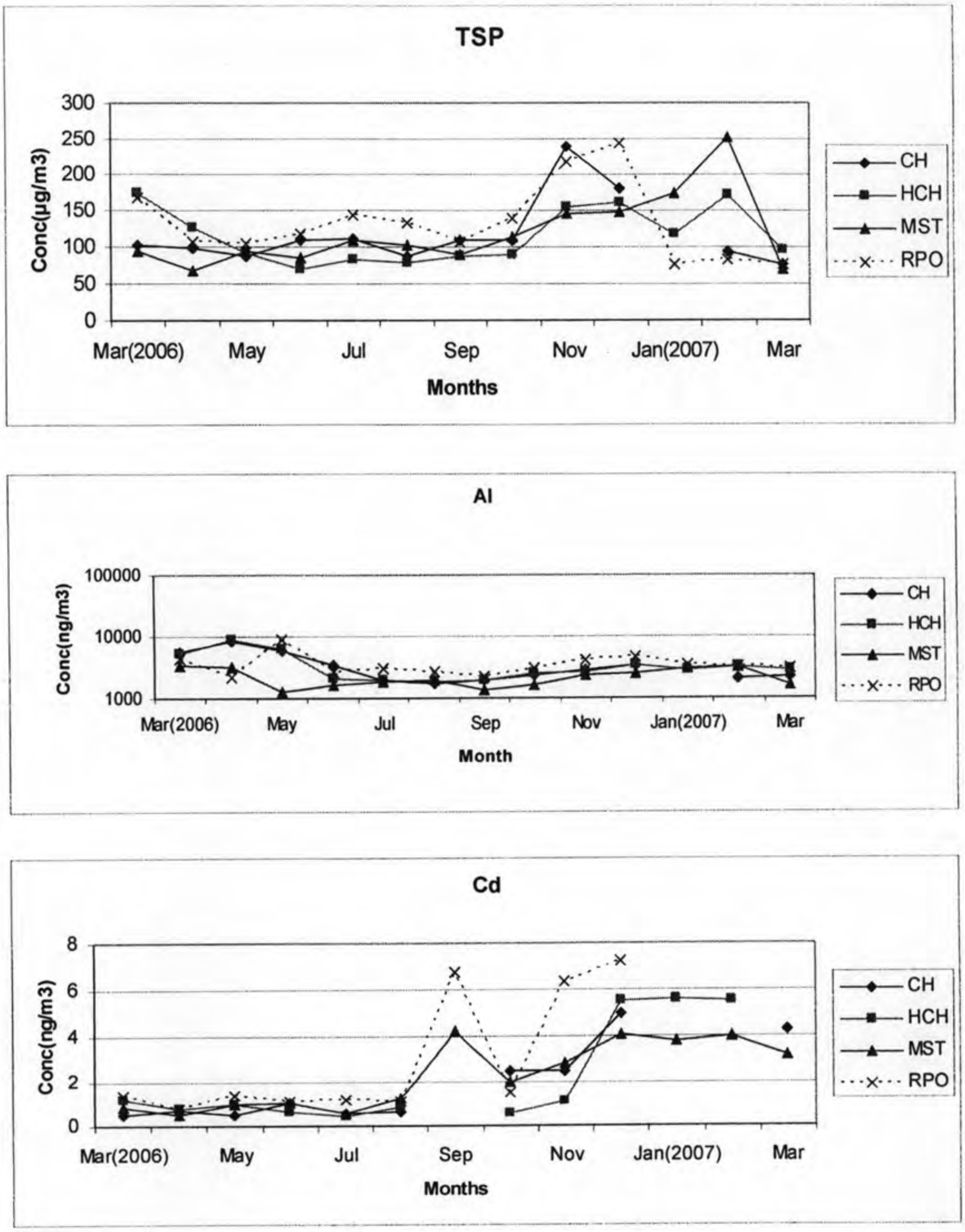
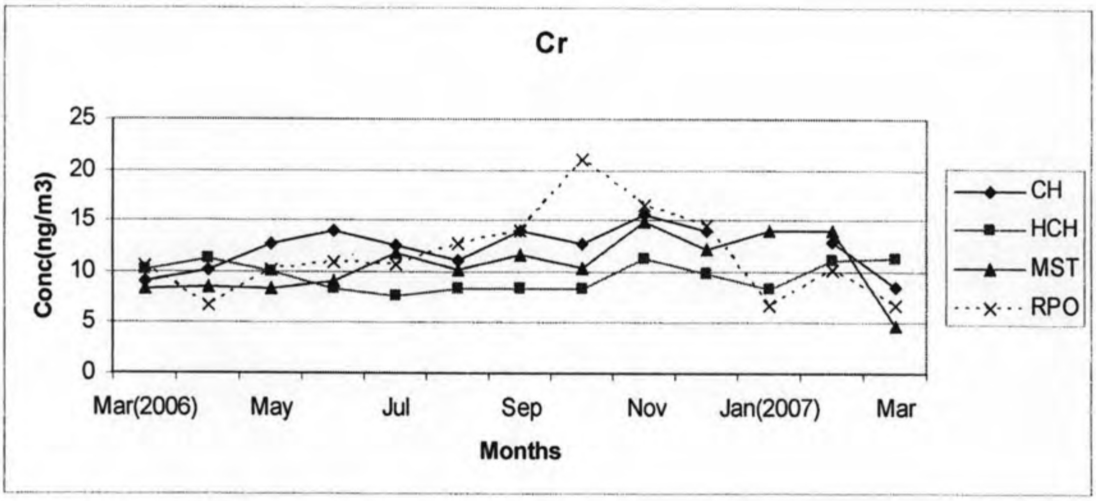
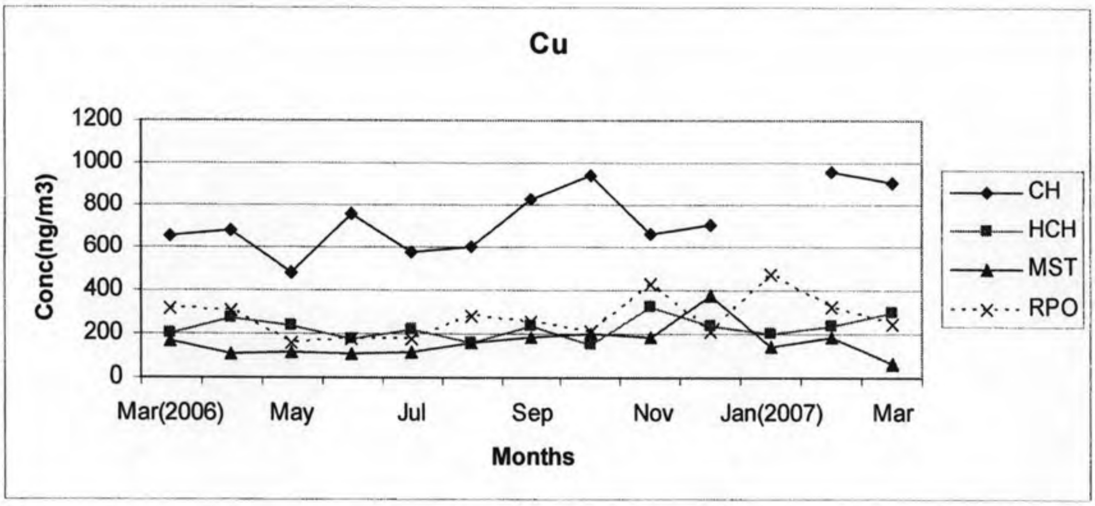


Figure 4.7 The monthly variations Concentrations of airborne trace metals and total suspended particles in air samples at the four stations on 12 sampling months.





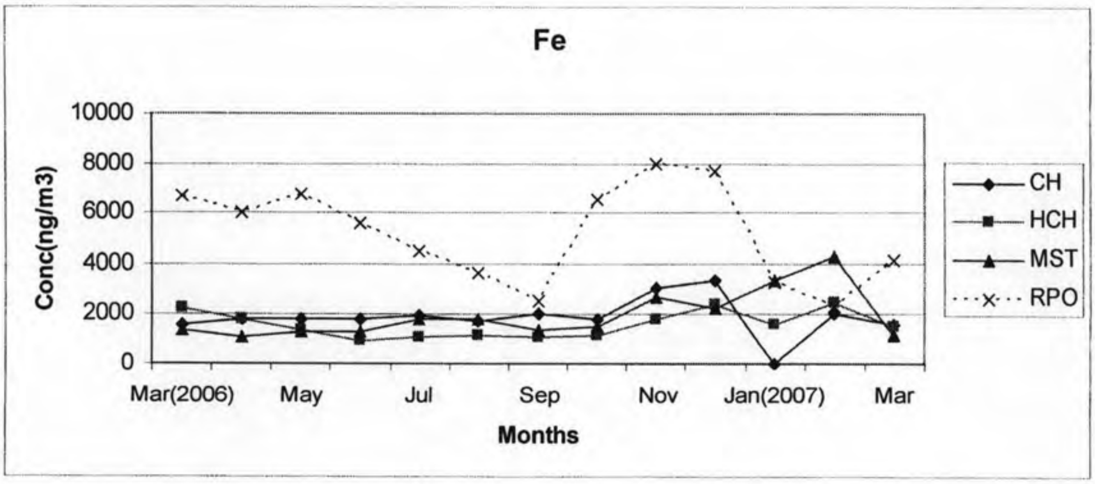
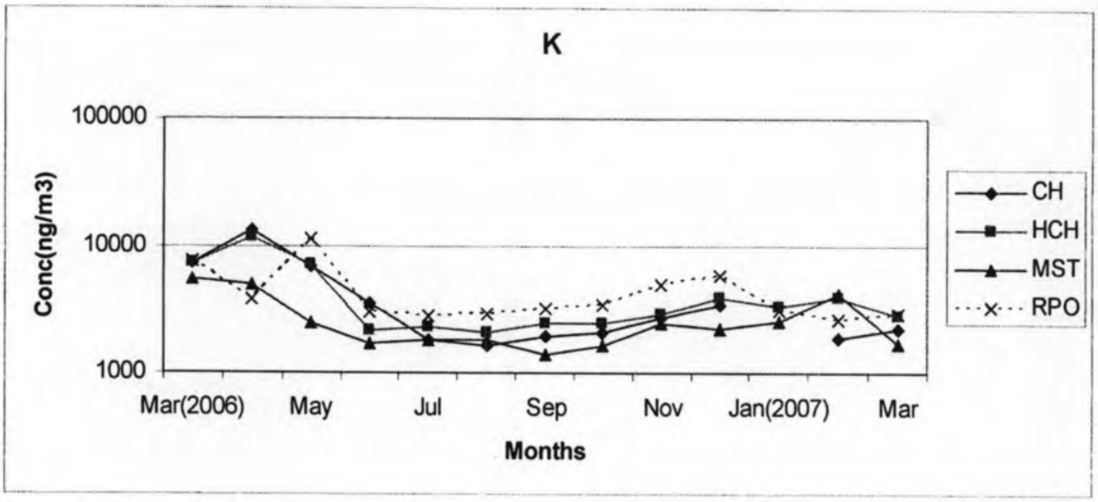
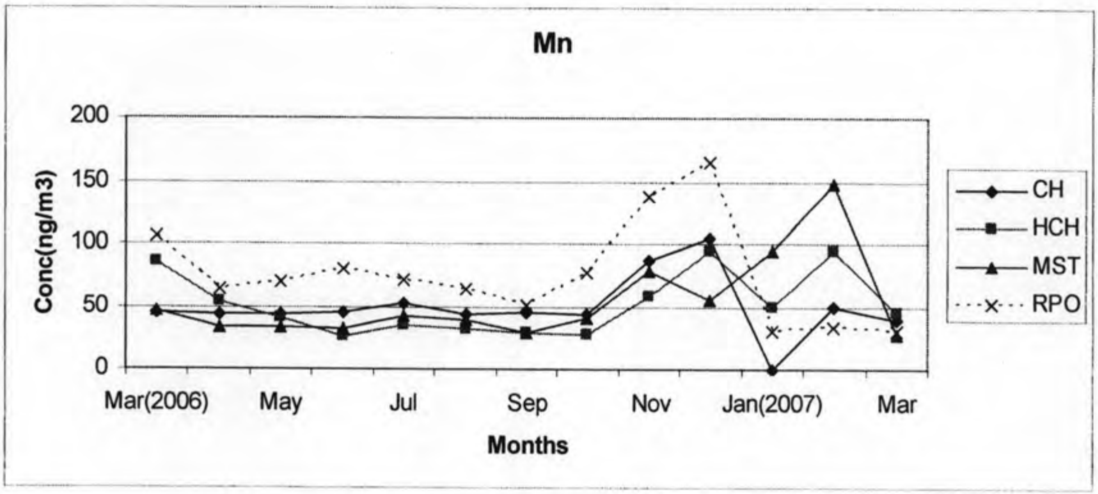


Figure 4.7 The monthly variations Concentrations of airborne trace metals and total suspended particles in air samples at the four stations on 12 sampling months **(continued).**





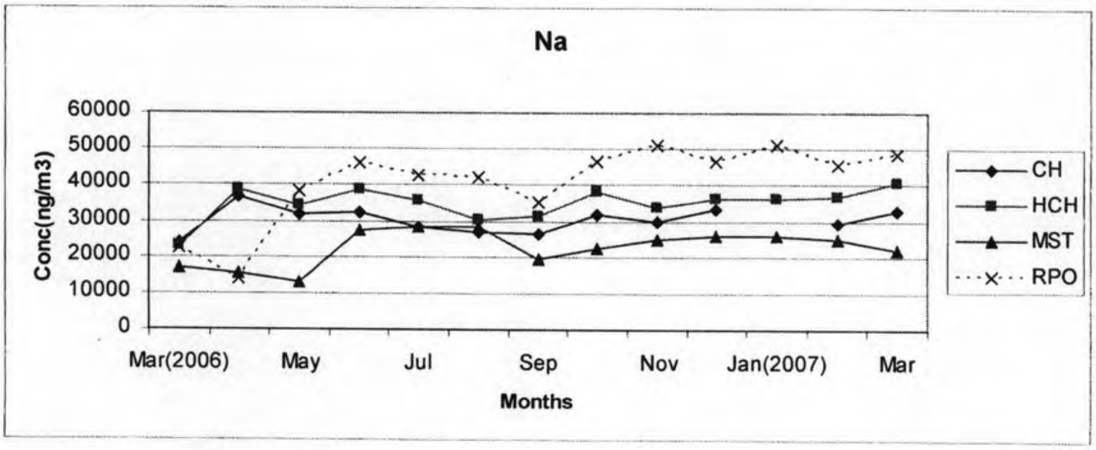
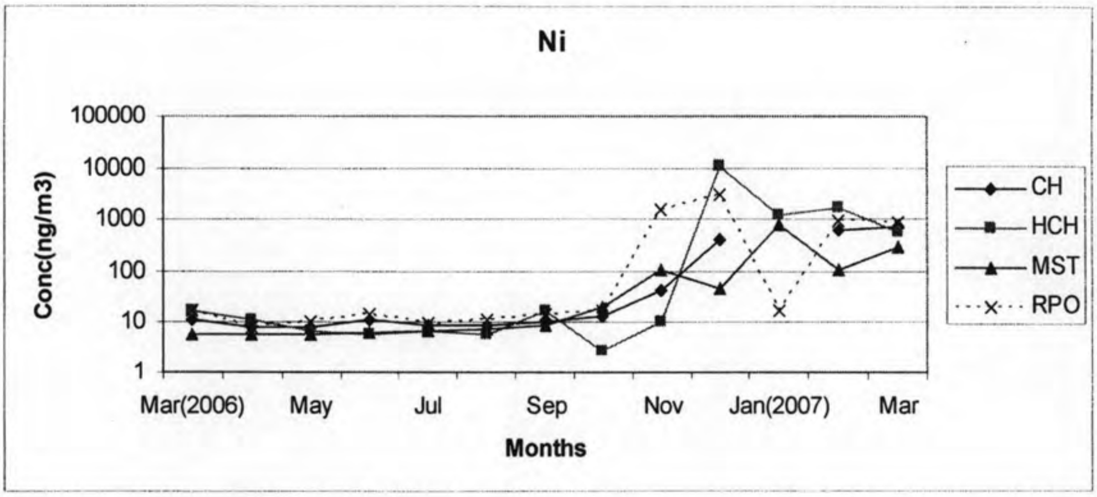
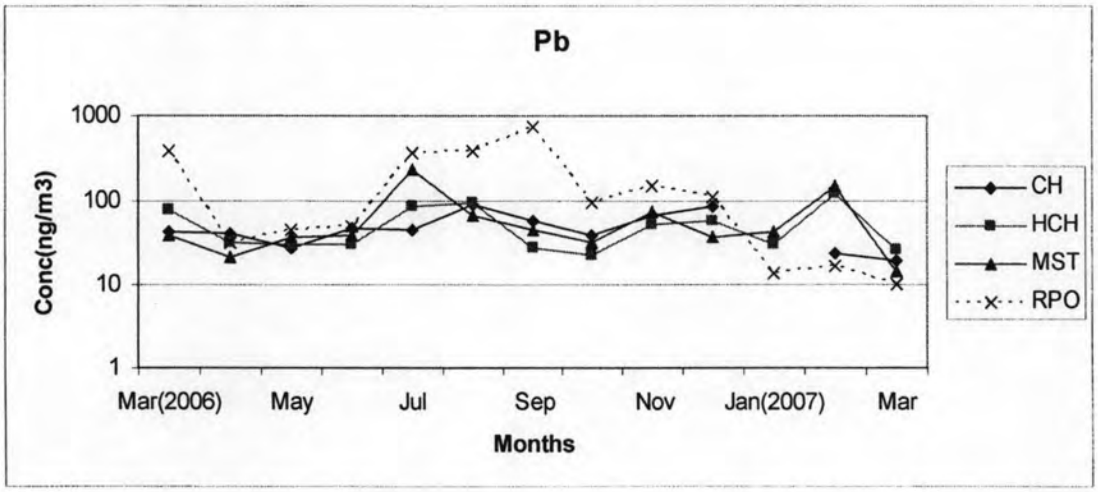


Figure 4.7 The monthly variations Concentrations of airborne trace metals and total suspended particles in air samples at the four stations on 12 sampling months **(continued).**





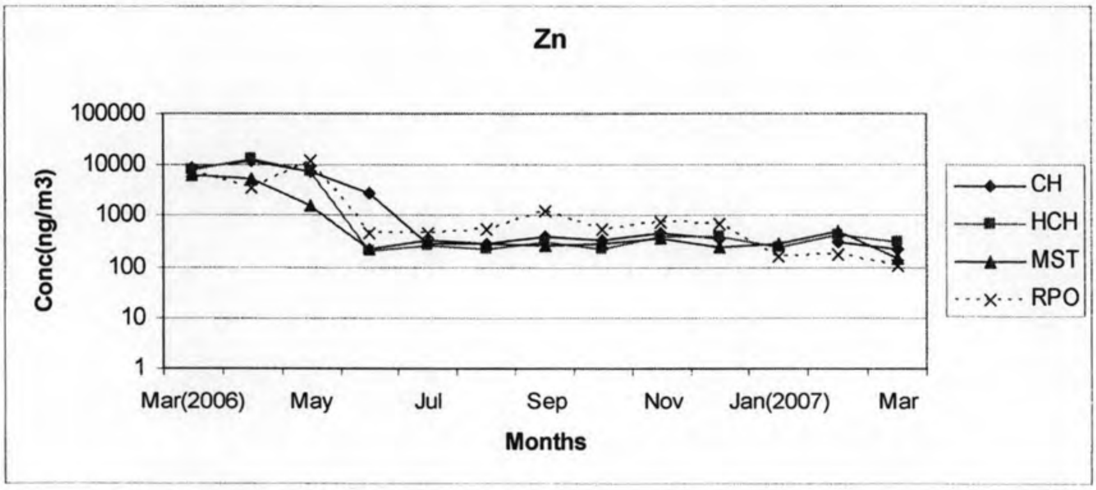


Figure 4.7 The monthly variations Concentrations of airborne trace metals and total suspended particles in air samples at the four stations on 12 sampling months **(continued).**

The average concentrations of weekend and weekdays were calculated from the data collected within the same period for each metallic element. The results are shown in Figure 4.8. Almost of the metal concentration in weekend and weekdays are not different at the CH site. The reasonable explanation for this phenomenon may be the site is located in dense areas which have many kinds of activities especially traffic activity at all days. The vehicles are crowded in the areas in both the weekend and weekdays for different purposes. The CH is situated in commercial area and also has many office buildings. People traveling to the workplace cause the high traffic congestion on the working days. On the weekend, these areas are crowded with people who traveling for their shopping purpose. This might be the reason of that why there is no significant difference between weekdays and weekend at the site. The significant different of Ni between weekday and weekend can be observed at HCH and RPO site. The previous study showed that Ni in the atmosphere can come from steels industry (Kumar *et al.*, 2001), oil combustion (Fang *et al.*, 2006), tailpipe emission from diesel engine (Lim *et al.*, 2007). At the weekday, the area of the HCH which is close to big market, school and resident houses, the MST which is close to big hospital and university campus, and the RPO which is industrial area are crowed by the diesel truck for transporting purpose. This might be the reason of that why there is significant difference of Ni between weekdays and weekend at the sites.

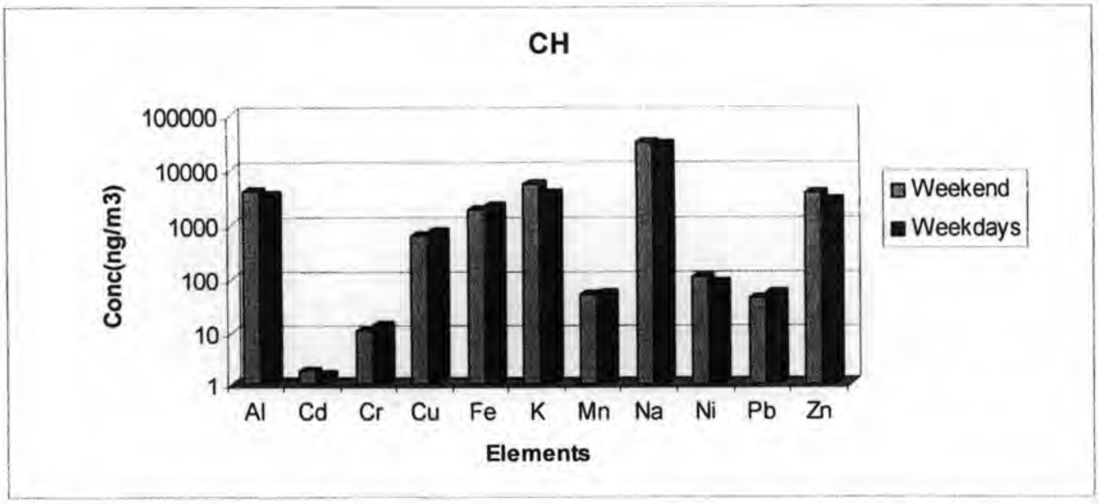
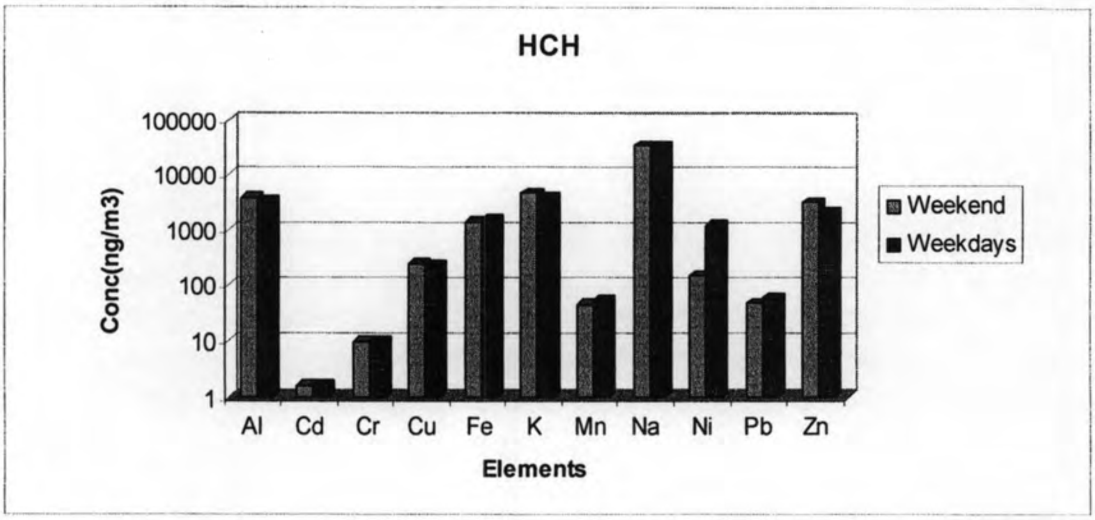
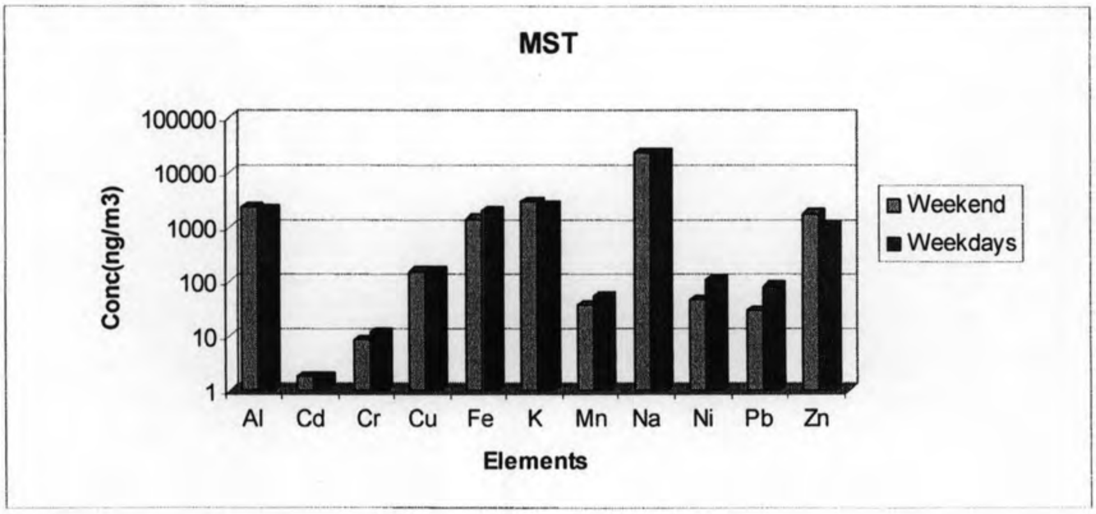


Figure 4.8 Comparison of trace element concentrations between weekend and weekdays.





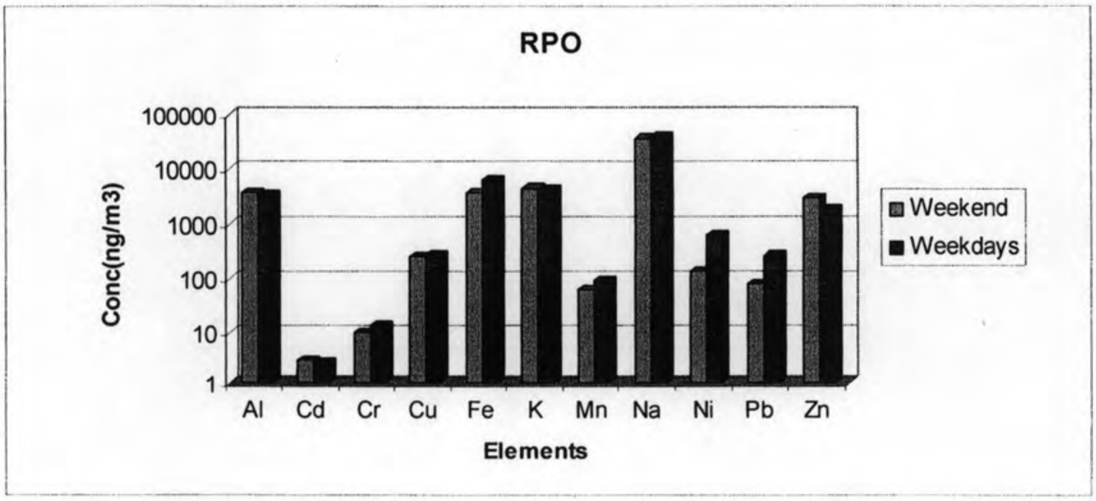


Figure 4.8 Comparison of trace element concentrations between weekend and weekdays **(continued).**

4.6 Enrichment factors and the sources of trace elements

Atmospheric concentrations of trace metals can vary significantly by their different origins. Nonetheless, the normalization of trace metals to crustal concentrations can be used to enable the "chemical character" of aerosol particles to be investigated effectively (Chester *et al.*, 2000). An enrichment factor (EF) can be defined to evaluate anomalies of specific chemical species of ambient aerosols, with respect to representative compositions of a reference material (e.g., average crust and sea water). The calculation of trace metal EFs in airborne particles, relative to soil or crustal abundances, has been used to evaluate anthropogenic versus natural sources (Veron *et al.*, 1992). EF of elements in particle was determined to assess the extent of non-crustal contributions to the elemental concentration levels (Wang *et al.*, 2006). Usually Si, Al or Fe is used as the reference element, but there is no universally accepted rule for its choice. In this study, Fe was used as a reference element as done by other investigators based on the earth's crustal mean abundances of the elements given by Taylor (1964) (Bilos *et al.*, 2001; Manoli *et al.*, 2002, Wang *et al.*, 2006).

The abundance of elements in the earth crust shown in Table 4.8 was taken from Taylor (1964). The EF of element E in aerosols is defined as below

$$EF = \frac{[E]_{TSP} \;/\; [R]_{TSP}}{[E]_{crust} \;/\; [R]_{crust}}$$

E = Element in particulate sample

R = Referent element of crustal material

Table 4.8 Abundance of chemical elements in the continental crust averages (Taylor, 1964).

Element	Crustal average
Al	8.23%
Cd	0.2 ppm
Cr	100 ppm
Cu	55 ppm
Fe	5.63%
K	2.09%
Mn	950 ppm
Na	2.36%
Ni	75 ppm
Pb	12.5 ppm
Zn	70 ppm

The results of EF really can provide useful evidence for the sources identification of the elements in aerosols, and avoid the coagulation problem by using individually detected elemental concentrations in total suspended particles (TSP). The EF close to unity suggests that the element is dominantly from crustal materials or the anthropogenic sources contribute only a minor fraction. The higher values than 10 may imply sources other than crustal dust. These sources include human activities (e.g., combustions, etc.) and other processes (e.g., forest fires, volcanic eruptions, sea salts, etc.). It should be noted that there is a potential problem to use enrichment factors for the sources of identification because the crustal composition of elements varies from one site to another, so is the possibility of fractionation during the process of soil-derived aerosols formation.

If EF approaches unity, crustal soils are most likely the predominant source of element. A conservative EF value of about 100 was chosen in this study as the criterion to indicate a significant proportion of a given element, which has a non-crustal source (Kim *et al.*,2002; Lopez *et al.*, 2005). In the other word, if EF is over 100, the element would have a significant contribution from anthropogenic sources. The concentrations and EF values of individual elements in TSP are presented in Table 4.9.

Table 4.9 Mean EF values of elements at sampling sites

Sites	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn
CH	1.23	197.15	3.48	366.92	1.00	5.99	1.54	37.04	30.49	114.14	1261.61
HCH	1.54	255.27	3.80	165.25	1.00	7.25	1.83	63.10	291.61	163.10	1054.28
MST	0.96	271.73	3.57	93.07	1.00	4.71	1.55	34.30	22.18	157.59	870.34
RPO	0.52	150.07	1.48	68.15	1.00	2.58	0.95	22.70	55.46	231.88	340.69

Figure 4.9 shows EF values of individual metals for all sampling sites. Overall, the EF patterns of metals in each site are quite similar except Ni. The EF value of Ni in HCH site is significantly different from others. The EF value of Cu at the CH site is slightly higher than those found in other sites.

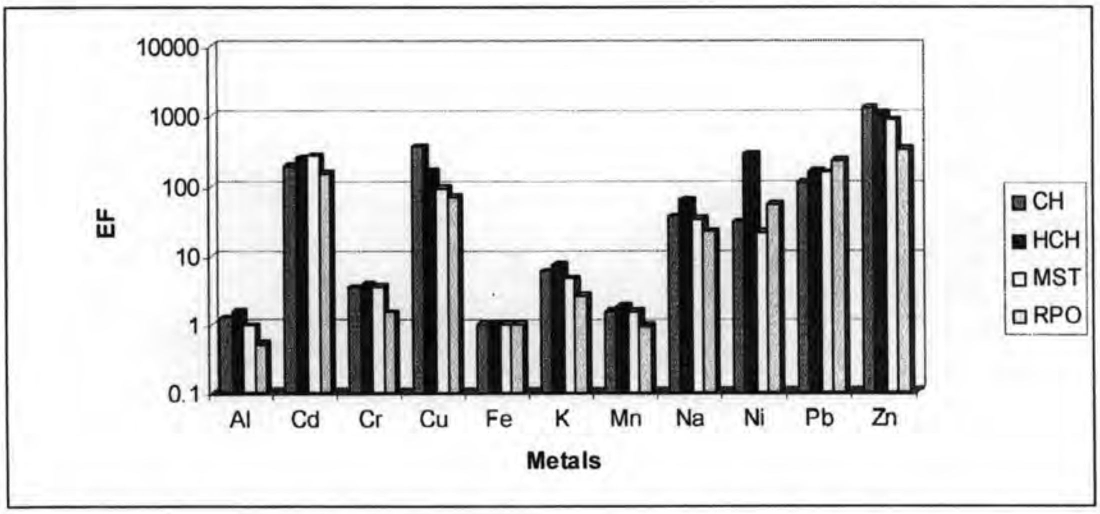


Figure 4.9 EF values for elements at all sampling sites using Fe as crustal reference.

The elements can be classified into three groups according to their EF values. The first group is elements with EF values lesser than 10 included Al, Cr, K, and Mn. These elements with their EF values indicate elements of crustal sources. The second group is the elements with intermediately enriched EF (EF values between 10 and 100) included Na, and Ni. The elements in this group also appear to be enrich even if to a lesser extend. It can be said that the elements in this group are from the combination of anthropogenic and natural sources. The last group is elements with EF values greater than 100 included Cd, Cu, Pb, and Zn. This group indicates obviously elements of anthropogenic sources.

On the basis of the EF values at the four sampling stations, TSP collected at the CH site appears as enriched in Cd, Cu, Pb, and Zn, whereas Al, Cr, K, and Mn are lower, compatible with prevailing natural sources. Zn shows the highest EF value at the CH (1261) and the lowest at the RPO (340). For Cu, the highest mean EF value is also found at the CH site and the lowest at the RPO. In the case of Cd, the EF found in the highest and lowest values are at the MST and the RPO, respectively. Pb with the highest value is found at the RPO, while the lowest is at the CH. The high EFs calculated for Pb, Zn, Cd and Cu indicate that they are presented in the airborne particles in concentrations too high to be explained in terms of normal crustal weathering processes (Bilos *et al.*, 2001). On a global basis, anthropogenic inputs of these elements predominate over natural sources accounting for 96%, 66%, 85% and 56% of the total emissions, respectively (Nriagu, 1989). Among these anthropogenic inputs, vehicle particle emissions are an important source (Bilos *et al.*, 2001). The previous study on high EF values of Pb, Zn, Cd and Cu using Fe as a reference element have also suggested the vehicular emissions source of these metals (Cadle *et al.*, 1997). The previous studies report that, the highly enriched elements are generally volatile elements, primarily emitted from high-temperature processes (e.g. fossil fuel combustion and smelting), and these elements are usually associated with small and medium sized aerosol particles and can be readily transported to remote areas (Wang *et al.*, 2005; Hedberg *et al.*, 2005). Cu and Zn are also reported to be derived from the metal industries especially smelters (Hedberg, *et al.*, 2005).

The intermediately enriched elements Na can be described to sea salt and the re-suspension of road dust and soil. Na is one of the most abundant components in sea salt (Begum *et al.*, 2004), paved road dust and soil (Samara *et al.*, 2003). Na itself can be attributed to refuse burning (Begum *et al.*, 2004), cement source and oil burning (Samara *et al.*, 2003). Ni is intermediately enriched elements found in the study and can be from oil combustion (Hedberg *et al.*, 2005). Less enriched elements included Al, Mn and K are from natural sources especially soil source (Begum *et al.*, 2004; Fang *et al.*, 2006). The soil factor is predominant source of the elements like Al, Mn in the study. K is mainly associated to a local wood burning source (Hedberg, 2005). The finding of these EF values shows that human activities have an influence on the airborne metal contents.

4.7 Correlation among elements and meteorological parameters

Pearson's correlation coefficients are obtained between metals measured in TSP aerosol at all four sampling sites. Meteorological parameters data in the study are available only at two sites, the HCH and the RPO monitoring sites. The statistical summary of the prevailing meteorological conditions during the study period are presented in Table 4.10. Airborne metal levels were also tested for correlation with meteorological parameters.

Table 4.10 Statistical summary of prevailing meteorological parameters during the study period

Sites		Temperature (^{o}C)	Wind Speed (m/s)	Relative Humidity (%)	Pressure (mmHg)
HCH	Mean	28.1	0.7	68.2	758.4
	Median	28.0	0.6	69.5	758.1
	SD	1.7	0.4	10.7	2.2
	Max	31.2	2.1	86.5	764.1
	Min	23.4	0.0	47.8	754.9
RPO	Mean	27.9	1.2	69.4	757.1
	Median	27.9	1.3	70.8	756.6
	SD	2.2	0.6	9.8	2.1
	Max	33.9	2.4	84.4	763.2
	Min	22.1	0.1	44.2	753.6

As shown in Table 4.11, low and medium correlation coefficients are mostly found between meteorological parameters and metals. Only RH-TSP, RH-Fe and RH-Mn at the HCH site have high negative correlation coefficients which r is greater than 0.7. There are found at values -0.75, -0.73 and -0.75, respectively. This can be implied that increasing of humidity will decrease the level of TSP, Fe and Mn in the ambient air at the HCH site.

High correlation coefficients of Al-K (r = 0.99), Fe-Mn (r = 0.94), K-Zn (r = 0.97), Al-Zn (r = 0.97), TSP-Fe (r = 0.93), and TSP-Mn (r = 0.95) are observed at the HCH sampling site. At the RPO sampling site, high correlation coefficients display on Al-K (r = 0.94), K-Zn (r = 0.92), Al-Zn (r = 0.83) and TSP-Mn (r =0.93). Table 4.12 illustrated the high Pearson's correlations of TSP-Fe (r = 0.92), TSP-Mn (r = 0.88), Al-K (r = 0.94), Al-Zn (r = 0.96), Fe-Cr (r = 0.72), Fe-Mn (r = 0.87), K-Zn (r = 0.94) at the CH site. These results indicate that the higher correlation coefficients with metallic elements in three sites might come from the same pollutant sources at the sampling period. While, the high Pearson's correlations of TSP-Cr (r = 0.78), TSP-Fe (r = 0.96), TSP-Mn (r = 0.95), Al-K (r = 0.88), Cr-Fe (r = 0.82), Cr-Mn (r = 0.72), Fe-Mn (r = 0.96) K-Zn (r = 0.91) are observed at the MST site. The high correlation of TSP-Mn, Fe-Mn, and K-Zn implies that there are from the same source, which is crustal soil source and biomass burning at all sampling site.

Table 4.11 Pearson's correlation matrix of TSP metallic elements and meteorological parameters measured at (a) HCH and (b) RPO sites

(a)	Temp.	WS	RH	P	TSP	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn
HCH																
Temp.(^{0}C)	1.00															
WS (m/s)	0.20	1.00														
RH (%)	0.09	**-0.45**	1.00													
P (mmHg)	-0.27	0.02	**-0.35**	1.00												
TSP	**-0.43**	0.05	**-0.75**	**0.52**	1.00											
Al	0.09	-0.10	**-0.42**	-0.19	0.33	1.00										
Cd	**-0.57**	0.21	**-0.63**	**0.70**	**0.64**	-0.05	1.00									
Cr	-0.04	-0.23	-0.35	0.19	**0.55**	**0.48**	0.11	1.00								
Cu	0.30	-0.24	-0.07	0.11	0.16	0.23	-0.17	**0.40**	1.00							
Fe	-0.30	0.11	**-0.73**	**0.45**	**0.93**	**0.50**	**0.61**	**0.66**	0.25	1.00						
K	0.04	-0.10	**-0.49**	-0.19	0.40	**0.99**	-0.01	**0.48**	0.18	**0.52**	1.00					
Mn	**-0.44**	0.15	**-0.75**	**0.51**	**0.95**	**0.36**	**0.70**	**0.52**	0.08	**0.94**	**0.41**	1.00				
Na	0.05	0.06	0.05	0.00	-0.10	**0.38**	0.02	0.20	0.00	0.10	0.28	0.05	1.00			
Ni	-0.30	0.07	**-0.37**	0.29	0.35	-0.02	**0.56**	0.16	-0.11	**0.38**	0.01	**0.46**	0.07	1.00		
Pb	-0.23	**0.45**	**-0.51**	0.28	**0.45**	-0.12	0.28	0.22	0.02	**0.37**	-0.06	**0.48**	-0.13	0.05	1.00	
Zn	0.15	-0.14	-0.34	-0.34	0.26	**0.97**	-0.20	**0.40**	0.19	**0.40**	**0.97**	0.26	0.22	-0.11	-0.15	1.00

Correlation is significant at the 0.05 level (2-tailed)

Table 4.11 Pearson's correlation matrix of TSP metallic elements and meteorological parameters measured at (a) HCH and (b) RPO sites **(continued).**

(b)	Temp.	WS	RH	P	TSP	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn
RPO																
Temp. (^{o}C)	1.00															
WS (m/s)	0.13	1.00														
RH (%)	-0.20	-0.13	1.00													
P (mmHg)	-0.18	-0.34	**-0.32**	1.00												
TSP	-0.10	**-0.55**	**-0.52**	**0.47**	1.00											
Al	-0.02	0.01	-0.05	0.43	0.24	1.00										
Cd	-0.30	**-0.47**	**-0.44**	**0.62**	**0.67**	0.17	1.00									
Cr	-0.19	**-0.67**	0.00	0.34	**0.67**	0.28	**0.53**	1.00								
Cu	0.19	-0.12	-0.20	0.42	0.27	-0.08	0.34	0.10	1.00							
Fe	0.09	-0.19	-0.08	0.02	**0.45**	0.27	0.24	0.36	-0.02	1.00						
K	0.17	-0.09	-0.16	**0.45**	0.31	**0.94**	0.14	0.25	-0.03	0.33	1.00					
Mn	-0.01	**-0.51**	**-0.47**	0.32	**0.93**	0.27	**0.64**	**0.61**	0.16	**0.66**	0.37	1.00				
Na	**-0.42**	-0.17	0.08	0.14	0.33	**0.42**	0.41	**0.56**	0.05	0.10	0.18	0.26	1.00			
Ni	-0.36	-0.26	**-0.45**	**0.54**	**0.73**	0.16	**0.62**	**0.40**	0.26	0.22	0.19	**0.57**	0.30	1.00		
Pb	0.23	-0.21	-0.13	0.04	0.16	-0.01	-0.04	0.29	0.04	-0.16	0.07	0.05	0.01	-0.07	1.00	
Zn	0.33	0.08	0.01	0.15	-0.01	**0.83**	-0.17	-0.02	-0.13	0.20	**0.92**	0.08	-0.11	-0.13	0.05	1.00

Correlation is significant at the 0.05 level (2-tailed)

Table 4.12 Pearson's correlation matrix of TSP metallic elements measured at (a) CH and (b) MST sites

(a) CH	TSP	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn
TSP	1.00											
Al	-0.05	1.00										
Cd	**0.61**	-0.14	1.00									
Cr	**0.63**	0.14	0.37	1.00								
Cu	0.00	0.10	0.12	0.14	1.00							
Fe	**0.92**	0.03	**0.68**	**0.72**	-0.03	1.00						
K	-0.13	**0.94**	-0.18	-0.01	0.14	-0.06	1.00					
Mn	**0.88**	-0.02	**0.66**	**0.49**	-0.05	**0.87**	-0.11	1.00				
Na	0.15	**0.59**	0.08	**0.44**	**0.51**	0.22	**0.54**	0.17	1.00			
Ni	0.27	-0.10	**0.66**	0.19	0.25	0.37	-0.12	0.24	0.15	1.00		
Pb	0.38	-0.24	0.20	0.12	-0.14	0.29	-0.25	**0.40**	-0.12	-0.10	1.00	
Zn	-0.20	**0.96**	-0.29	-0.03	0.07	-0.14	**0.94**	-0.19	**0.43**	-0.19	-0.27	1.00

(b) MST	TSP	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn
TSP	1.00											
Al	0.30	1.00										
Cd	**0.56**	0.09	1.00									
Cr	**0.78**	0.32	**0.49**	1.00								
Cu	**0.45**	0.12	**0.51**	**0.45**	1.00							
Fe	**0.96**	0.37	**0.62**	**0.82**	0.36	1.00						
K	0.10	**0.88**	-0.16	0.06	-0.01	0.12	1.00					
Mn	**0.95**	**0.42**	**0.56**	**0.72**	0.33	**0.96**	0.25	1.00				
Na	0.34	0.14	0.19	**0.41**	0.11	0.36	-0.25	0.22	1.00			
Ni	**0.58**	0.35	**0.46**	**0.50**	0.06	**0.69**	0.10	**0.65**	0.17	1.00		
Pb	0.20	0.02	-0.04	**0.40**	0.00	0.24	-0.06	0.20	0.31	-0.01	1.00	
Zn	-0.29	**0.69**	**-0.41**	-0.23	-0.14	-0.27	**0.91**	-0.15	**-0.43**	-0.13	-0.13	1.00

Correlation is significant at the 0.05 level (2-tailed)

4.8 Principal component analysis

The multivariate methods of analysis are commonly used to identify the combined effect of several measured variables and the influence of external parameters on the selected metal distribution. Principal component analysis (PCA) is the most common multivariate statistical method used in environmental studies. PCA is considered as a useful tool for determining the relationships among the variables and for revealing groups within the data (Shah *et al.*, 2006). It reduces data set and extracts a small number of latent factors for analyzing relationships among the variables.

The statistical program, SPSS is used for varimax rotated factor analysis in the present study. The eleven trace metals at each site are considered as variables for factor analysis. Only the factors with cumulative percentage variance higher than 70% and the eigenvalue greater than one were selected. Due to the different magnitudes of elemental concentrations for each element, these were normalized taking zero as the mean value and unity as standard deviation. From this set of normalized concentrations, eigenvalues and eigenvectors of the correlation matrix were extracted and the result is truncated into a few factors (Mouli *et al.*, 2006). Varimax rotation is applied to the factor-loading matrix and the final factors should be related to the sources, which yielded three or four factors and the results including variance percentage associated with each factor are shown in Table 4.13. The results revealed that three and four factors explain the main part of the data variance.

At the HCH sampling site, the results show three possible factors representing three different contributing sources for airborne elements. Factor 1 explains 37.8% of the total variance of the data and has high loading for Al (0.981), K (0.964) and Zn (0.955), which can be identified as soil and/or road dust, construction, vehicle, and biomass burning. Particulate Zn in ambient air may have its origin from automobile sources (Karar *et al.*, 2006). Zn and K can be also found in biomass burning (Gaudichet *et al.*, 1995; Fang *et al.*, 2006). Soil, re-suspended dust, and construction may be the possible sources of Al, Fe, Mn (Fang *et al.*, 2006; Kumar *et al.*, 2001). Factor 2 is relative to vehicular emission, oil combustion and construction with high loading of Cd (0.899), Mn (0.853), Fe (0.755), Ni (0.748), and 25.4% variance of data set. The presence of Mn and Pb suggests the influence of vehicular traffic. Manganese has been used as an additive to enhance automobile performance. The manganese tricarbonyl compounds constitute the group of organomanganese compounds of toxicological significance. These manganese tricarbonyl compounds are used as an additive in unleaded petrol (Karar *et al.*, 2006). Cu can be found primarily in the fine fraction of biomass burning emission and also found in vehicular emission (Gaudichet *et al.*, 1995). Even though phasing out of leaded gasoline measurement had been introduced to Thailand since 1991 and direct emission of Pb from vehicular exhaust has decreased for many years, Pb is still persistent in from earlier vehicular exhaust emissions because of its longer residence time in the environment (Karar *et al.*, 2006). Pb can also be emitted from an incinerator (Fang *et al.*, 2006). Considering the high load of Pb (0.665), Cu (0.626) and 12.6% variance in the Factor 3, it represents sources from vehicular emission and incineration.

At the RPO sampling site, 36.3% of the total variance of the data is observed in Factor 1. High loading of Zn (0.967), K (0.961), and Al (0.932) indicates that the contributing sources in Factor 1 of the RPO are similar to the Factor 1 of the HCH site. Factor 2 has 23.7 % variance and high loading of Na (0.904) which can be implied that it is influenced by sea salt. The loading of Cr (0.775), Cd (0.612) represents the vehicular emission and industry. Factor 3 is relative to construction, vehicular emission, and industry with high loading of Mn (0.776), Fe (0.704), Cu (0.701), Ni (0.603), and 11.8% variance. Leaded gasoline has been banned in Thailand since 1996 and therefore lead would not be a good indicator for vehicle emission in Bangkok atmosphere. Thus, high loading of Pb (0.919), and 9.6 % variance in Factor 4 should indicate the industry sources.

At the CH sampling site, the results show three factors. Factor 1 explains 34.2% of the total variance of the data and has high loading for Al (0.981), K (0.946), Zn (0.952) and Na (0.664) which can be identified as soil and/or road dust, vehicle emission, construction, biomass burning and sea salt. Particulate Zn in ambient air may be from non-catalyst automobile exhaust, lubricating oil used in two-stroke engine where engine oil is mixed with fuel. The combustion process in a two-stroke engine is such that significant quantity of unburned fuel is released along with lube oil. Zn is normally used as additive in this kind of lube oil (Begum *et al.*, 2004). Zn is also found in tire wear (Watson *et al.*, 2001) and domestic heating emissions from galvanized parts of heating appliances (Chow *et al.*, 1992). The factor characterized by high Al, Mg, Si, Ca and mixed with K, Fe, Mn, Zn could be represented by metal smelting source (Begum *et al.*, 2004). The high loading of Na which can be implied that it is influenced by sea salt and road dust (Samara *et al.*, 2003). Factor 2 is relative to vehicular emission, oil combustion and construction with high loading of Fe (0.963), Mn (0.910), Cr (0.743), Cd (0.739) and 30.3% variance of data set. Considering the high load of Cu (0.806) and 11.7% variance in the Factor 3, it represents source from vehicular emission according to Fang *et al.*(2006).

At the MST sampling site, 38.4% of the total variance of the data is observed in Factor 1. High loading of Ni (0.902), Fe (0.896), Mn (0.871), Cr (0.641) and Cd (0.627) indicates that the contributing sources in Factor 1 of the MST are similar to the Factor 2 of the HCH site. The possible sources of this factor are vehicular emission, oil combustion and construction. Factor 2 of MST has 25.7 % variance and high loadings of K (0.982), Zn (0.923), Al (0.876) which are closely similar to Factor 1 of HCH site. It can be implied that the factor is influenced by soil or road dust, construction, vehicular emission, and biomass burning. Factor 3 is relative to incineration and sea salt with high loading of Pb (0.880), Na (0.641) and 11.6% variance. Factor 4 is high loading of Cu (0.956), and 9.1 % variance should indicate the vehicular emission sources.

This study gets along with the previous study on the identification and the contribution of TSP major sources in Bangkok Metropolitan Area using chemical mass balance conducted by Suwanthanee (2002). The former study revealed that diesel and motorcycle emission, and biomass burning were important sources at all sampling stations. Moreover, the study was also found that marine aerosol was the minor source. The present study has also confirmed that traffic emission, soil/dust re-suspension and biomass burning are influences on the air particulate in Bangkok atmosphere.

Even though PCA is one of the most effective tool and very popular in source apportionment research, it is still difficult to ensure the exact sources without having any specific source results obtained in the vicinity of the study area.

Table 4.13 Rotated component matrix for the data of the metallic element composition at the HCH, RPO, CH and MST sites (factor loadings < 0.2 are omitted)

Elements	HCH			RPO			
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4
Al	**0.981**	-	-	**0.932**	0.320	-	-
Cd	-	**0.899**	-	-	**0.612**	0.547	-
Cr	0.573	0.298	0.471	-	**0.775**	0.321	0.328
Cu	0.395	-	**0.626**	-	-	**0.701**	0.372
Fe	0.483	**0.755**	0.373	0.314	-	**0.704**	-
K	**0.964**	-	-	**0.961**	-	-	-
Mn	0.286	**0.853**	0.336	-	0.481	**0.776**	-
Na	0.349	-	-	-	**0.904**	-	-
Ni	-	**0.748**	-	-	0.523	**0.603**	-
Pb	-	0.334	**0.665**	-	-	-	**0.919**
Zn	**0.955**	-	-	**0.967**	-0.200	-	-
Eigenvalue	4.163	2.795	1.382	3.991	2.607	1.298	1.058
Variance(%)	37.843	25.410	12.564	36.281	23.702	11.797	9.616
Cumulation(%)	37.843	63.253	75.816	36.281	59.983	71.781	81.397

Elements	CH			MST			
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4
Al	**0.981**	-	-	-	**0.876**	-	-
Cd	-	**0.739**	-	**0.627**	-	-	0.550
Cr	-	**0.743**	-	**0.641**	-	0.505	0.396
Cu	-	-	**0.806**	-	-	-	**0.956**
Fe	-	**0.963**	-	**0.896**	-	0.269	0.254
K	**0.946**	-	-	-	**0.982**	-	-
Mn	-	**0.910**	-	**0.871**	-	-	0.224
Na	**0.664**	0.245	0.542	-	-	**0.641**	-
Ni	-	0.448	0.588	**0.902**	-	-	-
Pb	-	0.454	-	-	-	**0.880**	-
Zn	**0.952**	-	-	-	**0.923**	-	-
Eigenvalue	3.764	3.331	1.283	4.224	2.825	1.278	1.001
Variance(%)	34.214	30.278	11.662	38.399	25.682	11.622	9.101
Cumulation(%)	34.214	64.492	76.154	38.399	64.081	75.703	84.805

A three dimension plot of the PCA loadings in all sampling sites are presented in Figure 4.10 and the relationships among the metals are also illustrated. In the three dimension plot at the HCH site, Cd, Fe and Mn are strongly correlated, considered on the short distance of metals. All four sites, there are high correlation among Al, K and Zn which can be implied that there are the same sources of these elements at all sampling sites.

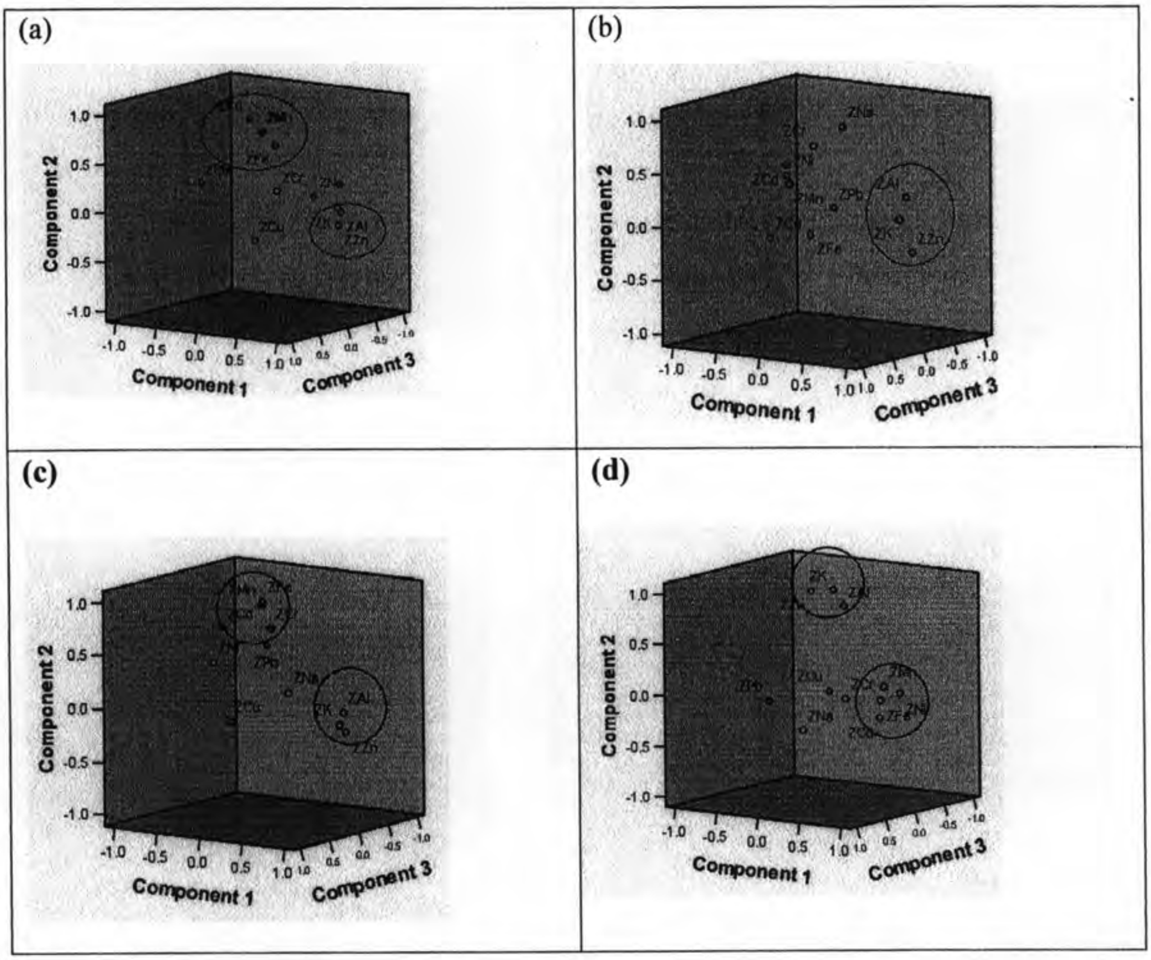


Figure 4.10 PCA loading three dimension plot for eleven heavy metals (a) HCH and (b) RPO (c) CH and (d) MST

4.9 Comparison with other studies

The trace element concentrations (ng/m^3) in comparison for ambient air particulates at several locations are shown in Table 4.13. Fe is found as the most abundant element in the previous studies. The highest concentration of Fe is 265,500 ng/m^3 found at the Mumbai traffic junction sampling sites. Al is the second highest metal concentration showed in Table 4.13. The Al concentration found in the Mumbai traffic junction is 58,000 ng/m^3, while the Al in the present study is only about 3,512.4 ng/m^3 or 16 times lesser than those of the Mumbai sampling site (Kumar *et al.*, 2001). The range of average concentration of Cd measured in the study is from 1.6 to 2.7 ng/m^3. The amount of Cd found in present study is similar to the concentrations found in Dhaka, Islamabad, and Seoul (Salam *et al.*, 2003; Shah *et al.*, 2006; Kim *et al.*, 2004). Concentration of Cr in the study is slightly different to Bursa (Tasdemir *et al.*, 2006). The highest concentration of Cu is collected in Tartous, Damascus (4,283 ng/m^3), which is 6 times greater than the CH site (Al-Masri, 2006). Cu in the Thailand study is slightly higher than those in Taichung, Taiwan (ranging 198.6-218.8 ng/m^3) (Fang *et al.*, 2003; Fang *et al.*, 2004).

The highest concentration of K found at Gandhinagar, Mumbai in India is 5,140 ng/m^3 while the highest concentration of K found in the study at Ratburana is 4,452.7 ng/m^3. The highest concentration of Mn is measured (average 1,470 ng/m^3) at Gandhinagar, Mumbai in India. In Thailand study, average concentrations of Mn ranged from 49.0 to 81.7 ng/m^3 and these values are enormously lower than at Gandhinagar, Mumbai in India (average 1470 ng/m^3) (Kumar *et al.*, 2001). The range of average concentration of Ni measured in the study is from 88.1 to 929.4 ng/m^3. The amount of Ni found in the present study is the highest comparing with those in other places. The highest concentration of Pb is also measured in Mumbai, India (ranging 820–1,060 ng/m^3) meanwhile average concentrations of Pb in the present study is 5-16 times lesser than those (Kumar *et al.*, 2001).

Even though the concentration of Ni in this study is the highest comparing with others, there are two more elements found in the present study (Na and Zn) which are in the highest rank when compared with other studies. The average amount of Na found in the present study is about 31 times higher than those of Dhaka (Salam *et al.*, 2003). The highest concentration Zn are in the range of 1,310.2 -2,933.8 ng/m^3. It is about 3 times higher than Zn levels found in Taiwan (Fang *et al.*, 2004).

Table 4.13 Comparison of heavy metal concentrations (ng/m^3) in total suspended particulate in the world

Country	Sampling site	Character	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn	Reference
Spain	Seville	Urban	-	-	-	26.7	654.0	-	16.5	-	-	63.7	-	Espinosa *et al*, 2001
Italy	Tito Scalo	Industrial	-	-	-	58.0	521.0	-	27.0	-	-	60.0	304.0	Ragosta *et al.*, 2002
Pakistan	Islamabad	Urban	-	2	42	-	930	-	57	-	9	210	542	Shah *et al.*, 2006
India	Sakinaka, Mumbai	Traffic junction	56100	-	150	370	165500	2490	850	20700	160	1060	-	Kumar *et al.*, 2001
	Gandhinagar, Mumbai	Traffic junction	58000	-	50	1550	265500	5140	1470	18200	100	820	-	
Taiwan	Taichung	Traffic	-	-	-	-	4420.0	-	-	-	-	44.0	209.0	Fang *et al.*, 2002
	Taichung	Rural	-	-	-	-	2700.0	-	-	-	-	39.0	105.0	Fang *et al.*, 2002
	Taichung	Farm	-	-	-	198.6	1182.6	-	83.7	-	-	573.6	395.3	Fang *et al.*, 2003
	Taichung	Suburban	-	-	-	218.8	2848.9	-	85.6	-	-	299.4	1165.7	Fang *et al.*, 2004
Japan	Sapporo	Urban city	-	-	2.61	20.9	625	-	16.8	-	3.81	43.9	149	Fang *et al.*, 2005
	Tokyo	Urban city	-	-	6.09	30.2	677	-	40.1	-	5.63	125	299	
Vietnam	Ho Chi Minh	Urban	-	-	-	-	2904	-	-	-	-	146	203	Hien *et al.*, 2001

Table 4.13 Comparison of heavy metal concentrations (ng/m^3) in total suspended particulate in the world **(continued).**

Country	Sampling site	Character	Al	Cd	Cr	Cu	Fe	K	Mn	Na	Ni	Pb	Zn	Reference
Korea	Taejon	Industrial	-	-	31.8	54.9	1839	-	66.1	-	33.6	260	220	Kim *et al.*, 2002
	Seoul	-	-	3.1	15	208	2397	-	79.7	-	19	77	-	Kim *et al.*, 2004
UK	Brownfields	Rural	-	0.6	-	-	260	-	6	-	2	30	63	Allen *et al.*, 2001
	Birmingham	Roadside	-	0.5	-	-	204	-	6	-	-	27	30	Harrison *et al.*, 2003
Bangladesh	Dhaka	Urban	-	2.5	-	-	24800	1550	-	1270	-	279	801	Salam *et al.*, 2003
Argentina	La Plata	Urban	-	0.41	4.32	-	1183	-	26	-	3.15	64.5	273	Bilos *et al.*, 2001
Brazil	Santa Cruz	Industrial	5770	1	421	335	38903	-	1216	-	-	101	2120	Quiterio *et al.*, 2004
China	Beijing	Urban	-	-	-	-	51000	-	1210	-	51	46	274	Mori *et al.*, 2003
Turkey	Bursa	Urban	-	0.7	10.7	396.6	2165.4	-	51.1	-	5.1	77.2	250.5	Tasdemir *et al.*, 2006
Damascus	Tartous	Traffic	-	-	-	4283	-	-	-	-	-	193	133	Al-Masri *et al.*, 2006
	Darya	Industrial	-	-	-	2504	-	-	-	-	-	284	134	
Thailand (Present study)	**CH**	Commercial	3512.4	1.6	12.6	704.0	2061.0	4251.7	53.8	30357.5	92.8	51.1	2933.8	
	HCH	Residential	3463.6	1.6	9.5	227.5	1527.8	4219.1	49.0	34939.8	929.4	53.5	2463.9	
	MST	Traffic	2171.5	1.8	10.7	147.1	1824.9	2613.9	49.3	22762.7	88.1	67.3	1310.2	
	RPO	Industrial	3510.3	2.7	12.0	263.1	5578.6	4452.7	81.7	39911.9	461.9	197.4	2186.7	