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PM_{10} Metal Distribution in an Industrialized City

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The dense population in Taiwan leads to high level of suspended particulate pollution, which represents serious problem. This problem is particularly acute in the highly industrialized and densely populated cities of Kaohsiung in southern Taiwan. In this area, the percentage of days with PSI (Pollutant standards index) over 100 was highest in Taiwan. Anthropogenic contribution became more evidence as the dominant source of many pollutants including most metal species (Nriagu, 1989). The results of Michellozzi et al. (1998) have indicated that the mass concentrations of some particulate pollutants vary according to seasons. However, the spatial and temporal distribution of metal elements adsorbed in aerosols is still incomplete in Taiwan. According to Antonio et al. (2001), metal-loaded particles pose a latent risk to public health. In this study, 110 samples taken in 2002/2003 at five sampling sites (A, B, C, D and E) in Kaohsiung county, were divided into summer, autumn, winter and spring samples and analyzed for metal elements.

MATERIALS AND METHODS

Five sites (A, B, C, D, and E) located in Kaohsiung county of southern Taiwan were selected in this study. The sampling sites were in proximity to the air quality monitoring stations of the environmental protection agency of Taiwan (EPA). The samples were taken simultaneously by PEM-PM_{10} (MSP) and Harvard samplers (Air Diagnostics and Engineering). Each sample was collected continuously on three consecutive days for 24 hours from September 2002 to August 2003. The filters were digested following the procedure of NIEA A301.11C, which is the EPA reference method in Taiwan, and metal elements were quantified by ICP-MS (Agilent 7500). Additionally, nonparametric correlations and the median test analysis for all 110 samples were analyzed using SPSS 13.0 software.

RESULTS AND DISCUSSION

The average metal element mass concentrations in ambient air at the five sampling sites over the entire measurement period are shown in Fig 1 for

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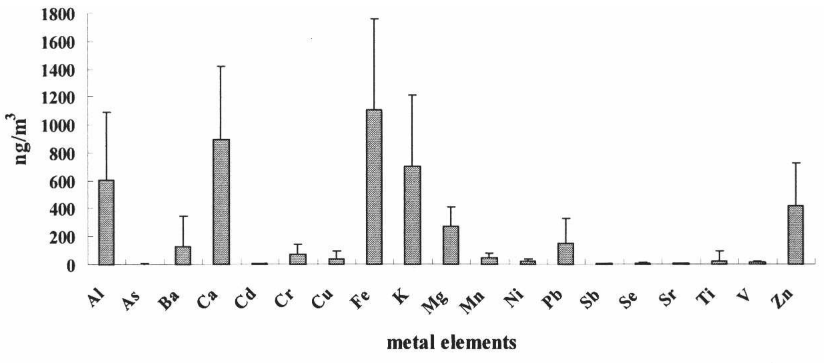

Figure 1. The average mass concentration (mean ± standard deviation) of metal elements in ambient air and measured on PM_{10} particles (n=110) at the five sampling sites over the periods September 2002 to August 2003.

particles smaller than 10μm (PM_{10}). The metal elements were classified into anthropogenic (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr, Ti, V and Zn) and crust (Al, Ca, Fe, K and Mg) groups according to Wang, et al. (2003). The highest concentrations were found in crust elements such as: Fe, Ca, K, Al and Mg (1108, 897, 700, 609 and 275 $ng.m^{-3}$), respectively, and three anthropogenic elements, Zn, Pb and Ba (418, 156 and 127 $ng.m^{-3}$). Fe, Ca, K, Al, Mg, Zn, Pb and Ba account for 24.5%, 19.8%, 15.5%, 13.4%, 6.07%, 9.22%, 3.43% and 2.80% of total metal elements mass concentrations, respectively. Arsenic was found to have the lowest of the 20 investigated metal element mass concentrations with a mean value of 3.54 $ng.m^{-3}$. The mass concentration of Pb of 156 $ng.m^{-3}$ is similar to the result of Vasconcelos and Tavares (1998) (145~505 $ng.m^{-3}$, sampling site near an old incinerator and a busy street) and Kim, et al. (2003) (120 $ng.m^{-3}$ for non-Asian Dust period in a moderately developed urban area), however, it is higher than the results of Beceiro-Gonzalez, et al. (1997) and Bilos, et al. (2001) (27 and 10 $ng.m^{-3}$, in a moderately polluted to unpolluted area).

Aluminum, iron and calcium are the most common metal elements formed in earth's crust (Taylor, 1964). The pattern for enrichment factor (EF) is a reference value of contamination status (Kim, et al.2002). The EF will provide information to judge either the enrichment (or depletion) of a given element relative to the reference element (Al, in this study). The EF was defined as follows: $EF = \{X/Al\}_{sample}/\{X/Al\}_{crust}$ (X denotes a metal of interest). The EF values were grouped into three categories: (1) <10, Al, Ca, Fe, K, Mg, Mn, Sr, Ti and V, (2) 10~1000, As, Ba, Cr, Cu, Ni, and Zn,

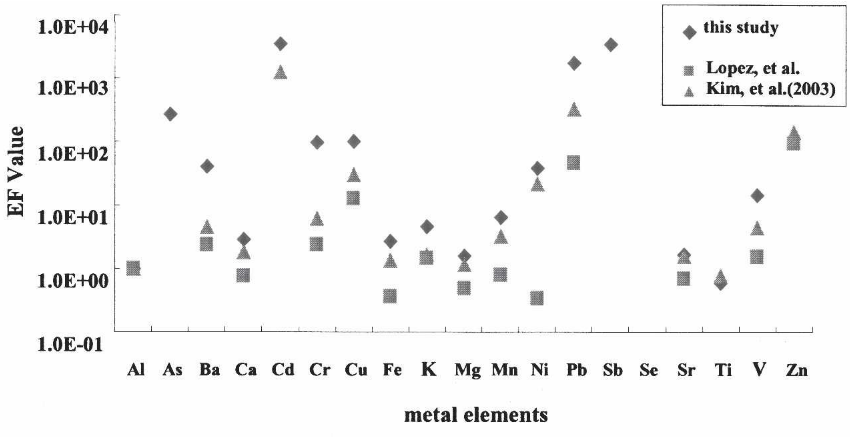

Figure 2. The enrichment factor (EF) ratio for each metal element.

(3) >1000, Cd, Pb, Sb and Se. Additionally, the EF for the 20 analyzed metal elements for various studies is shown in Figure 2.

All the metal elements for EF were higher in this study than the EF calculated for the same elements by Lopez et al. (2005) and Kim et al. (2003). According to Lopez et al. (2005), the sampling site was located near a heavy traffic motorway and several industrial areas in which paper, steel transforming and sugar-processing industries are placed. Furthermore, the sampling site in Kim's study (2003) was located on the NE sector of Seoul, a moderately developed urban area. The highly polluted atmosphere in Kaohsiung county requires attention since it is a great concern on the residents exposure to these metals inducing the adverse health effects in this area.

Table 1 gives the spearman's correlation coefficients among metals. There are 119 pairs of metals which showed a spearman's correlation coefficients with a level significance lower than 0.05. Significant Spearman's correlation coefficients among metals were found in most of metals. The highest coefficient in 19 metals was found between Sr and Sb with r = 0.712 and $p<0.01$. The element of Mn were correlated the best (r = -0.094~ 0.637) with the individual metal. Furthermore, the most toxic element of As had a significant association (r = -0.293~0.675) with other metals except for Ca, Cu, Ni, and Ti.

The seasonal variability of metal distributions is shown in Figure 3. The result indicates that the concentrations of most metal elements tend to peak in either autumn or winter except for Ba, Cu, K, Ni and V. The mean PM_{10} concentration of the autumn and winter samples is significantly higher than those of the spring and summer samples, particularly for As, Ca, Cd, Cu, Cr, Fe, K, Mn, Pb, Se, Sb, Sr, Ti, and V (Table 2). The strong winds of autumn and winter decrease the chances of wet deposition removal.

Table 1. Spearman's coefficients correlation among metals analyzed by statistical approaches.

	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	Pb	Sb	Se	Sr	Ti	V	Zn
Al	1																		
As	0.329**	1																	
Ba	0.364**	0.239*	1																
Ca	-0.044	0.167	-0.086	1															
Cd	0.192*	0.199*	-0.073	0.107	1														
Cr	0.149	-0.293**	0.135	-0.233*	-0.005	1													
Cu	0.053	0.013	0.092	0.329**	0.256**	-0.099	1												
Fe	0.600*	0.540**	0.401**	0.190*	0.052	0.110	0.223*	1											
K	0.447*	0.399**	0.301**	0.245**	0.199*	-0.216*	0.255**	0.508**	1										
Mg	0.093	0.252**	0.045	0.525**	0.006	-0.238*	0.171	0.258**	0.445**	1									
Mn	0.265**	0.486**	0.197*	0.403**	0.355**	-0.094	0.362**	0.550**	0.512**	0.431**	1								
Ni	0.145	0.049	-0.042	0.307**	0.260**	0.137	0.284**	0.229*	0.287**	0.345**	0.537**	1							
Pb	0.224*	0.475**	-0.019	0.245**	0.617**	-0.118	0.316**	0.356**	0.457**	0.355**	0.562**	0.336**	1						
Sb	0.236*	0.611**	0.143	0.303**	0.276**	-0.260**	0.355**	0.485**	0.464**	0.239*	0.637**	0.315**	0.537**	1					
Se	0.236*	0.603**	0.238*	0.260**	0.244*	-0.026	0.228*	0.490**	0.271**	0.263**	0.462**	0.176	0.377**	0.647**	1				
Sr	0.358**	0.675**	0.231*	0.208*	0.142	-0.146	0.108	0.590**	0.401**	0.320**	0.548**	0.273**	0.465**	0.712**	0.687**	1			
Ti	0.473**	0.147	0.289**	-0.457**	-0.076	0.227*	-0.208*	0.311**	0.152	-0.229*	-0.085	-0.123	-0.039	-0.137	-0.162	-0.027	1		
V	0.149	-0.244*	0.018	0.269**	0.315**	0.239*	0.350**	0.069	0.042	0.119	0.191*	0.310**	-0.004	0.005	0.181	-0.136	-0.208*	1	
Zn	0.141	0.282**	0.256**	0.366**	0.342**	-0.286**	0.472**	0.275**	0.497**	0.370**	0.587**	0.479**	0.507**	0.436**	0.191*	0.353**	-0.035	0.118	1

**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed).

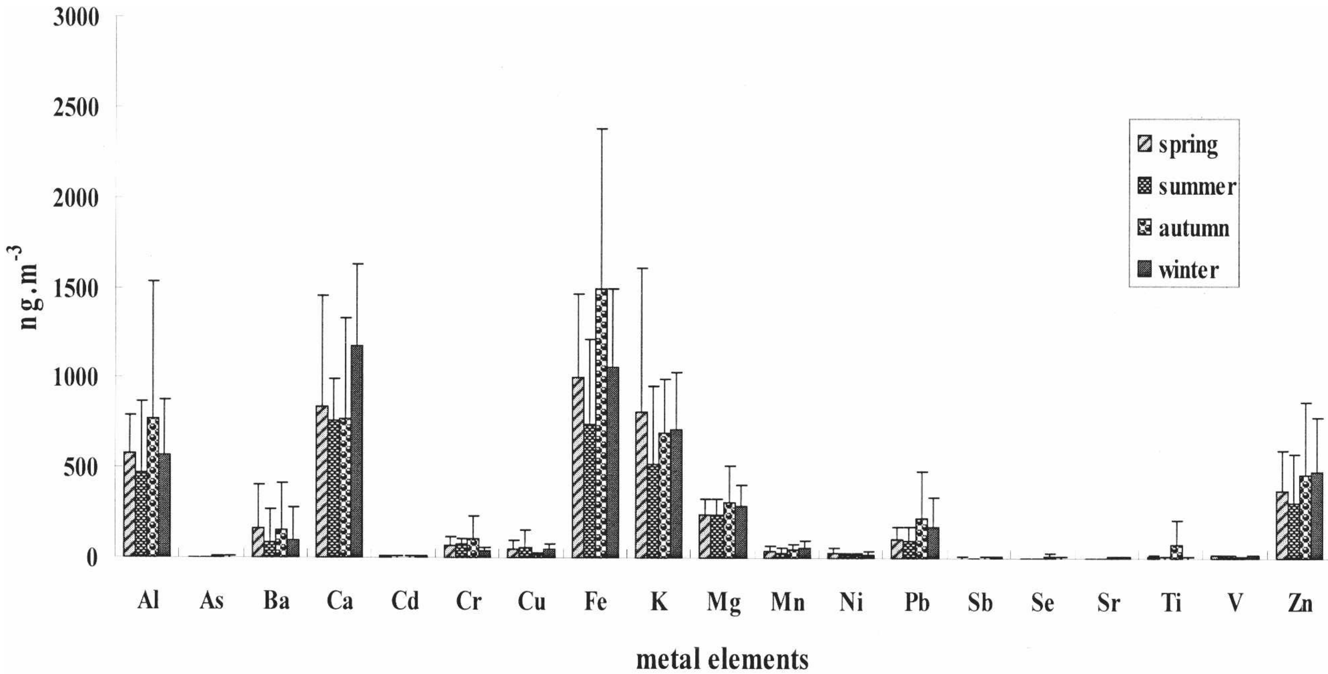

Figure 3. The average concentration of metal elements of PM_{10} particles during various seasons.

Table 2. Results of median test.

Seasons	Spring (n=30)	Summer (n=20)	Autumn (n=30)	Winter (n=30)	p [a] Value
Al [b]	578 ± 208 [c]	469 ± 398	773 ± 758	570 ± 307	0.057
As	2.60 ± 1.56	0.472 ± 0.312	6.43 ± 4.84	3.62 ± 1.28	<0.001***
Ba	159 ± 243	83.9 ± 188	155 ± 259	94.1 ± 183	0.133
Ca	835 ± 619	765 ± 230	772 ± 555	1170 ± 453	<0.001***
Cd	5.14 ± 3.55	4.56 ± 6.64	3.39 ± 4.22	6.95 ± 6.66	<0.001***
Cu	25.1 ± 30.3	18.7 ± 9.79	15.9 ± 11.0	22.4 ± 16.2	<0.001***
Cr	64.6 ± 55.9	81.4 ± 25.2	104 ± 126	42.1 ± 19.2	<0.001***
Fe	1010 ± 455	743 ± 468	1500 ± 890	1070 ± 427	0.001**
K	813 ± 795	520 ± 434	694 ± 302	714 ± 317	0.002**
Mg	245 ± 85.6	246 ± 82.9	309 ± 200	291 ± 111	0.706
Mn	40.4 ± 23.1	30.3 ± 26.1	45.8 ± 34.7	58.7 ± 35.3	0.007**
Ni	25.1 ± 30.3	18.7 ± 9.79	15.9 ± 11.0	22.4 ± 16.2	0.254
Pb	110 ± 62.9	95.9 ± 76.9	222 ± 261	175 ± 167	0.002**
Se	2.77 ± 0.822	1.43 ± 0.324	9.73 ± 16.9	4.80 ± 2.12	<0.001***
Sb	3.79 ± 2.07	1.50 ± 0.826	4.70 ± 2.56	8.87 ± 5.20	<0.001***
Sr	2.78 ± 0.812	1.45 ± 0.318	5.79 ± 2.96	7.32 ± 5.15	<0.001***
Ti	11.7 ± 8.21	4.52 ± 3.22	73.6 ± 135	2.52 ± 2.45	<0.001***
V	18.1 ± 4.85	17.0 ± 3.26	6.07 ± 3.98	16.3 ± 6.85	<0.001***
Zn	380 ± 216	313 ± 269	463 ± 403	481 ± 304	0.083

[a] Median test, [b] Unit : ng/m^3, [c] Mean ± standard deviation
* p<0.05, ** p<0.005, *** p<0.001

Furthermore, autumn is the harvest season for farmers, who often burn the straw after harvesting. The variation of seasonal concentration was from the lowest, As (0.47 ng.m^{-3}) in summer, to the highest, Fe (1497 ng.m^{-3}) in autumn. The ratio of the highest to the lowest seasonal mass concentration of the analyzed metals was classified into three categories: (1) <5.0: Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, V and Zn (2) 5.0~10.0: Sb, Se and Sr (3) > 10: As (13.6) and Ti (29.2). The high variability of As mass concentration needs further investigation because it is harmful for human health. Yatin et al. (2000) indicated the As easily attaches to fine particles, which accumulate in the alveolei and thus cause adverse health effect to humans. The meteorological parameters play an important role in the distribution of metal elements during their transportation process (Kim et al., 2002). The air pollutants of metals in our sampling sites may be from the highly polluted factories in the industrial area located in Kaohsiung city due to seasonal and sea wind. It is concerned on public health of residents living in Kaohsiung Areas, further studies are needed to forcus on the long-term monitoring of arsenic concentrations in the fine particulate in the atmosphere.

Episodes of higher concentration of metal elements in autumn and winter were found in this study. The seasonality pattern showed the possible relationship with higher occurrences of asthma and respiratory diseases in Taiwan. To learn more about the health effect in an industrialized area, further studies are necessary to investigate the metal elements on $PM_{2.5}$ and the relationship between particulate mass concentration and respiratory diseases.

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