THE DISTRIBUTION CHARACTERISTICS OF TRACE ELEMENTS IN AIRBORNE PARTICULATES FROM AN URBAN INDUSTRIAL COMPLEX AREA OF KOREA USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

JONG-MYOUNG LIM, JIN-HONG LEE* and YONG-SAM CHUNG[1]
Chungnam National University,
220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea
[1]Korea Atomic Energy Research Institute
150 Deokjin-dong, Yuseong-gu, Daejeon 305-353, Korea
*Corresponding author. E-mail : jinlee@cnu.ac.kr

An instrumental neutron activation analysis was used to measure the concentrations of about 24 elements associated with airborne particulates (PM10) that were collected in the most polluted urban region of Daejeon city, Korea from 2000 to 2002. Using the measurement data for various elements, both the extent of elemental pollution in the study area and the seasonality in their distribution characteristics were examined. Examinations of their distribution patterns indicated that most elements with crustal origin tend to exhibit seasonal peaks during spring, while most elements with anthropogenic origin tend to exhibit seasonal peaks during fall or winter. In order to explain the factors regulating their mobilization properties, the data were processed by a factor analysis. Results of the factor analysis suggested competing roles of both industrial and natural source processes, despite that the study site is located at a downwind position of the industrial complex. Based on the overall results of this study, it is concluded that the site may be strongly impacted by man-made sources but the general patterns of elemental distributions in the study area inspected over a seasonal scale are quite consistent with those typically observed from natural environment.

KEYWORDS : Instrumental Neutron Activation Analysis, Air Pollution, PM10, Factor Analysis

1. INTRODUCTION

Urban particulate matters, PM10 (aerodynamic equivalent diameter, AED, less than 10μm) are particularly important because of their potential for deposition on human respiratory system, while accompanied by many harmful trace elements (such as As, Cd, Cr, Cu, Mn, Pb, Se, and Zn) [1,2]. The trace elements in airborne particulates originating from various source processes (soil, vehicle exhaust, combustion of fossil fuel, incinerators, and industrial processes) can also affect the environment, not only in a locally limited region but also in a wide area by long range transportation. Thus, trace element data obtained by long-term monitoring is very useful for risk assessment and source identification.

An analytical method aiming to the quantitative determination of trace elements in airborne particulate samples should be sensitive and precise, while potent enough to simultaneously identify the diversity of elements. Among the methods for quantification of trace elements in PM10, instrumental neutron activation analysis (INAA) has unique features including high-precision, non-destruction, and multi-elemental capability [3,4].

In this study, measurements of 24 trace elements were conducted on airborne PM10 samples collected from an industrial sampling station in the most polluted urban area of Daejeon city in Korea. The city has been growing rapidly, and currently has a population of about 1.45 million population and 0.49 million vehicles. With consideration that relatively little effort has been directed toward measuring trace elements in urbanized areas of Korea, the measurements were made over a three-year period by combining a high-volume air sampling and INAA technique. Based on measurements on elemental compositions of PM10 samples, it was attempted to elucidate the factors regulating the elemental distribution characteristics and to diagnose

the element-pollution status of the study area.

2. EXPERIMENTAL

2.1 Site Characteristics and Sampling

The collection of PM10 samples was conducted from a local administrative office located in Daewha-dong district in Daejeon (Fig. 1). The sampling site is at the southern edge of the 1st and 2nd industrial complexes, which are home to more than 130 different types of business: 1) small scale industries producing metallurgical, mechanical, rubber /plastic, and chemical products, and 2) large scale industries dealing with soaps and cosmetics. Inspection of meteorological conditions indicates that the site is dominantly affected by winds rising from the NW, aside from temporary interruptions from the SE during the summer season. As seen in Fig. 1, the local office is located at a downwind position favorable enough to examine the extent of local pollution.

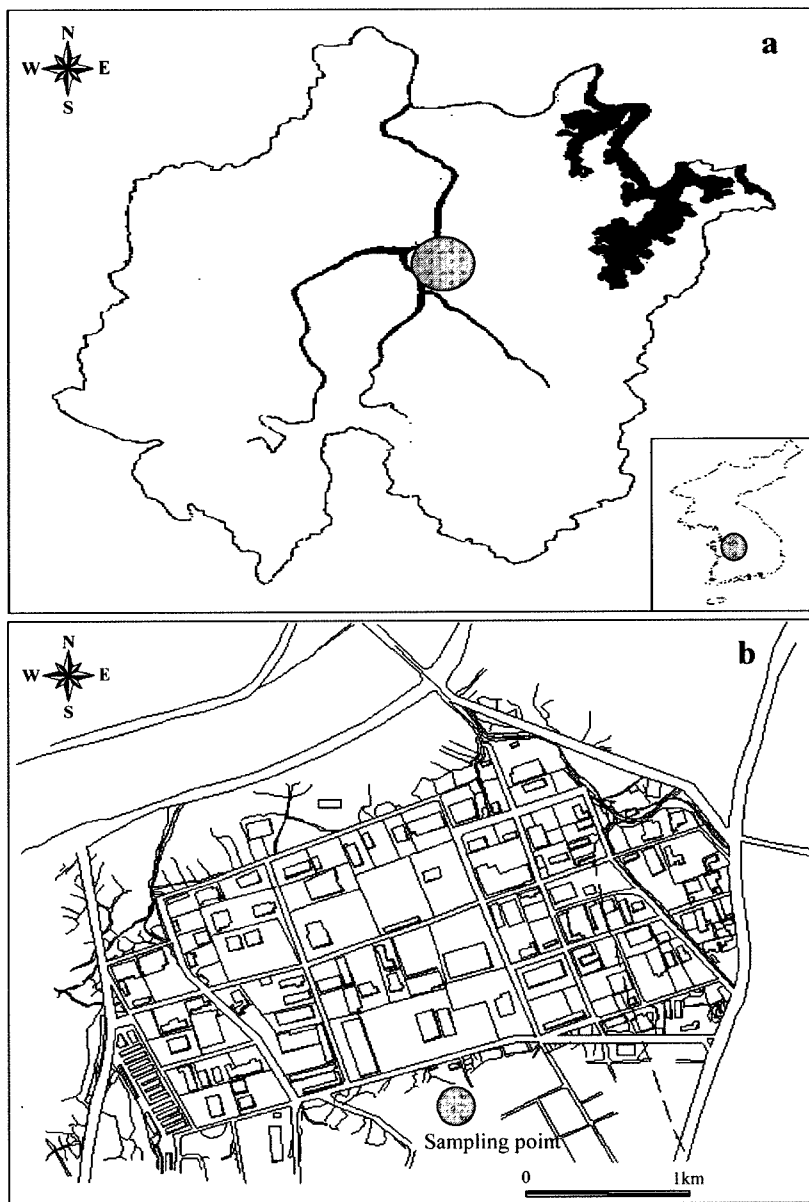The collection of PM samples was conducted with a high volume sampler (HVS: Model SAUV-10H, Graseby

Fig. 1. Areal Maps are Presented to Show Both Daejeon City in Korea and Daewha-Dong Site: (a) Daejeon City is Located in the Southwestern Region of Korea; and (b) the Study Site is on the Southern Edge of the First and Second Industrial Complex of the City

Table 1. Analytical Condition of INAA

HANARO	Irradiation hole	Neutron Flux			R_{cd}
		Thermal, Φ_{th}	Epithermal, Φ_e	Fast, Φ_f	
	NAA #1	2.95×10^{13}	2.13×10^{10}	3.78×10^{10}	≈ 250
	Irradiation facility	Irradiation time	Decay time	Counting time	Element
Short- 1st Detection Short-2nd Detection	PTS	2 min	10 min 40 min	500 sec 1200 sec	Al, Mg, Ti, V Ba, Cl, I, In, Mn, Na
Long-1st Detection Long-2nd Detection	PTS	4 hour	5~6 day 10~16 day	4000 sec 10000 sec	As, Br, K, La, Sb, Sm Ce, Co, Cr, Fe, Sc, Se, Th, Zn

Anderson Co.) at the top of the second floor (6.5 m high from the earth) of a local administrative building during a 24 hour time period at a weekly interval for a 33-month period from April 2000 through December 2002. Each sample was collected on 20×25 cm fibrous filter paper (Whatman No. 41) at a flow rate of 0.85 m^3 min^{-1}. This filter paper is made of cellulose with a small pressure drop and good mechanical strength[5]. Total volume of air passed through a filter was computed using a flow recorder for each sampling period. The flow rate was re-adjusted using an orifice calibrator (GMW-25) at every motor brush exchange (~ 500 hours). The collected total volume was calculated with the flow rate and collection time. 136 collected samples were pre-stored for 24-hour in a controlled atmosphere (20°C, 50% relative humidity) and transferred into polyethylene vials after weighing.

2.2 INAA

The PM10 samples were irradiated using thermal ne-utrons using the Pneumatic Transfer System (PTS, Φ_{th} = 2.95×10^{13} $cm^{-2}s^{-1}$, $R_{cd} \approx 250$) at the HANARO research reactor at the Korea Atomic Energy Research Institute. For neutron flux monitoring, activation wires were comprised of Au-Al, Co, Fe, and Mn (Reactor Experiments Inc., R/X activation wire, 99.99% purity). Analytical conditions were optimized by pre-adjustment of the system. The details of the INAA system are provided in Table 1. The measureme-nts were carried out using a high-purity Ge detector with a relative efficiency of 25%. This measuring system has a resolution of 1.9 keV (FWHM) at 1332.5 keV of ^{60}Co with a peak-to-Compton ratio of 45:1. The detector was connected to a personal computer and a 8k multi-channel analyzer (EG&G ORTEC, 919A MCB). During the measurement of the activated samples, the dead time was maintained below 10%. Energy and efficiency calibrations were performed using multi-nuclide reference sources (NEN Products Inc., NES-602, 2.54 cm diameter disc type) that are certified by NIST (National Institute of Standards and Technology, U.S.A.). Gamma Vision software (EG&G

ORTEC) was used for the following: (1) energy and efficiency calibrations, (2) acquisition of gamma-ray spectra, and (3) peak analysis. The counting loss of both short (such as Al and V) and long half-life species was corrected by the inverse value of the mean decay ratio (F_m), which was computed by a new Windows PC-code, Labview software (KAERI, Korea). For instance, the activity of Al can be computed by the $1/F_m$ value (2.87), while it becomes negligible for long half-life species. The effect of nuclear interference from ^{28}Si (by the formation of ^{28}Al) was tested using high-purity Si powder (99.9%). With an Al production rate of about 2.7×10^{-3}, it may be assumed that such an effect can be ignored for the actual Al concentrations quantified.

2.3 Data Treatment

The elemental concentrations of both samples and blank filters were determined under the same analytical conditions. The absolute concentrations of elements were estimated by the absolute approach of Tolgyessy and Klehr [6] with the aid of Labview software with the nuclear data library [7,8]. The system was developed for rapid and simple treatment of data with the information of the gamma-ray spectrum obtained at preset analytical conditions. The detection limits (DLs) of the elements were calculated by Currie's quantitative definition [9] with an allowable uncertainty of 10%. The DLs of trace components were generally in the range of 0.01-10 ppm, which corresponded to about less than 25% of the measured concentrations. However, those of certain elements (e.g., Ba, K, and V) occasionally exhibited 30 – 45% of the measured values.

2.4 Analytical Quality Control

The standard reference material (SRM: NIST, the National Institute of Standards and Technology, U.S.A., SRM 2783, air particulate on filter media) was analyzed using the same method as that for the samples for analytical quality control. The analytical results are summarized in

Table 2. Analytical Results of NIST SRM 2783-Air Particulate on Filter Media

Element	Certified value (ng/filter)	This work (ng/filter)	Relative Error (%)	RSD(%)
	Mean ±Unc.(2s)[a]	Mean ±SD(1s)[b]		
Al	23210±530	22710±496	2.2	2.2
As	11.8±1.2	11±0.08	8.4	0.8
Ba	335±50	357±17.1	-6.6	4.8
Ca	13200±1700	13836±746	-4.8	5.4
Ce	23.4±3.5	25.70±2.33	-9.8	9.1
Co	7.7±1.2	7.84±0.42	-1.8	5.3
Cr	135±25	144±4.47	-6.8	3.1
Cu	404±42	386±33	4.4	8.7
Fe	26500±1600	28201±900	-6.4	3.2
K	5280±520	5279±138	0.0	2.6
Mg	8620±520	9826±1086	-14.0	11.1
Mn	320±12	332±5.45	-3.6	1.6
Na	1860±100	1840±25	1.1	1.3
Sb	71.8±2.6	75.73±6.62	-5.5	8.7
Sc	3.54±0.28	4.03±0.28	-13.7	6.9
Sm	2.04±0.15	2.11±0.18	-3.5	8.4
Th	3.23±0.59	3.52±0.35	-8.9	10.0
Ti	1490±240	1460±41	2.0	2.8
V	48.5±6	49.05±3.97	-1.1	8.1
Zn	1790±130	1864±142	-4.1	7.6

[a] Expanded uncertainty with coverage factor 2 (approximately 95% confidence)
[b] Standard deviation

Table 2. The concentrations of 20 elements determined in this method were compared statistically with the certified (or recommended) values. The deviation between these values and SRM's for Al, Ca, Co, Cu, K, Mn, Na, Sm, Ti, V, and Zn fell below 5%, while those for As, Ba, Ce, Cr, Fe, Sb, and Th were less than 10%. Those for Sc (-13.7%) and Mg (-14.0%) were within 15%. All RSD (relative standard deviation, %) of trace elements fell below 10% except Mg (11.1%), thus indicating that the analytical results are very precise.

3. RESULTS AND DISCUSSION

3.1 Mass Concentration of Trace Elements

A statistical summary of the elemental concentrations measured during the entire study period is provided in Table 3. In order to constrain uncertainties involved in the measurements, some outlying data sets were eliminated prior to the statistical analysis via two different screening steps. In the first step, about 1% of the data sets were removed on the basis of a signal-to-noise (S/N) ratio of

2. Following this treatment, the data sets with values exceeding ±3 SD from the mean were also excluded so as to rule out the possibility that the distribution patterns of certain elements are distorted by the presence of a few extreme values. Loss of data was also about 1% at this secondary step. According to the summary provided in Table 3, the distribution patterns of elements can be clearly distinguished, with their concentrations varying across four orders of magnitude. The means for In and Sm were the lowest with values of 0.1 and 0.14 ng m^{-3}, respectively, while that for Cl showed the highest value of 3,017 ng m^{-3}. The mean concentrations for each element were also compared on a logarithmic scale. Based on a simple comparison of magnitude, all elements can be grouped into five different categories: 1) < 10^0 ng m^{-3}: In, Sc, Sm, and Th; 2) < 10^1 ng m^{-3}: As, Ce, Co, Cr, I, La, Se, and V; 3) < 10^2 ng m^{-3}: Ba, Br, Cr, Mn, and Sb; 4) < 10^3 ng m^{-3}: K, Mg, Na, Ti and Zn; and 5) < 10^4 ng m^{-3}: Al, and Cl. In addition, it was shown that the concentration of major earth elements (such as Al, Fe, K, and Ti) was much higher than that of any other element.

In order to examine the relative status of toxic metal (such as As, Br, Cr, Mn, Sb, Se, V, and Zn) pollution

Table 3. A statistical Summary of Elemental Concentration from Study Area during 2000-2002 [a]

(unit: ng m⁻³)

Element	Mean	SD	Min	Max	N	N [b]
Al	1665	1862	153	16672	136	136
As	3.2	2.3	0.1	11	134	136
Ba	43	25	6.6	122	135	136
Br	25.4	17.7	2.63	80.4	133	136
Ce	2.1	1.7	0.2	10	135	136
Cl	3017	1404	807	7100	121	122
Co	1.10	0.66	0.14	3.12	135	136
Cr	17.3	14.9	3.3	79	133	135
Fe	1393	949	175	5520	135	136
I	6.9	4.6	1.0	24	131	133
In	0.1	0.1	0.0	0.2	129	132
K	843	582	84	2861	135	136
La	1.0	0.8	0.1	4.0	136	136
Mg	443	518	24	4897	131	132
Mn	48.2	31.0	4.8	149	135	136
Na	758	499	163	3617	130	130
Sb	12.3	8.3	1.2	37	134	136
Sc	0.27	0.30	0.02	1.85	135	136
Se	2.1	1.4	0.1	8.4	134	136
Sm	0.14	0.13	0.01	0.71	135	136
Th	0.37	0.31	0.03	1.79	136	136
Ti	104	105	14.1	897	136	136
V	5.52	3.70	0.39	32.0	136	136
Zn	146	77.7	19.6	369	135	136
PM10 [c]	85.8	40.3	17.5	253.2	136	136

[a] Total number of samples = 136
[b] Numbers of data prior to removing the OL data sets; the OLs were determined on the basis of ±3 from the mean.
[c] Expressed in $\mu g/m^3$

level in the study area, a comparison of the measurement data was made with measured data previously obtained from other urban areas on the globe [10]. A comparison of metal concentrations among different studies indicated that the magnitude of variability in the observed concentration levels can be distinguished either between metals or between sites. The pollution level of the study area, while differing in the diversity of metal species analyzed, closely resembles those defined [10] as 'the most polluted area'.

3.2 Seasonal Distribution of PM10 and Trace Elements

Since the measurements in the present study were made over a three-year period, evaluation of the elemental concentration change during such an extended period may be attempted in order to assess temporal changes in the environmental conditions in terms of the source/sink relationships for PM10 in the study area. A comparison of distribution patterns of both PM10 and each element was made at monthly intervals (Fig. 2). PM10 and those elements with crustal origin (such as Al, Fe, K, and Ti) were fairly dominant in spring. The dominant occurrences of peak levels during the spring season reflect the close similarity in the seasonal distribution pattern between PM10 and these elements, which are the major components of PM10. The concentrations of PM10 tend to increase in winter at which time strong winds rise accompanied by a reduced likelihood of wet deposition removal. This PM10 level can be significantly enhanced during the spring season with the frequent intrusion of Asian dust from China and Mongolia. Most of the anthropogenically originated elements are dominant in fall and winter. Some elements including As, Se, Cl, Zn, Br, and Sb have been reported as marker elements of fossil fuel and municipal waste combustion, vehicle exhaust, and industrial activities [11-13]. In fall and winter, the concentrations of these
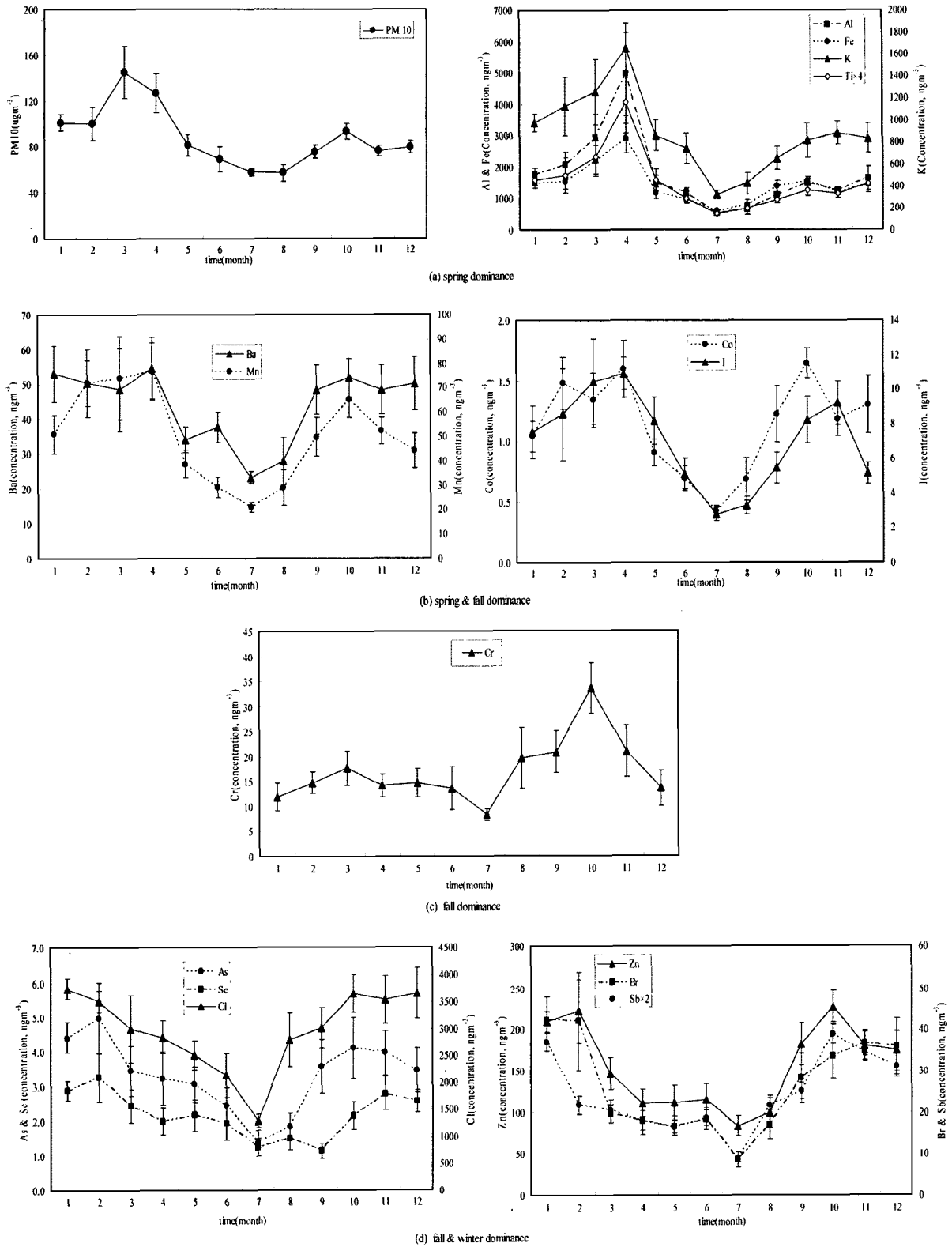
(a) spring dominance

(b) spring & fall dominance

(c) fall dominance

(d) fall & winter dominance

Fig. 2. . Monthly Distribution of PM10 and Elements in Study Area

Table 4. Result of Factor Analysis

Sources	Elements of high factor loading[a]	Variance[b] (%)
Soil dust	Al(0.96), Ce(0.88), Fe(0.83), K(0.93), Sc(0.94), Th(0.93), Ti(0.94)	42.3
Vehicle exhaust	Ba(0.47), Br(0.89), Sb(0.50), Zn(0.64)	12.7
Oil combustion	Cr(0.86), Se(0.60), V(0.54), Zn(0.43)	10.4
Coal combustion	As(0.76), Se(0.60), Zn(0.44)	8.0
Sea-salt	Cl(0.49), Na(0.80)	5.1
Incinerator	Ba(0.65), Sb(0.39), Mn(0.55), Zn(0.33)	5.0

[a] In the parenthesis, factor loading means simply the correlation coefficients between the variable(element) and the factor.
[b] Variance(%) means that amount of the data set is apportioned by the factor.

elements increase additionally by space heating and adverse meteorological conditions.

3.3 Pollution Sources Identification

A factor analysis (FA) is a numerical approach to account for statistical variance by deriving the least number of major factors. Hence, FA is useful in reducing the dimensionality of a large data set and in clarifying relationships between variables. The purpose of a FA is to determine the number of such common factors so as to account for an acceptable amount of variance in the observed data. The variables have been standardized such that the variance for each variable is 1. In this study, as a means to assess the major sources affecting elemental distributions in the study area, a varimax rotation factor analysis [14,15] was conducted using the measurement data. The results are shown in Table 4. The results of the factor analysis indicate that there are no more than six factors (with statistical significance) that appear to be significant in regulating the elemental concentration levels in the study area. These six factors can account for as much as 84% of the total variance.

The first factor was dominated by many major/minor crustal components (such as Al, Ce, Fe, K, Sc, Th and Ti). This can explain 42% of the variance. This factor may suggest the dominant contribution of re-suspended soil dust. The second factor was characterized by vehicular emissions (such as Ba, Br, Sb, and Zn) - the term applied to both gasoline and diesel emissions. This can explain 13% of the variance. In order to characterize the components of this second factor, bromine can be an alternative marker for this source, which is well known to come from the combustion of leaded gasoline. Although bromine is also a marker of marine aerosols, the strong correlation (coefficient of 0.899) of Br with Sb in the measurement data may justify the use of Br as a traffic marker.

A number of elements originating from the burning of oil fuel (such as Cr, Se, V, and Zn) for domestic heating systems appeared to be the most important components of the third factor, with an additional 10% of the variance.

The fourth factor was characterized by coal combustion for metal alloy and heating (such as As, Se, and Zn). This can explain 8% of the variance. Arsenic is usually considered as a coal burning tracer, while oil combustion has Se, V, and Ni as marker elements. Coal burning in the study area is utilized in only a small number of domestic heating systems. Thus, the majority of this factor arises from industrial processes for metal alloy (non-ferrous element smelter).

The fifth factor appears to be clearly associated with aged sea-salt (such as Cl and Na). The sixth factor has a high factor loading for Ba, Sb, Mn, and Zn, which are generally considered to be a major marker for municipal waste incinerators. The fifth and sixth factor can each explain 5% of the variance. Results of the factor analysis suggest important roles of both industrial and natural source processes, despite that the study site is located at a downwind position of a major industrial complex.

4. CONCLUSIONS

In order to examine the distribution characteristics of elements at a polluted Korean urban area, the measurements of 24 elements in airborne PM10 samples were made using the INAA technique. Results showed that all the elements exhibited occurrences in diverse concentrations ranging over several orders of magnitude. Examination of their distribution patterns indicated that most elements with crustal origin tend to exhibit seasonal peaks during spring, similar to the observed pattern for PM10 concentration. On the other hand, most elements with anthropogenic origin tend to exhibit seasonal peaks during fall or winter. In order to explain the factors regulating their mobilization properties, the data were processed by a factor analysis. Results of the factor analysis suggested important roles of both industrial and natural source processes, despite that the study site is located at a downwind position of a major industrial complex. Based on the overall results of this study, it is concluded that while the site may be strongly

impacted by man-made sources, the general patterns of elemental distributions in the study area inspected over a seasonal scale are quite consistent with that are typically observed from natural environments.

Acknowledgements

REFERENCES

[1] D.F.S. Natusch, J.R. Wallace, and C.A. Evans Jr., "Toxic Trace Elements: Preferential Concentration in Respirable Particles," *Science*, **183**, 202 (1974).

[2] D.W. Dockery and C.A. Pope III, "Acute Respiratory Effects of particulate Air Pollution," *Annual Review of Public Health*, **15**, 107 (1994).

[3] S. Landsberger, Trace Element Determination of Airborne Particles by Neutron Activation Analysis, in Elemental Analysis of Airborne Particles, p. 323, Gordon and Breach, Malaysia (1999).

[4] I. Salma and E. Zemplen-Papp, "Instrumental Neutron Activation Analysis for Studying Size Fractionated Aerosols," *Nucl. Instrum. Meth. in Phys. Reser.*, **A435**, 462 (1999).

[5] K.W. Lee and M. Ramamurthi, Aerosol Measurement: Principles, Techniques and Applications, p. 184, Van Nostrand Reinhold, New York (1992).

[6] J. Tolgyessy and E.H. Klehr, Nuclear Environmental Chemi-
cal Analysis, Ellis Horwood Series in Analytical Chemistry, p. 185, John Wiley and Sons, New York (1987).

[7] G. Erdtmann and W. Soyka, The Gamma Rays of the Radionuclides: Tables for Applied Gamma Ray Spectrometry, Vol. 7, p. 862, Weinheim, New York (1979).

[8] IAEA , "Handbook on Nuclear Activation Analysis Data," IAEA Tec. Rep. No. 273, p. 811 (1987).

[9] L.A. Currie, "Limit for Qualitative Detection and Quantitative Determination," *Anal. Chem.*, **40**, 586 (1968).

[10] K.H. Kim, J.H. Lee, M.S. Jang, "Metals in Airborne Particulate Matter from the First and Second Industrial Complex Area of Taejon City, Korea," *Environmental Pollution*, **118**, 41 (2002)

[11] H. Xudong, O. Ilhan, and A.K. Namik, "Emissions of Trace Elements from Motor Vehicles: Potential Marker Elements and Source Composition Profile," *Atmospheric Environment*, **28**, 1385 (1994).

[12] W. Zhao and P.K. Hopke, "Source Apportionment for Ambient Particles in the San Gorgonio Wilderness," *Atmospheric Environment*, **38**, 5901 (2004).

[13] P.K. Hopke, Receptor Modeling in Environmental Chemistry, p. 319, John Wiley & Sons, New York, NY. (1985).

[14] P.K. Hopke, E.S. Gladney, G.E. Gordon, W.H. Zoller, and A.G. Jones, "The Use of Multivariate Analysis to Identify Sources of Selected Elements in the Boston Urban Aerosol," *Atmospheric Environment*, **10**, 1015 (1976).

[15] B.A. Roscoe, P.K. Hopke, S.L. Dattner, M. Jenks, "The Use of Principal Component Factor Analysis to Interpret Particulate Compositional Data Sets," *J. of the Air Pollution Control Association*, **32**, 637 (1982).