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The chemical composition of fine and coarse particles in relation with the Asian Dust events

Ki-Hyun Kim[a,*], Gyoo-Hoon Choi[a], Chang-Hee Kang[b], Jin-Hong Lee[c], J.Y. Kim[d], Y.H. Youn[d], S.R. Lee[e]

[a] *Department of Earth & Environmental Sciences, Sejong University, Seoul 143-747, South Korea*
[b] *Department of Chemistry, Cheju National University, Cheju 690-756, South Korea*
[c] *Department of Environmental Engineering, Chung Nam University, Gung Dong, Taejon 305-764, South Korea*
[d] *Meteorological Research Institute, Sin Dae Bang, Seoul 156-720, South Korea*
[e] *Korean Institute of Geosciene and Mineral Resources (KIGAM), Daejeon 305-350, South Korea*

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Abstract

The distribution patterns of the particulate matter (PM) and the associated elements were investigated from Seoul, Korea during spring 2001. The results of our measurements were analyzed to explain the behavior of metallic components by comparing their compositions mainly in terms of between Asian Dust (AD) and non-AD (NAD) period and between fine and coarse particle fraction. The computation of enrichment factor (EF) indicated that the magnitude of EF values for most hazardous metals during the AD period were even smaller than the NAD counterpart. The existence of low EF values during the AD period may be ascribable to the excessive input of crustal components like Al accompanied by the AD event. In accordance with this finding, the effects of the AD events were also reflected in diverse manners, when assessed by the concentration ratios of a given element for both AD/NAD period and fine-to-coarse (F/C) fraction. Results of this comparative analysis generally suggest that AD events are prominent sources for major crustal components in the fine particle fraction of PM. In addition, comparison of our measurement data with those obtained within the Korean peninsula and in the near-by Asian areas indicates that the metallic distribution patterns of the study area may be affected more sensitively by anthropogenic signatures. The results of our analysis, if investigated in relation with air mass movement patterns by means of the back-trajectory analysis, demonstrate consistently that the PM data measured during the study period can be closely tied with the signatures of both AD events and anthropogenic processes.

Keywords: Asian Dust; Fine particulates; Coarse particulates; PM2.5; PM10; Air quality

1. Introduction

It is well-perceived that the Asian Dust (AD) occurs very periodically from the vast desert areas across China and Mongolia (Joussaaume, 1990; Kai et al., 1988). Its impact is seen to be widespread so as to influence the environmental conditions of not only the Asian continent but also across different continents such as the Americas (David et al., 2001; McKendry et al., 2001). In the recognition of the environmental significance of AD events, many studies were conducted over the past decades to elucidate the various aspects of AD events, including long-range transport of airborne pollutants (LRTAP) (Lin, 2001; Fang et al., 2002). According to those previous studies, the PMs introduced by the AD events can be transported along with westerlies of about 20 m s^{-1} wind speed.

*Corresponding author.
E-mail address: khkim@sejong.ac.kr (K.-H. Kim).

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The total quantity of particulate matter (PM) transported via AD events is estimated to amount to 800 Tg on annual basis (Zhang, 1995). It is further predicted that about the half of them are deposited near the source area (30%) and re-distributed on a local scale (20%). However, the other half of them are expected to be subject to long-range transport such that they can serve as one of the major PM sources all across the Asia and the Pacific. In light of the environmental significance of the AD events on PM mobilization across continents and between the earth's surface and atmosphere, they are believed to ultimately affect the global climate through the alteration of PM cycle and chemical composition in the global atmosphere (Chun et al., 2001).

In order to investigate the effects of the AD events as a major source process of airborne pollutants into the Asian continent, we established an experimental plan to routinely conduct the measurements of PMs and the associated metals from our local monitoring station located in Seoul, Korea. As part of this long-term study plan, we initiated the measurements from the spring months of the year 2001. In the course of our study, the patterns of particle fractionation were examined in relation with the metallic composition by measuring their compositional changes between fine (PM2.5) and coarse fraction (PM10–PM2.5). In addition, as the AD events were observed very frequently during the whole study period, their compositions were also compared between AD and non-AD (NAD) periods. By analyzing the measurement data obtained for this comparative analysis, we attempted to provide some insights into the factors and processes governing the atmospheric PM chemistry in relation with the AD events.

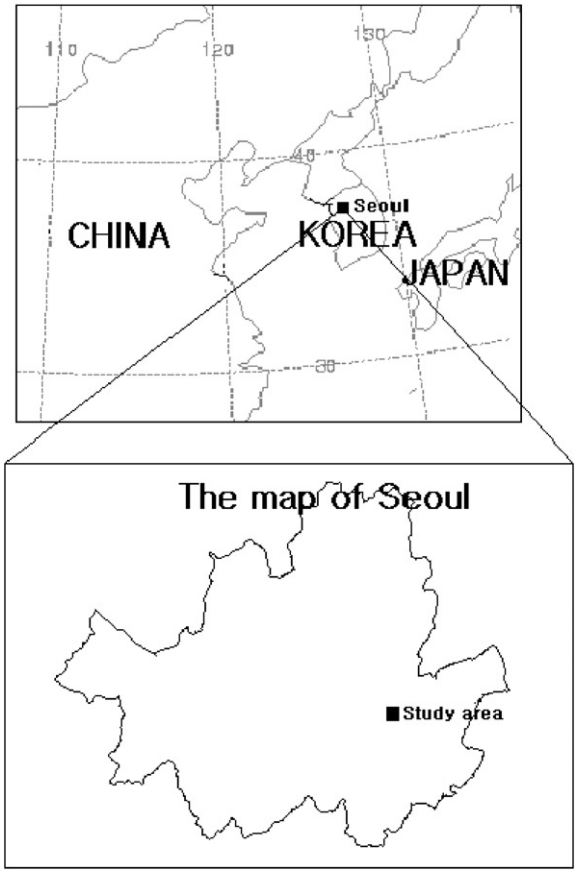

Fig. 1. A geographical location of the study site, Seoul is presented.

2. Experimental

The experimental site for the present study is located on the NE sector of Seoul, Korea (Fig. 1: 37°32′N (latitude) and 127°04′E (longitude)). The collection of PM samples was made on top of the 5th floor, Natural Science Building of Sejong University, which belongs to Gwang Jin district of Seoul city. This site can represent a moderately developed urban area. As the site is surrounded by diverse urban facilities including a large-scale public park (E), residential area (N and W), and commercial area (S), it is suspected to be influenced by the combined effects of various anthropogenic source types.

Our PM measurements were made for a total of 29 weekdays, during the period covering 19 March through 1 May 2001. For the simultaneous collection of PM2.5 and PM10 samples, we employed the PM-sampling system developed by URG Inc. (USA). Actual sampling of those samples was made at flow rates of $1\,m^3\,h^{-1}$ (or $16.67\,l\,min^{-1}$) using 0.5 μm pore size Teflon filter (Advantec MFS, Inc., Japan). The analysis of metallic components bound on both PM fractions were basically made by adopting the procedures described as EPA 3051A method. The PM-bound metals were extracted into an acid solution by a CEM microwave digestion system (Model MARS-5) in the following sequence. Filter samples were placed in a Teflon container and treated initially by the concentrated acid solutions (9 ml HNO_3 and 3 ml HCl). They were then heated up to 175°C for a 10 min duration under microwave and remained at the same condition for 5 min. These metal extracted solutions were then separated by PVDF syringe filter (0.45 μm, Whatman) and diluted with deionized water to make a final volume of 50 ml.

The extractants were then analyzed for their metallic components in each of the two PM fractions by ICP-AES system (Thermo Jarrell Ash, Model IRIS-DUO). The analysis of metallic components was made after dividing the whole elements into two data groups by considering the expected quantity of target analytes in samples such as: (1) radial plasma torch method for

components at high concentration level (Al, Fe, Ca, Na, K, Mg, and S) and (2) axial plasma torch method for low concentration level (Ti, Mn, Ba, Sr, Zn, V, Cr, Pb, Cu, Ni, Co, Mo, and Cd). Detection limits for individual elements investigated in this study can be classified into the following three concentration ranges:

(1) $10^{-2} \leqslant < 10^{-1}$ μg: Mn (0.01), Co, Cd, Zn (0.03), Ti, V, and Ni (0.06);
(2) $10^{-1} \leqslant < 1$ μg: Ba, Cu, Cr, Mo, Sr (<0.2), Fe (0.4), and Mg (0.6);
(3) 1 μg⩽: Pb, Ca (1.0), Na, S (1.5), A1 (2.0), and K (3.0).

3. Results

In the Korean peninsula, a detailed record of AD has been documented since 1988 by the Korean Meteorological Institute (METRI). Because the frequency with which AD events were previously observed in Seoul generally fell at a few days or less per year basis, the record for 2001 is the unprecedently high: (1) 11 days (four times) during March, (2) 9 days (three times) during April, and (3) none for May. However, as our measurements were basically confined to weekday period, we were able to catch 11 AD days (i.e., 20–23 March, 9–12 April, and 24–26 April) out of 29 experimental days, thus covering about one-half of AD days in spring 2001.

During the study, all the relevant meteorological and environmental parameters were measured concurrently with an automated weather monitoring system on the top of the building. During this study, the prevailing wind direction was mainly SE, but winds were also seen frequently from NW. This pattern was seen to be rather consistent between day and night period. The wind speeds were varying moderately throughout the study period with a mean of $2.1 \pm 0.5\,m\,s^{-1}$. Air temperature in this spring period was measured at $10.1 \pm 5.0°C$, while relative humidity (RH) was observed at $56 \pm 15\%$. Considering that RH values generally rise above 60% during spring, our study period was under relatively dry conditions. The PM concentrations measured during this study period were examined mainly in terms of fine (PM 2.5) and coarse particle fraction (PM10–PM2.5). In many cases however, the data for the original PM 10 were also provided for reference. According to this grouping scheme, the concentrations for those PM fractions averaged 49.3 ± 29.2 (fine; $N = 29$), 50.5 ± 35.0 (coarse; $N = 28$), and $95.5 \pm 46.1\,\mu g\,m^{-3}$ (PM10; $N = 28$), respectively. It is thus found that the concentrations of fine and coarse fractions observed during this study are highly compatible with each other on a quantitative basis.

4. Discussion

4.1. Comparison of concentrations between AD and NAD

In the present work, the compositional changes of PM were investigated to account for the effects of competing factors to regulate the metal distribution characteristics between different particle fractions and between different (AD and NAD) periods. Comparison of metal concentration levels shown in Fig. 2 is compatible with the general expectation in that most crustal components are abundant, while hazardous metals exist at their traceable quantities (e.g. Foltescu et al., 1994). A brief inspection on the data between the AD and NAD periods indicates that most elements tend to exhibit enhanced concentration levels during the former (refer to Table 1). Whereas several metals including Co, Mo, Cd, and Sr belong to a group with the lowest concentration levels (at or below $10\,ng\,m^{-3}$), most of major crustal components are found to have the concentrations larger than those at the lower end members by two to three orders of the magnitude (e.g., around or above $1000\,ng\,m^{-3}$). The difference between the levels of each element during AD and NAD may represent the contribution from the AD event. It should however be stated that such differences in concentration levels between the periods are less prominent in trace metals than in major crustal components. The results of our analysis also indicate that the overall distribution patterns, if compared in a relative sense, are quite compatible.

As a means to investigate the influence of the AD events on the metal composition of PM, the concentration ratios between the AD and NAD events (X(AD/NAD)) can be evaluated for each element (Fig. 3A and Table 2). The AD/NAD ratios for different PM fractions were computed to be: 1.7 (fine), 2.6 (coarse) and 2.0 (PM10). These computed ratios indicate that the PM quantity of most particle fractions was raised by a factor of around two due to the AD event; this is because the PM concentrations during the NAD period generally remained at a constant level. If the ratio for certain element is concerned, the value of above unity is likely to reflect directly the influence of the AD event. (On the other hand, if the ratio is below unity, the AD event might have exerted controls in an opposite manner.) Although exceptions were seen from a number of elements (e.g., S, Pb, and Cd), most elements in both PM2.5 and PM10 fractions persistently exhibited ratios above unity.

The existence of high AD/NAD ratios (e.g., >2.5) in PM10 fraction was typically seen from the major crustal components such as: Al (3.4), Mg (3.3), Ti (2.6), Fe (2.6), and Ca (2.5). It is interesting to find that their ratios are even higher in fine rather than in PM10 or in coarse PM fractions. Hence, as another means to investigate the

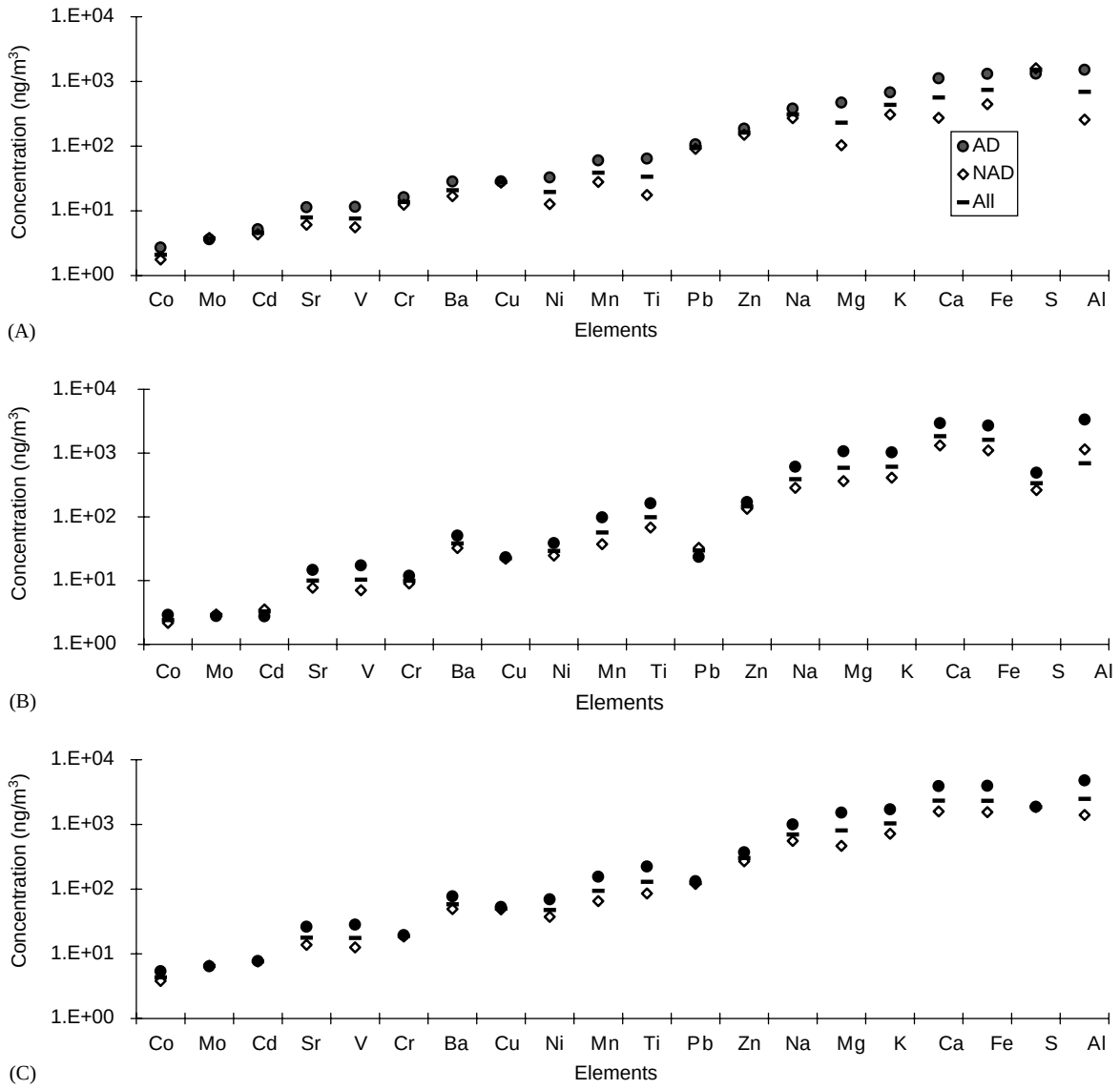

Fig. 2. Comparison of the concentration levels of each chemical component is made among (A) fine (PM2.5), (B) coarse (PM10-PM2.5), and (C) PM10 particle fractions. Considering the wide range of distribution, the concentration data are plotted on a logarithmic scale.

influence of AD on the metallic composition, we evaluated relative composition of metallic components between fine and coarse fractions both with and without AD effects. In Table 3, the concentrations of elements in both fine and coarse fractions were divided by those determined as PM10 fraction. The results of this computation indicate that the mass of most major crustal components (e.g., Al, Mg, Ca, Ti, and Fe) is dominated by coarse than fine fraction both during AD and NAD period. However, it is noted that their proportions in fine fraction appear to increase sharply during AD period. Hence, it may be possible to conclude that the AD events can be one of the most important sources of crustal components in the fine particle fraction.

Among various changes induced by the AD, that of the PM mass concentration may be pointed out as one of the most sensitive indicators. Although the generally windy conditions during the AD event may also have the potential to stimulate the PM emissions from local sources, the major causes of those changes are believed to be the long-range transport of PM-rich air mass. In

Table 1
A statistical summary of both fine and coarse PM[a] fractions and the associated constituents determined during the spring 2001: All measurements are made on a daily basis for a total of 29 days between March and May[b]

Parameters	All	AD	NAD	Parameters	All	AD	NAD	Parameters	All	AD	NAD
Fine	49.3	68.2	39.3	Coarse	50.5	86.9	33.2	PM10	95.5	144	72.5
Al	691	1514	258	Al	1853	3353	1143	Al	2490	4790	1400
Fe	743	1310	444	Fe	1615	2701	1100	Fe	2321	3960	1544
Ca	565	1117	274	Ca	1836	2940	1313	Ca	2336	3916	1587
Na	309	381	271	Na	390	611	285	Na	699	999	556
K	435	676	308	K	610	1028	411	K	1038	1712	720
Mg	231	472	103	Mg	588	1064	363	Mg	806	1523	466
S	1504	1320	1601	S	337	493	263	S	1867	1874	1864
Ti	33.7	64.4	17.6	Ti	98.7	163	68.0	Ti	130	223	85.6
Mn	39.0	60.1	27.9	Mn	56.8	98.1	37.2	Mn	94.2	156	65.1
Ba	20.8	28.4	16.9	Ba	38.3	50.8	32.4	Ba	58.4	77.6	49.3
Sr	7.91	11.4	6.09	Sr	9.99	14.7	7.74	Sr	17.8	26.2	13.7
Zn	163	187	150	Zn	146	171	134	Zn	302	372	270
V	7.62	11.6	5.55	V	10.3	17.3	7.04	V	17.6	28.3	12.6
Cr	13.7	16.2	12.4	Cr	9.93	11.9	8.99	Cr	18.8	19.5	18.5
Pb	96.4	107	90.9	Pb	29.7	23.5	32.6	Pb	124	133	120
Cu	27.8	28.6	27.3	Cu	22.4	23.1	22.1	Cu	50.1	53.0	48.7
Ni	19.6	32.8	12.7	Ni	29.2	38.7	24.7	Ni	47.8	69.8	37.4
Co	2.09	2.70	1.77	Co	2.41	2.91	2.17	Co	4.32	5.39	3.82
Mo	3.75	3.63	3.82	Mo	2.89	2.79	2.93	Mo	6.50	6.43	6.54
Cd	4.62	5.18	4.33	Cd	3.28	2.75	3.53	Cd	7.66	7.73	7.63

[a] The unit of PM is $\mu g\ m^{-3}$, while all the rest are $ng\ m^{-3}$.
[b] Note that $N = 29$ for fine and $N = 28$ for coarse and PM10 fractions.

light of the generally sensitive influence of AD on the PM mass change, the AD/NAD ratios were also evaluated by applying the PM-normalization procedure, such as the formula given in Fig. 3b. It is found that the results of this modified analysis differ dramatically from those computed for simple AD/NAD ratio. This normalization procedure in fact helped decrease ratios significantly for almost all elements. Although the normalized ratios of crustal components are reduced by about two to three times, their ratios still remain to exceed the unity. On the other hand, the normalized ratios for the dominant portion of trace metals dropped below unity. It may thus be possible to conclude that, as changes in PM concentrations exceed those of trace metals, the increased PM levels can lead to dilution effect (relative depletion) of most trace metals, especially in the coarse fraction during the AD event.

4.2. Comparison of fine-to-coarse ratios between AD and NAD periods

Information concerning the fractionation between fine and coarse particle size is a valuable key to a better understanding of the behavior of metallic constituents (Bilos et al., 2001; Fowler et al., 1994). To describe fractionation characteristics of metals in our study period between AD and NAD periods, fine-to-coarse (F/C) ratios for each metal were derived and compared (Table 2). The results of this analysis indicate that most of hazardous trace metals have F/C ratio values above unity (even before the grouping of periods), such as in the case of Pb (5.83). However, unlike the patterns seen from the crustal components, the values for trace metals generally exhibit values above 1.0, regardless of AD/NAD distinction. This type of results can in fact commonly be found from studies conducted previously in Korea (Lee and Kim, 1992; Choi and Song, 1999) as well as abroad (e.g., Manoli et al., 2002). If we extend this type of comparison to the two separate data groups of AD and NAD periods, the patterns appear to change considerably between periods and among components (Table 2). The results of this computation clearly indicate significant reduction in the F/C ratios of major crustal components across AD and NAD period (e.g., Al, Fe, Ca, Mg, Ti, etc.). As already seen from the computation of AD/NAD ratio, this observation supports the idea that the AD event can contribute significantly to the enhancement of major crustal components in fine particle fraction. In addition, the results for Pb are overwhelming to show roughly three-fold increase in its ratio during the AD period relative to NAD period.

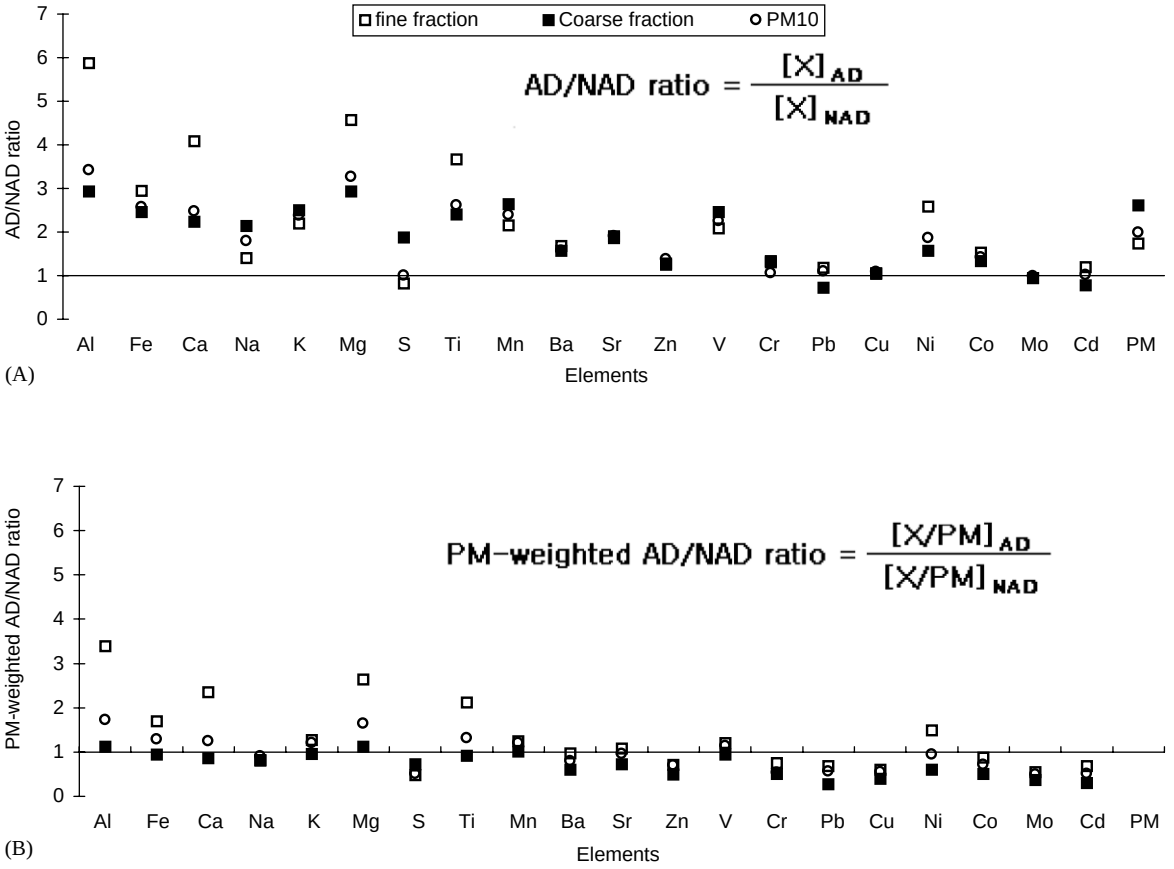

Fig. 3. Computation of the concentration ratios between Asian dust and non-Asian dust period. Comparison is made for fine, coarse, and PM10 fractions. Concentrations are compared: (A) directly using the values representing both AD and NAD periods; and (B) after normalization by the mass concentrations of PM for each period.

4.3. Comparison of EF values between the AD and NAD periods

As one simple means to evaluate the extent of metal pollution in the atmosphere of the study area during the study period, the concept of enrichment factor (EF) can be employed (Kim et al., 2002). If we derive EF values on the basis of the major crustal component (like Al), the results can provide basis to judge either the enrichment (or depletion) of a given element relative to that reference element (Al) (Fig. 4). Comparative analysis of EF values was however limited on PM10 data sets; this is because all the computation is conducted to compare the concentration ratios in all airborne particles against those ratios representing earth's crust (soils collected from the earth's surface without fine and coarse size fractionation in principle). If the computed EF values for a given element exceeds far above unity (e.g., 10 or 100), it can imply that the extent of enrichment is significant for that element compared to its crustal composition (Perry et al., 1999; Zhang and Arimoto, 1993). It was seen that several toxic metals like Zn, Pb, Cu, and Ni showed EF values above a few tens or hundreds, suggesting the possibly important role of man-made sources. However in accord with the general expectation, most of crustal components showed much smaller values of <10. Similarly to our observations, Lee et al. (1996) also observed consistently low EF values for crustal components by conducting field measurements of TSP from four distinctive urban locations in Korea. The results of previous studies made in other locations around the globe are also highly compatible with the results of the present study (e.g., Gao and Anderson, 2001).

Despite the general compatibility in EF values between different studies, the detailed features are commonly found to differ to a certain extent. For example, while our EF value for Cd is dramatically lower (by about two orders of magnitude) than that of Lee et al. (1996), our results for Cr and Ni are noticeably higher than their results. Because sources of crustal

Table 2
Relative composition of elemental components between periods (AD vs. NAD) and particle fractions (fine vs. coarse) is compared using their concentration data provided in Table 1

Components	AD/NAD ratios			F/C ratios	
	Fine	Coarse	PM10	AD	NAD
PM	1.7	2.6	2	0.8	1.2
Al	5.9	2.9	3.4	0.5	0.2
Fe	3	2.5	2.6	0.5	0.4
Ca	4.1	2.2	2.5	0.4	0.2
Na	1.4	2.1	1.8	0.6	1
K	2.2	2.5	2.4	0.7	0.7
Mg	4.6	2.9	3.3	0.4	0.3
S	0.8	1.9	1	2.7	6.1
Ti	3.7	2.4	2.6	0.4	0.3
Mn	2.2	2.6	2.4	0.6	0.8
Ba	1.7	1.6	1.6	0.6	0.5
Sr	1.9	1.9	1.9	0.8	0.8
Zn	1.2	1.3	1.4	1.1	1.1
V	2.1	2.5	2.2	0.7	0.8
Cr	1.3	1.3	1.1	1.4	1.4
Pb	1.2	0.7	1.1	4.5	2.8
Cu	1	1	1.1	1.2	1.2
Ni	2.6	1.6	1.9	0.8	0.5
Co	1.5	1.3	1.4	0.9	0.8
Mo	1	0.9	1	1.3	1.3
Cd	1.2	0.8	1	1.9	1.2

Table 3
Relative composition of elemental components between fine and coarse fraction of PM is compared against PM10 using the concentration data provided in Table 1. The AD/NAD ratios for each fraction are also computed separately

Period ratio	AD		NAD	
	C(fine)/C(PM10)	C(coarse)/C(PM10)	C(fine)/C(PM10)	C(coarse)/C(PM10)
PM	47	60	54	46
Al	32	70	18	82
Fe	33	68	29	71
Ca	29	75	17	83
Na	38	61	49	51
K	40	60	43	57
Mg	31	70	22	78
S	70	26	86	14
Ti	29	73	21	79
Mn	39	63	43	57
Ba	37	65	34	66
Sr	43	56	44	56
Zn	50	46	56	50
V	41	61	44	56
Cr	83	61	67	49
Pb	81	18	76	27
Cu	54	44	56	45
Ni	47	56	34	66
Co	50	54	46	57
Mo	56	43	58	45
Cd	67	36	57	46

components are by and large homogeneous among different locations, the observation of large differences in EF values between different anthropogenic metals may be accounted for by considering variabilities in such factors as their emission source types and the associated emission strengths. It may be thus reasonable to judge that the behavior of toxic metals can be distinguished from major crustal components for their high F/C ratios and EF values. These findings may reflect the general tendency of toxic metals, as metals can readily incorporate with anthropogenically formed, fine particle fraction.

Results of our comparative analysis further indicate that EF ratios can vary widely between AD and NAD periods. While toxic metals generally exhibit high EF ratios, their values observed during the AD period are in general much smaller than the NAD period. Because sufficient amount of major crustal components is transported via the AD event, their enhanced concentration levels can induce dilution effects on computed EF values of anthropogenically driven metals during the AD relative to NAD period; this dilution effect is highly compatible with what we observed from normalization of concentration ratios for AD/NAD as discussed above.

4.4. Geographical distributions of metals in relation with the AD

In order to assess information concerning the geographical distribution characteristics of metals in Korea during the spring of 2001, we made a comparative analysis of metal concentration data between our study and those measured at other locations at the similar time period (Table 4). To this end, we used the measurement data from Gwang Ju (hereafter as GJ), southwestern area of Korea as the reference point. The PM measurement project at GJ were conducted by the KJIST scientists as part of ACE-ASIA project to investigate aerosol behavior in the Asian continent (e.g., Kim et al., 2001). Through comparative analysis of the data sets at two different locations, we intended to examine how effectively the AD events impacted metal distribution patterns among different locations. While our site represents an urbanized environment, GJ can be considered as suburban area. Hence, when the concentration data between the two sites are compared by magnitude, the concentrations for the major crustal components were generally higher at GJ than our site. On the other hand, the patterns for the toxic metals were

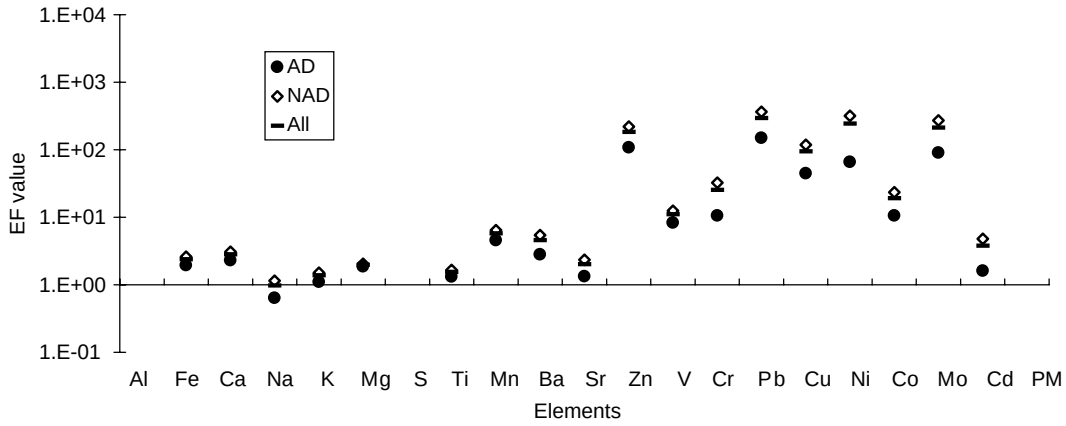

Fig. 4. The plots of EF ratio computation for each elemental component. The concentration data derived for PM10 fraction were used for this comparison.

reversed so that their concentrations at our site are generally larger than those of GJ.

To extend our examination of spatial variability, we also used the data sets of the suspended particulate matter (SPM) obtained on a continuous basis from various urban locations in Japan. In Japan, abundant data sets of metal distribution have been collected from many different locations through the establishment of National Air Surveilance Network (NASN) since 1974 (Var et al., 2000). For the purpose of comparative analysis with our data sets, we used the results of those authors for five different large, urban locations (i.e., Sapporo, Sendai, Tokyo, Nagoya, and Osaka) between the period of 1974 and 1996. Because their measurements focused on SPM, their results will be most compatible with our PM10 data sets. As shown in Table 4, the concentrations for most of major crustal components are much higher in Seoul than those of all the locations in Japan. This difference may in part be explained by the difference that our measurement was conducted during spring period only, while Japanese data represent the results for the entire year. However, the influence of geographical factors may not be ruled out; it is noted that the concentration of Na, well known as a sensitive indicator for sea-salt evasion, tends to be high in most Japanese locations. The concentrations of metallic components determined from our study site were in most cases higher than those determined in urban locations of Japan, except for a few cases (e.g., Na, Zn, and Pb data for Tokyo and Zn, V, Cr, and Pb data for Osaka). In line with this observation, the results derived from Hong Kong area show generally enhanced levels of soil components, while those of toxic metals tend to be lower (Fang et al., 1999). Thus, the results of these comparative analyses suggest that our study site in Seoul may be affected more sensitively by anthropogenic source processes than other Asian urban locations investigated in similar manners.

4.5. Factors affecting the compositional changes of PM

To describe the influence of air mass movement patterns on the compositional changes of PM-bound elements, we investigated our data sets in relation with the back-trajectory analysis. The results of back-trajectory analysis for the period covering our study indicated that air masses were generally transported into the study area via three different pathways: (1) type I: air masses transported from San Dong peninsula across the Yellow Sea (6 days consisting of 2 AD and 4 NAD days); (2) type II: air masses coming from Japan area via the East Sea (4 days with 2 AD and 2 NAD days); and (3) type III: air masses from Mongolia en route of North Korea (19 days with 7 AD and 12 NAD days). It may be most desirable to compare the concentration ratios between AD and NAD for each of all three types. However because of the paucity of the data sets for types I and II, such comparison can be attempted most meaningfully for type III. The normalized results shown in Fig. 5 indicate that as seen from the comparison without consideration of air mass origin, the differences in concentration levels between the two periods appear to be rather distinctive for similar air mass movement patterns: the enhancement of concentration during the AD is dominant for most, but such pattern is more significant for crustal than toxic metal. It should also be noted that their relative distribution patterns are highly compatible regardless of particle size fraction; however, the changes in absolute values are rather significant for major crustal components between fine and coarse fraction. The overall results of this grouping of data sets in relation with air mass movement patterns clearly indicate that the effects of AD events can be

Table 4
A comparison of elemental concentrations of both PM2.5 and PM10 (or TSP) measured among different studies in the Asian measurement sites

(a) Data for PM2.5

(1) Seoul (This study)				(2) Gwang Ju		
Element	All	AD	NAD	All	AD	NAD
Al	691	1514	258	777	2300	382
Fe	743	1310	444	681	1538	459
Ca	565	1117	274	525	1467	280
Na	309	381	271	337	490	297
K	435	676	308	545	1192	377
Mg	231	472	103	289	762	166
S	1504	1320	1601	2557	2840	2484
Ti	33.7	64.4	17.6	19.8	64.2	8.23
Mn	39.0	60.1	27.9	68.2	57.1	71.2
Ba	20.8	28.4	16.9	10.3	5.57	11.7
Sr	7.91	11.4	6.09	3.95	10.2	2.26
Zn	163	187	150	90.7	96.6	89.0
V	7.62	11.6	5.55	5.22	8.69	4.33
Cr	13.7	16.2	12.4	5.57	7.31	5.12
Pb	96.4	107	90.9	48.2	52.9	47.8
Cu	27.8	28.6	27.3	9.71	10.1	9.61
Ni	19.6	32.8	12.7	4.44	4.77	4.35
Co	2.09	2.70	1.77	1.18	0.94	1.24
Mo	3.75	3.63	3.82			
Cd	4.62	5.18	4.33	2.54	2.02	2.68

(b) Data for PM (or TSP)

(3) Seoul (This study: PM10)				(4) Japan (TSP)					(5) Hong Kong (TSP)	
Element	All	AD	NAD	Sapporo	Sendai	Tokyo	Nagoya	Osaka	Hong Kong	Lantau
Al	2490	4790	1400	908	626	429	440	555		
Fe	2321	3960	1544	625	514	677	418	941	5183	7585
Ca	2336	3916	1587	672	570	469	329	542	2759	4236
Na	699	999	556	729	704	637	622	921		
K	1038	1712	720							
Mg	806	1523	466							
S	1867	1874	1864						4292	6020
Ti	130	223	85.6	53.3	42.5	40.2	34.2	51.7		
Mn	94.2	156	65.1	16.8	18.6	40.1	26.4	50.7		
Ba	58.4	77.6	49.3							
Sr	17.8	26.2	13.7							
Zn	302	372	270	149	182	299	196	328		
V	17.6	28.3	12.6	5.19	4.00	8.90	9.59	14.3	16.2	18.2
Cr	18.8	19.5	18.5	2.61	3.63	6.09	5.85	43.7		
Pb	124	133	120	43.9	39.2	125	71.5	174	81.5	110
Cu	50.1	53.0	48.7	20.9	11.4	30.2	15.5	20.9	48.0	28.1
Ni	47.8	69.8	37.4	3.81	2.84	5.63	5.58	8.70	6.7	10.9
Co	4.32	5.39	3.82						1.6	2.3
Mo	6.50	6.43	6.54							
Cd	7.66	7.73	7.63						2.3	3.0

Sources: (4) Var et al. (2000) and (5) Fang et al. (1999).

considerably distinguishable between air masses of the similar geographical origin.

To simplify the comparison among three different air mass movement patterns, the compositional data for the first and second types were also normalized by the most dominant trend, the third type as seen in Fig. 6. The results of this analysis turned out to be largely different between different particle fractions. In case of fine

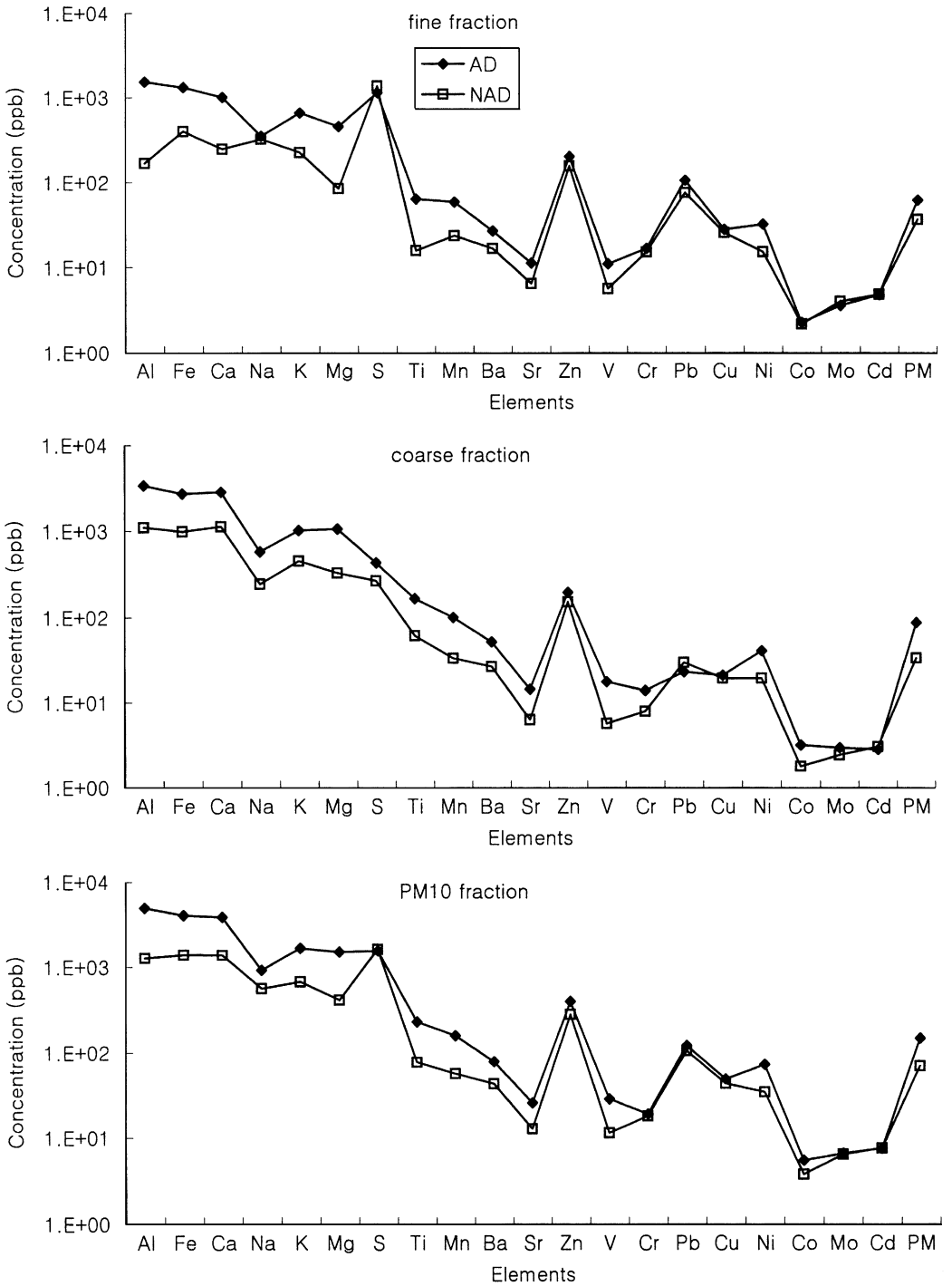

Fig. 5. The elemental concentrations measured during the air mass movement patterns of type III (from Mongolia desert via N. Korea) are compared using the mean values for the AD (7 days) and NAD (12 days) period.

particle fraction, most anthropogenic metals measured during the type I period were systematically higher than those of type II period. However, contrary patterns were evident for certain elements like Na, Mg, Cr, and Ni; note that some of those can directly reflect the influence of sea-salt evasion. In case of coarse particle fraction, the results are quite different. While the dominance of type I can still be found from several

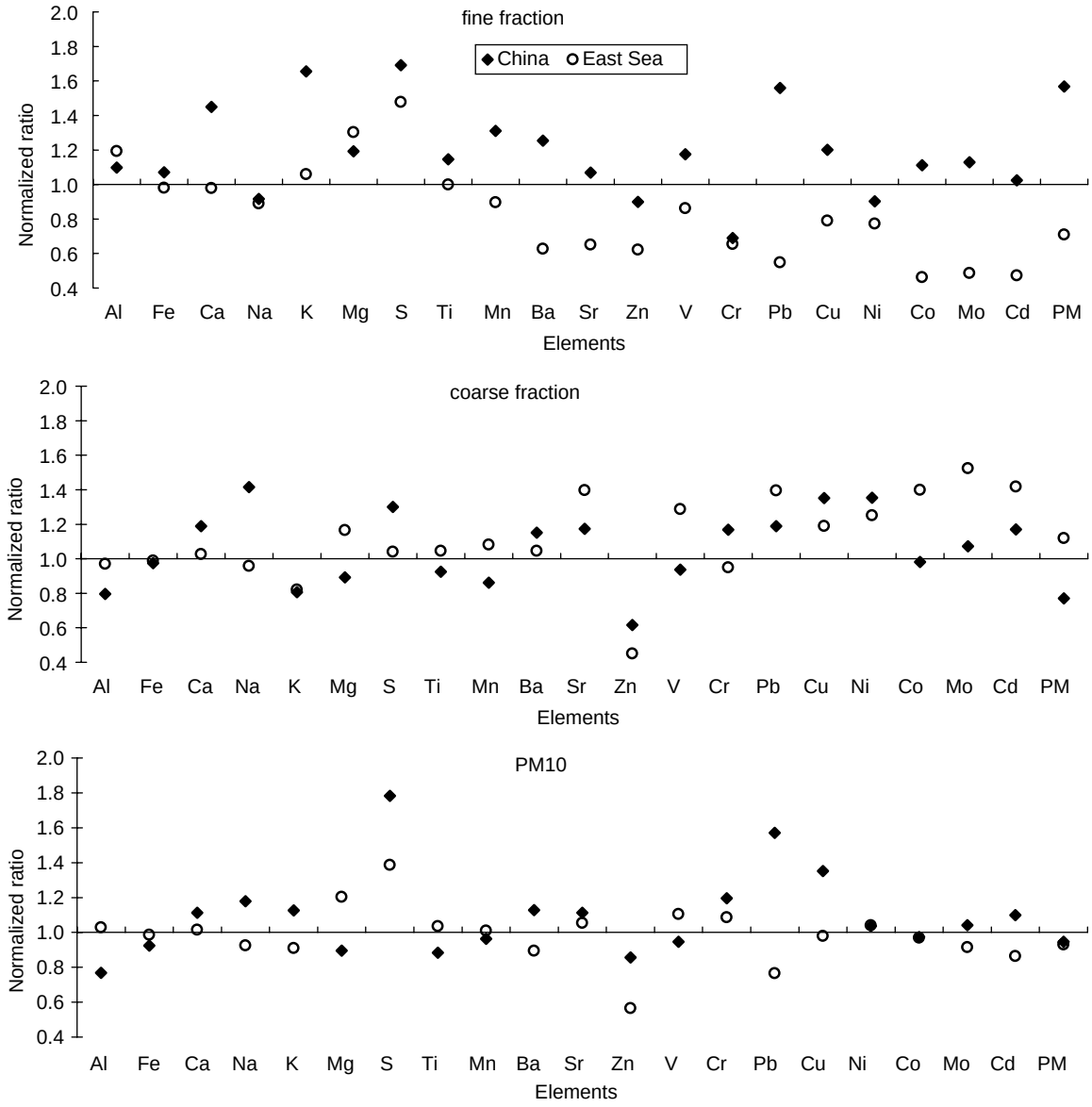

Fig. 6. The relative distribution patterns among different components of both fine and coarse particle fractions. The concentration data for the two different air mass movement patterns (China (type I) and East Sea (type II) of Korea) are normalized using the most common backward trajectory pattern (type III) of those coming en route of N. Korea.

crustal components, the concentrations determined during type II period are significantly high for most metals of anthropogenic origin. The patterns seen for the fine particle fraction may be reasonable in that toxic metals can readily incorporate various inland sources during its formation and transport. By contrast, the modified pattern for coarse particle fraction appears to be much complicated to explain. It is however suspected that as the air mass of type II generally moved slowly, the surviving coarse particles may have increasing chances for enriching minor trace constituents.

To provide some insights into the factors governing the metal distribution patterns in terms of two different criteria (i.e., different particle size and different periods), we conducted a correlation analysis to address the overall patterns of inter-parameter relationships. To this end, correlation analysis was tested for each of the four data groups: (1) Group I or F_{AD}: fine particle during AD; (2) Group II or F_{NAD}: fine particle during NAD; (3) Group III or C_{AD}: coarse particle during AD; and (4) Group IV or C_{NAD}: coarse particle during NAD. The results of this correlation analysis run for each of the

Table 5
A statistical summary of correlation analysis for the four PM data groups measured during spring 2001: Comparison of abundance patterns of strongly correlated pairs between AD and NAD and between fine and coarse particle fractions

Group No.	I	II	III	IV
Component[a]	F_{AD}	F_{NAD}	C_{AD}	C_{NAD}
(1) General				
PM vs. X_A[b]	2 (0/2)[c]	10 (0/10)	9 (0/9)	6 (1/5)
MET vs. X_A	4 (4/0)	18 (13/5)	1 (1/0)	20 (11/9)
(2) Inter-elemental relationships				
X_C vs. X_C	11 (1/10)	15 (2/13)	16 (5/11)	15 (6/9)
X_C vs. X_M	25 (8/17)	31 (7/24)	21 (10/11)	24 (11/13)
X_M vs. X_M	18 (9/9)	36 (15/21)	9 (4/5)	44 (13/31)
Sum	60 (22/38)	110 (37/73)	56 (20/36)	109 (42/67)

[a] Definitions for individual components of four data groups: Capital letters F and C imply fine and coarse, respectively, while subscripts AD and NAD denote the period of Asian Dust and non-Asian Dust, respectively.

[b] Definitions for matching pairs: Capital letters PM and MET denote particulate matter and meteorological parameters. In addition, X denotes element of interest. Subscripts A, C, and M denote type of elements such as: all (A) = crustal (C) + metal (M). Here, simple terms of crustal and metal are used to represent major crustal components and sub-nanogram level trace metals, respectively.

[c] The sum of strongly correlated cases of (1) $P<0.05$ (first number in the parenthesis) and (2) $P<0.01$ (second number in the parenthesis) is provided for each matching pair.

above category are summarized to address the general characteristics of those major factors on different data groups (Table 5). Our comparison initially focused on the general relationships between parameters such as between mass concentration of PM and all individual elements (without grouping of major crustal and trace elements) and between basic meteorological parameters and all elements. This comparison was further extended to pairs of between different PM-bound components such as: (1) crustal vs. crustal, (2) crustal vs. metal, and (3) metal vs. metal. (Hence, subscript of capital letter A (used as "all") in Table 3 corresponds to the sum of crustal (C) and metal (M).) According to this analysis, the results are found to contrast depending on the established criteria. Comparison made in terms of different periods (AD vs. NAD such as groups I vs. II or III vs. IV) exhibit highly clear patterns. The results for each pair determined during NAD (II and IV) have considerably abundant cases of strong correlations (in our study $p<0.05$ and $p<0.01$) relative to the AD period (I and III). (The only exceptions are seen from coarse particle data between PM and all elements (X_A) and between crustal components (X_C).) If the results of the correlation analysis are compared between fine and coarse fraction at the identical period group (such as group I vs. III or group II vs. IV), the distinctions are not as evident as that seen in terms of AD vs. NAD. Consequently, the results of this comparative study suggest that within a given particle-size fraction, the occurrence of AD is more critical in disturbing relationships among most parameters. However, when AD occurs, its effect is unlikely to be crucial to distinguish the compositional patterns between different particle fractions.

5. Conclusion

As a means to investigate the influence of the Asian Dust (AD) on compositional changes of PM, we measured the concentrations of 20 elements bound on both fine (PM2.5) and coarse particle fraction (PM10–PM2.5) from a northeastern area of Seoul, Korea. The results of our analysis conducted for 29 days of March–May 2001 indicate that the signatures of the AD event can be explored in various manners. To this end, the elemental composition of PMs was examined primarily by evaluating their concentration ratios between AD and NAD period (AD/NAD ratio) and between fine and coarse particle fraction (F/C ratio). The computation of AD/NAD ratio indicated the generally enhanced input of major crustal components during AD, especially in fine particle fraction. The occurrences of AD event hence appear to be most significant source processes of major crustal components on fine particle fraction.

Knowing that the absolute content of PM changes significantly across AD and NAD period, we also calculated those ratios after PM-normalization. The results of the modified analysis demonstrated that the patterns can change dramatically by considering such effect. Most strikingly, the observations of AD dominance were no longer seen for toxic metals, when their contents were evaluated by PM-weighted AD/NAD ratio. The reduction of the ratio by normalization procedure indicates that their relative concentrations can be diluted by excessive input of PM during AD. Similar to these observations, computation of EF values clearly pointed out that the relatively low EF values of most elements during the AD period are due to the introduction of massive amount of crustal components.

Because of abundance of AD events during the spring period of 2001, we were also able to compute the concentration ratios between the AD and NAD period for one specific type of air mass movement pattern. (The results of back-trajectory analysis indicated that the dominant portion of air masses was transported to the study area from Mongolia desert via northern Korea and the west coast of the Korean peninsula.) The results of this analysis were also consistent in that absolute content of most elements can increase with the inflow of AD event. In addition, to characterize the factors

affecting the compositional changes of PM, we also tested correlation analysis among all measured parameters for the four different data groups between different particle fractions and between different measurement periods. It was seen that the data obtained during the NAD period are correlated more significantly than the AD period, while no such distinctions were seen between different particle fraction for the same period type. The overall results of our comparative analysis thus consistently indicate that the effects of the AD events on the compositional change of PM can be remarkably significant to exhibit various signals in metal distribution patterns in both absolute and relative sense.

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