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The Distribution Characteristics of Elemental Components between Fine and Coarse Particle Fractions in Chongju, Korea

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ABSTRACT

The distribution characteristics of airborne particulate matter (PM) were investigated in terms of the relationships between different constituents (elements) and between different particle ranges (fine vs. coarse) from the city of Chongju, South Korea for approximately a year (October 1995 to August 1996). For the purpose of our study, the elemental compositions of both fine (FP: $PM_{2.5}$) and coarse particle (CP: $PM_{2.5\text{-}10}$) fractions were determined by proton induced x-ray emission (PIXE). Based on our study, the annual mean concentrations of PM in FP and CP fractions were found to be 41.4 and 29.6 μm^{-3}, respectively. The major elemental components of CP were found to be in the order of Si, Ca, Al, Fe, K, and Cl, while those of FP were S, Cl, Si, K, and Fe. If the temporal patterns of PM were compared across seasons, the most prominent pattern was found to be a relative depletion in coarse-mode concentrations during the summer's possibly due to efficient wet scavenging. On the other hand, the summing term for all elements showed consistently a summertime depletion pattern for all particle fractions. Our analysis of the relative relationships between PM and elements confirmed that the contribution of elemental components to PM mass concentrations can differ significantly across different particle size ranges and seasons.

(Key words: Fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particles, Dichotomous sampler, Proton induced x-ray emission (PIXE), Ionic composition, Chongju)

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1. INTRODUCTION

By operational definition, particles less than 2.5 μm in diameter belong to the fine particle (FP) fraction, whereas those greater than 2.5 μm are of the coarse particle (CP) fraction (e.g., Seinfeld 1986). Like physical differences in particle size, sources of each particle fraction have been distinguished from each other in various respects. The formation of fine particles occurs primarily as the result of various man-made activities (including the combustion of fossil fuels or secondary chemical reactions in the atmosphere). In fact, a number of previous studies have demonstrated that toxic metallic species (such as arsenic, selenium, cadmium, and zinc) are more concentrated in the fine, rather than coarse, particle fraction (e.g., Kim et al. 2003). By contrast, coarse particles are produced primarily by such processes as wind erosion, primary emissions, sea spray, and mechanical processes (Pakkanen et al. 2001a, b). Hence, the coarse particle mode of PM is known to consist mainly of crustal components such as iron, calcium, and silicon (Mishra et al. 2004).

A better knowledge of the size distributions of the ambient aerosols can provide valuable clues in predicting the pathways leading to their formation and transformation in the atmosphere (Gramotnev and Ristovski 2004; Hazi et al. 2003). Moreover, because of the great differences in origin and associated physicochemical properties between different particle size ranges, diverse statistical treatment is also allowable for the apportionment of sources (e.g., Polisar et al. 2001) and/or for the evaluation of health risks (e.g., Lall et al. 2004). A prerequisite for the application of such sophisticated tools is detailed information concerning the chemical composition of particles. This means the acquisition of a quantitative data set is fundamental to the establishment of strategies to control urban aerosol pollution problems.

Although numerous studies have been performed to investigate the atmospheric chemistry of PM, information concerning the behavior and fate of PM is still insufficient in certain respects; for example, changes in chemical composition across different particle size ranges (e.g., Yao et al. 2003). In this study, in order to investigate the factors and processes controlling the distribution of airborne PM, measurements were undertaken to simultaneously analyze PM samples in both fine and coarse mode in the city of Chongju, a moderately urbanized area in Korea. Through a thorough investigation of both absolute and relative relationships between different elements, we attempted to elucidate the main mechanisms that contribute to the formation of PM in Chongju, Korea. In addition, based on these measurement data, we discuss the fundamental factors that underlie the temporal distribution of airborne PM.

2. METHODS

In this study, both fine and coarse particle samples were collected and analyzed simultaneously for the period, October 1995 through August 1996 from a total of 58 individual experiments. The sampling site location was on the roof of the Chongju National College of Science and Technology building (15 m above ground level), which is located in a commercial-residential complex in central Chongju City. There are no large buildings around the sampling site to disrupt wind flow patterns. The site is approximately 3.8 km from the nearest highway, Kyung Bu line, and 56 km away from the west coastal area. The city represents a moderately urbanized area (154 km^2), about 115 km from Seoul, the capital of Korea (Fig. 1). It lies within a topographic basin surrounded by mountains to the east and south and is open to the west and north. The prevailing wind at the study site is either southwesterly or northwesterly. The climate of Chongju is characterized by large variations in temperature, from a monthly mean of -1.3°C in January to 26°C in August. Its population (570,000) is growing rapidly, and at present the number of vehicles on the road (145,000) is approximately five times that of 1990. It has been shown that the major emission sources of the city are industry, domestic heating, and vehicles with the main fuel sources in industry and heating being heavy and light oils (Chongju 1996). Major industries include electronics, metal assemblies, textiles, food, etc. These industrial sources are approximately 1.5 km from the monitoring site located northwest of downtown Chongju. The city experiences air pollution problems due to the combined effects of the topography, meteorological conditions, increasing fuel usage by industry, vehicles and continuous growth in population.

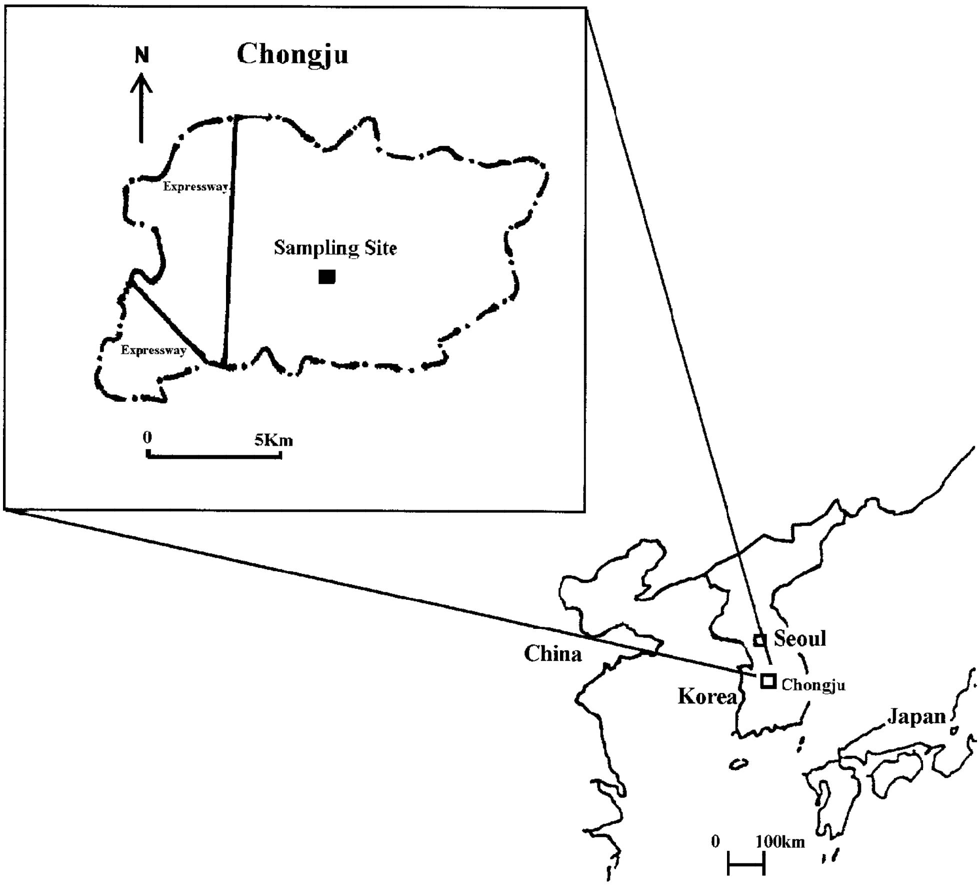

Fig. 1. A geographical location of the study site, Chongju in Korea.

The Korean Peninsula during the spring months comes under the influence of Asian dust storms, which contain high concentrations of earthen components originating from regions in northern China and/or the Mongolia plateau. Chung and Yoon (1996) found that the chief layer of a dust cloud moved to the east and southeast by a steering airflow at 850 - 500 hPa; and they estimated atmospheric loadings for this cloud to be 1.5 Mton.

The collection of PM samples was performed routinely from 8 a.m. in the morning at 24 h intervals using a dichotomous sampler (Model SA241, Andersen Co.). Instead of covering every month throughout the year, we conducted continuous sampling over intervals of 3 to 4 days for two representative months in each season. The particles entering the dichotomous sampler with an aerodynamic diameter below 10 (PM_{10}) were divided into two size fractions by means of a virtual impactor with a 2.5 cutoff point. These two particle fractions are referred to as fine (FP: $d_a < 2.5$ μm) and coarse particle fractions (CP: 2.5 μm < d_a <10 μm), respectively. The sampler was operated at a total flow rate of 16.7 liters min^{-1} (the flow rates of coarse and fine fractions were 1.67 and 15 $lmin^{-1}$, respectively). Particles were collected on 37 mm Teflon membrane filters (1 μm pore size) and supported by rubber o-rings (Gelman Sciences). The $PM_{2.5}$ mass was determined gravimetrically using a microbalance (Cahn C-35), which is sensitive to changes as small as 0.1 μg. All Teflon filters were pre- and post-weighed (below 35°C and 50% relative humidity), and the net weights were corrected with three unsampled control filters. All Teflon filters were conditioned before and after sampling in a clean chamber (Nikko auto dry desiccator) for at least 24 hrs.

Elemental composition was analyzed using a proton induced x-ray emission (PIXE) by the Element Analysis Corporation (Lexington, KY, USA); this instrument has the capacity to analyze up to 72 elements (sodium to uranium). Three blank filters were analyzed and used to correct the mass of each element contained in the sample filters. Information regarding the detection limit (DL) values for the series of elements measured is shown in Table 1, which includes sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), and lead (Pb). These values were calculated on the basis of analyzer sensitivity using 24-hr samples collected separately at coarse (1.67 $lmin^{-1}$) and fine-mode flow rates (15 $lmin^{-1}$). The accuracy of the measurements of these species was typically within 10% of the standard value. The precision was typically computed between 1 to 10% on the basis of replicate analysis of air samples.

3. RESULTS AND DISCUSSIONS

3.1 The Overall Pattern of PM Experimental Results

In Table 2, a statistical summary of our compositional analyses of both FP ($d_a < 2.5$ μm) and CP mode (2.5 μm < d_a < 10 μm) samples is presented using some major parameters derived from our measurement data. (Data for the PM_{10} fraction represent the sum of both FP and CP fractions, as they were collected separately by the dichotomous sampler.) To make a meaningful comparison of the relative roles for the two particle fractions between the different elemental components, a comparison of the results was made using the following terms: (1) two absolute values: PM (μg m^{-3}) and Σ(element) (ng m^{-3}); and (2) two relative values derived as concentration ratios: Σ(element)/PM (%) and F/C ratio (unitless). Here, the summing term for element [Σ(element)] was derived by summing up the individual concentrations of all elements investigated in this study (Fig. 2).

Table 1. Detection limit (DL) values of elements for the analysis of the fine and coarse particles (ng m^{-3}) in this study.

Species	$PM_{2.5}$	$PM_{2.5-10}$
Na	25.5	20.3
Mg	14.1	11.3
Al	11.7	9.30
Si	11.0	8.70
S	10.3	8.30
Cl	10.3	8.20
K	9.60	7.60
Ca	14.7	11.7
Ti	6.90	5.50
V	5.10	4.10
Cr	2.60	2.00
Mn	2.10	1.70
Fe	3.40	2.70
Ni	4.40	3.60
Cu	2.40	1.90
Zn	2.10	1.70
Br	4.50	3.60
Pb	10.8	8.70

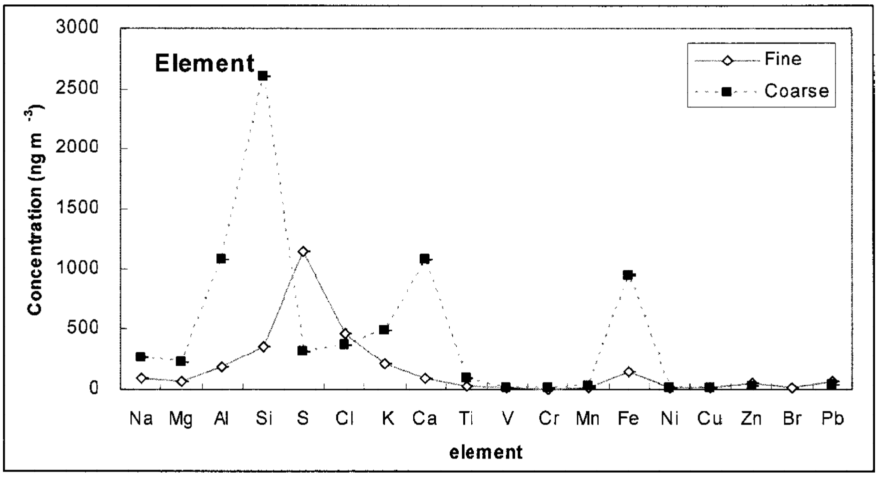

Fig. 2. Comparison of the mean concentrations of elemental components between fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particle fractions.

The results shown in Table 2 indicate several interesting aspects of PM geochemistry. First of all, the mean PM concentrations are larger in FP (41.4 μg m^{-3}) than in CP (29.5 μg m^{-3}). This is compatible with results from many previous studies conducted in diverse urban areas in that $PM_{2.5}$ mass can account for 27 ~ 80 % of PM_{10} mass (Zhuang et al. 1999, Alonso et al. 1997, Chan et al. 1997, Harrison et al. 1997, Chow et al. 1996). On the other hand, the pattern for elemental mean concentration data is completely reversed with the values for FP and CP fractions at 2.76 and 7.54 μg m^{-3}, respectively. Our results thus indicate the absolute dominance of elemental components in the CP mode. To analyze the diverse features of PM chemistry, all the different individual constituents used for the derivation of the summation term in Table 2 are analyzed independently in Table 3. For the computation of each statistical term shown in the tables, we excluded concentration values below detection limits (BDL) to place limitations on uncertainties in such lower-bound concentration ranges. However, to describe the occurrence patterns of such lower-bound concentration values, the frequency of all BDL occurrences are given additionally in tables with respect to all and seasonally divided data sets. Per our classification of data in terms of detectibility, the acquisition patterns of valid data sets appear to contrast quite sharply between various data groups. For example in the case of many elements (e.g., Na, Mg, Cl, Ti, Cr, Mn, Ni, and Cu), the occurrences of BDL readings occurred primarily in the FP fraction. By contrast, the opposing patterns were also evident for a few elements (including V, Ni, and Pb), such that their BDLs were found predominantly in the CP, rather than FP, fraction. Moreover, if these elemental data are compared on a seasonal basis, BDL values were observed most commonly during summer, probably due to enhanced washout of these constituents with the aid of heavy or frequent precipitation. Specially, the major unidentified elements (manganese and titanium) that are wet scavenged in the summer (Table 3).

Table 2. A statistical summary of PM and PM-related parameters measured from Chongju city during the whole study period. For all particle fractions, the numbers of measurements for each season (spring, summer, fall, and winter) correspond to 15, 13, 15, and 15, respectively.

Element	Season	Fine					Coarse					PM_{10}					F/C	F/PM10
		Mean	SD	Med	Min	Max	Mean	SD	Med	Min	Max	Mean	SD	Med	Min	Max		
PM μg m^{-3}	All	41.4	20.3	34.3	10.2	94.4	29.5	17.4	26.4	7.38	114	71.0	29.0	66.7	19.4	153	1.40	0.58
	Spring	35.1	10.0	33.0	22.3	62.6	44.7	25.7	37.2	20.9	114	79.9	27.6	72.0	50.3	153	0.79	0.44
	Summer	38.6	20.4	42.0	10.2	69.5	16.6	4.78	17.3	7.38	23.5	55.3	22.5	56.5	19.4	91.1	2.32	0.70
	Fall	43.5	26.1	29.2	16.5	88.5	26.8	10.1	23.3	15.5	47.3	70.3	35.2	56.6	32.0	127	1.62	0.62
	Winter	48.1	20.9	42.6	23.5	94.4	28.3	6.57	27.2	18.8	43.5	76.4	25.5	69.8	43.5	138	1.70	0.63
Σ(element) ng m^{-3}	All	2,764	1,227	2,657	355	5,818	7,542	4,447	6,103	2,426	25,991	10,303	5,315	8,613	3,688	31,808	0.37	0.27
	Spring	3,347	917	3,075	1,888	5,818	9,675	6,333	7,864	2,426	25,991	13,019	6,978	11,273	5,502	31,808	0.35	0.26
	Summer	1,579	847	1,158	355	3,292	4,297	1,029	4,339	2,596	5,863	5,874	1,509	5,981	3,688	8,042	0.37	0.27
	Fall	3,183	1,167	2,775	1,834	5,287	7,625	2,533	7,595	4,261	11,728	10,802	3,502	11,199	6,230	15,972	0.42	0.29
	Winter	2,787	1,205	2,565	1,367	5,480	8,138	4,251	6,669	4,995	22,394	10,926	5,030	9,968	7,116	27,341	0.34	0.26
Σ(element)/PM %	All	7.42	3.23	7.38	2.37	14.9	26.4	7.75	26.1	10.8	62.9	14.8	4.33	13.8	7.17	24.5	0.28	0.50
	Spring	10.0	3.05	10.4	5.10	14.9	21.3	6.05	21.6	10.8	36.0	15.9	4.42	14.6	10.0	22.9	0.47	0.63
	Summer	4.63	2.39	3.13	2.37	9.26	27.1	7.95	26.4	19.1	50.2	11.8	3.70	10.8	7.17	21.0	0.17	0.39
	Fall	8.48	2.50	8.27	3.91	12.9	29.0	3.45	28.5	20.7	33.1	16.7	3.56	16.2	12.0	22.0	0.29	0.51
	Winter	6.19	2.21	6.23	2.72	11.5	28.3	10.2	24.9	20.3	62.9	14.6	4.28	13.7	8.91	24.5	0.22	0.43

Table 3. A statistical summary of element concentrations measured from Chongju City during the entire study period. (all concentrations are in ng m^{-3})

Element	Season	Fine							Coarse							PM_{10}								
		Mean	SD	Med	Min	Max	N (all)*	N (BDL)*	Mean	SD	Med	Min	Max	N (all)	N (BDL)	Mean	SD	Med	Min	Max	N (all)	N (BDL)	F/C	F/PM_{10}
Na	All	95.4	30.3	94.8	40.1	192	34	24	265	94.7	258	88.8	500	58	0	354	106	378	150	534	34	24	0.36	0.27
	Spring	87.1	35.7	80.3	40.1	139	9	6	230	106	215	95.6	500	15	0	278	112	236	155	450	9	6	0.38	0.31
	Summer	97.8	39.7	97.8	69.8	126	2	11	251	101	229	153	437	13	0	426	135	426	331	522	2	11	0.39	0.23
	Fall	96.6	20.7	102	61.3	129	15	0	274	85.9	309	88.8	427	15	0	370	101	405	150	534	15	0	0.35	0.26
	Winter	102	40.8	86.7	66.1	192	8	7	302	79.4	299	190	461	15	0	391	68.3	412	269	478	8	7	0.34	0.26
Mg	All	71.3	27.0	65.3	35.4	148	33	25	231	105	198	123	625	57	1	315	108	262	207	738	32	26	0.31	0.23
	Spring	73.8	26.5	67.4	40.6	117	11	4	300	159	258	133	625	14	1	357	158	338	207	738	10	5	0.25	0.21
	Summer							13	152	19.4	147	123	179	13	0							13		
	Fall	71.1	20.2	69.5	41.3	112	15	0	230	55.4	215	155	303	15	0	301	68.3	265	219	416	15	0	0.31	0.24
	Winter	67.9	41.7	52.2	35.4	148	7	8	235	81.2	204	156	493	15	0	285	89.3	251	207	433	7	8	0.29	0.24
Al	All	183	216	131	36.4	1561	55	3	1069	644	895	366	3810	58	0	1285	753	1079	438	4407	55	3	0.17	0.14
	Spring	236	154	179	98.5	597	15	0	1443	927	1183	386	3810	15	0	1679	1058	1457	493	4407	15	0	0.16	0.14
	Summer	88.5	46.7	66.4	36.4	170	10	3	609	173	636	366	912	13	0	737	180	782	438	978	10	3	0.15	0.12
	Fall	161	53.4	150	82.2	284	15	0	1054	378	1177	490	1575	15	0	1215	403	1327	600	1736	15	0	0.15	0.13
	Winter	216	376	127	58.5	1561	15	0	1109	557	1058	556	2875	15	0	1326	707	1164	643	3129	15	0	0.19	0.16
Si	All	360	337	291	41.4	2177	57	1	2596	1888	2044	765	11162	58	0	2982	2185	2344	829	13338	57	1	0.14	0.12
	Spring	598	547	389	207	2177	15	0	3771	2840	2836	831	11162	15	0	4368	3317	3325	1038	13338	15	0	0.16	0.14
	Summer	133	74.4	115	41.4	307	12	1	1288	384	1305	765	1959	13	0	1433	442	1508	829	2048	12	1	0.10	0.09
	Fall	347	124	340	167	657	15	0	2446	864	2559	1228	3468	15	0	2792	946	2900	1395	3809	15	0	0.14	0.12
	Winter	317	170	296	105	664	15	0	2706	1573	2258	1382	7797	15	0	3024	1699	2628	1574	8460	15	0	0.12	0.10
S	All	1136	576	967	234	3002	58	0	324	229	250	68.4	1160	58	0	1460	675	1305	331	3768	58	0	3.51	0.78
	Spring	1388	522	1280	725	2310	15	0	271	170	206	68.4	729	15	0	1659	574	1382	1002	2767	15	0	5.13	0.84
	Summer	1078	677	854	234	2918	13	0	230	132	189	77.2	446	13	0	1308	713	1081	331	3082	13	0	4.68	0.82
	Fall	1124	667	856	536	3002	15	0	407	288	284	160	1160	15	0	1531	873	1196	726	3768	15	0	2.76	0.73
	Winter	945	358	829	473	1568	15	0	376	257	318	169	1103	15	0	1321	485	1264	648	2225	15	0	2.52	0.72
Cl	All	459	357	378	32.7	1702	51	7	367	248	304	22.5	969	58	0	834	496	795	150	2398	51	7	1.25	0.55
	Spring	300	172	354	34.4	592	15	0	225	157	178	22.5	483	15	0	524	243	599	190	873	15	0	1.33	0.57
	Summer	60.8	16.8	61.8	32.7	80.1	6	7	235	213	148	44.8	652	13	0	216	62.0	189	150	297	6	7	0.26	0.28
	Fall	620	408	488	298	1702	15	0	478	250	474	179	969	15	0	1098	450	977	531	1893	15	0	1.30	0.56
	Winter	618	332	488	285	1498	15	0	511	226	453	224	899	15	0	1128	427	1162	556	2398	15	0	1.21	0.55

* N(all) denotes the number of all measurement data, while N(BDL) that below detection limit. The latter data sets were not used for computation..

Table 3. Continued. (all concentrations are in ng m^{-3})

Element	Season	Fine							Coarse							PM_{10}								
		Mean	SD	Med	Min	Max	N (all)	N (BDL)	Mean	SD	Med	Min	Max	N (all)	N (BDL)	Mean	SD	Med	Min	Max	N (all)	N (BDL)	F/C	F/PM_{10}
K	All	214	143	196	13.4	750	57	1	496	313	402	153	1808	58	0	715	408	616	217	2292	57	1	0.43	0.30
	Spring	250	102	231	88	484	15	0	641	441	513	153	1808	15	0	891	515	743	294	2292	15	0	0.39	0.28
	Summer	77.9	56.5	60.7	13.4	219	12	1	304	87.7	277	167	432	13	0	384	123	383	217	595	12	1	0.26	0.20
	Fall	318	172	338	106	750	15	0	485	174	520	243	749	15	0	803	320	747	349	1499	15	0	0.66	0.40
	Winter	185	100	159	68.7	378	15	0	530	329	451	310	1641	15	0	715	387	652	417	1964	15	0	0.35	0.26
Ca	All	99.0	77.1	77.6	19.0	438	55	3	1072	731	940	244	4653	58	0	1208	795	1037	292	4916	55	3	0.09	0.08
	Spring	150	110	123	48.1	438	15	0	1320	812	1181	244	3080	15	0	1470	914	1251	292	3517	15	0	0.11	0.10
	Summer	43.5	20.7	36.5	19.0	82.5	10	3	556	180	526	337	835	13	0	647	189	640	383	883	10	3	0.08	0.07
	Fall	99.4	37.4	97.1	50.0	172	15	0	1134	415	1143	469	1752	15	0	1233	435	1237	519	1827	15	0	0.09	0.08
	Winter	85.0	63.4	60.4	19.4	264	15	0	1209	989	990	502	4653	15	0	1294	1041	1058	551	4916	15	0	0.07	0.07
Ti	All	21.1	15.1	15.1	7.47	65.5	19	39	98.3	65.4	81.9	26.9	393	58	0	142	93.8	121	56.1	459	19	39	0.21	0.15
	Spring	36.4	18.1	32.9	13.7	65.5	6	9	131	94.1	92.0	26.9	393	15	0	225	133	187	101	459	6	9	0.28	0.16
	Summer							13	56.0	18.4	58.9	28.3	83.7	13	0							13		
	Fall	11.2	2.92	10.3	7.47	15.1	8	7	93.8	31.9	104	47.1	139	15	0	99.1	33.5	85.4	56.1	153	8	7	0.12	0.11
	Winter	18.7	7.03	19.6	8.69	27.4	5	0	106	66.0	90.5	48.6	326	15	0	112	17.1	106	90.3	135	5	0	0.18	0.17
V	All	15.1	6.65	14.1	6.17	34.1	34	24	13.0	5.68	12.1	4.79	25.2	15	43	32.1	12.7	27.9	18.3	59.3	13	45	1.16	0.47
	Spring	13.2	5.27	13.7	6.17	21.0	8	7							15							15		
	Summer	10.8	5.65	10.8	6.78	14.8	2	11							13							13		
	Fall	17.8	8.29	16.2	8.44	34.1	15	0	17.0	5.59	17.5	8.06	25.2	6	9	42.9	10.4	40.6	31.8	59.3	6	9	1.05	0.41
	Winter	13.2	2.89	13.5	8.45	18.0	9	6	10.3	4.11	9.54	4.79	19.0	9	6	22.9	3.88	23.9	18.3	27.9	7	8	1.28	0.58
Cr	All	5.11	4.49	2.94	2.72	11.8	4	54	7.04	3.19	5.44	4.14	13.8	10	48	7.28	4.80	6.46	2.44	13.8	4	54	0.73	0.70
	Spring							15	9.44	3.72	9.31	5.37	13.8	4	11	8.89	4.36	7.54	5.37	13.8	3	12		
	Summer	11.8					1	12	4.87	0.69	4.95	4.14	5.51	3	10							13	2.43	
	Fall	2.94	0.30	2.94	2.72	3.15	2	13	4.79	0.23	4.79	4.62	4.95	2	13							15	0.61	
	Winter	2.73					1	14	8.43					1	14	2.44					1	14	0.32	1.12
Mn	All	11.4	4.45	11.8	4.00	18.7	43	15	21.2	12.6	18.7	4.28	79.3	58	0	35.7	15.3	34.1	14.5	97.7	43	15	0.54	0.32
	Spring	10.7	4.72	10.9	4.00	18.4	11	4	29.0	19.0	24.4	6.24	79.3	15	0	45.0	22.3	36.5	20.6	97.7	11	4	0.37	0.24
	Summer	11.3	3.83	11.6	6.43	15.7	4	9	12.5	4.89	12.4	4.28	18.8	13	0	27.4	4.37	29.1	21.0	30.5	4	9	0.90	0.41
	Fall	10.9	4.10	10.9	5.60	18.7	15	0	20.9	7.15	20.3	11.8	34.6	15	0	31.8	10.9	31.2	17.4	53.3	15	0	0.52	0.34
	Winter	12.7	4.98	13.8	4.54	18.6	13	2	21.1	8.72	19.4	9.31	45.4	15	0	34.9	12.0	36.7	14.5	61.7	13	2	0.60	0.36

Table 3. Continued. (all concentrations are in ng m^{-3})

Element	Season	Fine							Coarse							PM$_{10}$								
		Mean	SD	Med	Min	Max	N (all)	N (BDL)	Mean	SD	Med	Min	Max	N (all)	N (BDL)	Mean	SD	Med	Min	Max	N (all)	N (BDL)	F/C	F/PM$_{10}$
Fe	All	146	97.3	120	17.5	549	58	0	949	602	814	251	3775	58	0	1095	686	915	294	4325	58	0	0.15	0.13
	Spring	192	136	166	43.7	549	15	0	1294	903	933	251	3775	15	0	1486	1022	1099	294	4325	15	0	0.15	0.13
	Summer	77.4	71.7	64.5	17.5	291	13	0	575	208	561	311	898	13	0	652	265	626	341	1189	13	0	0.13	0.12
	Fall	157	54.9	146	71.1	280	15	0	935	335	997	456	1353	15	0	1092	381	1143	527	1539	15	0	0.17	0.14
	Winter	147	76.7	121	71.4	345	15	0	942	502	894	506	2511	15	0	1089	567	1016	602	2856	15	0	0.16	0.13
Ni	All	8.70	3.54	7.99	4.53	20.3	37	21	6.76	2.60	5.74	3.82	13.7	23	35	16.9	6.14	16.4	8.35	31.4	19	39	1.29	0.52
	Spring	7.72	2.23	7.24	4.64	12.0	10	5	5.40	1.06	5.31	4.32	7.19	6	9	12.2	1.40	12.0	10.8	14.1	4	11	1.43	0.63
	Summer	6.34					1	12	5.39					1	12							13	1.18	
	Fall	9.29	3.92	8.99	4.53	17.7	14	1	8.39	3.04	7.98	3.82	13.7	8	7	19.6	6.79	19.7	8.35	31.4	8	7	1.11	0.47
	Winter	9.02	4.09	7.99	5.35	20.3	12	3	6.33	2.46	5.25	4.43	11.2	8	7	16.4	5.80	16.4	10.8	26.7	7	8	1.42	0.55
Cu	All	13.2	9.39	9.81	3.26	59.6	47	11	8.28	4.69	6.76	3.19	23.6	56	2	22.0	13.0	18.1	7.46	83.2	46	12	1.59	0.60
	Spring	9.18	5.36	8.19	3.26	21.8	13	2	6.30	2.34	5.85	3.29	11.1	15	0	15.1	5.66	14.1	7.46	27.8	13	2	1.46	0.61
	Summer	13.0	6.55	13.1	4.47	22.3	7	6	6.90	2.09	6.18	3.87	10.9	12	1	20.2	7.03	21.1	10.5	28.8	7	6	1.88	0.64
	Fall	11.4	5.68	8.80	4.35	23.5	15		10.2	5.53	9.29	3.19	21.8	14	1	22.2	10.1	19.5	9.40	42.3	14	1	1.12	0.52
	Winter	19.8	14.2	18.3	7.47	59.6	12	3	9.58	6.14	6.79	4.22	23.6	15	0	30.2	19.5	28.0	13.8	83.2	12	3	2.06	0.65
Zn	All	55.0	28.0	47.6	13.0	140	55	3	27.7	14.9	25.8	5.84	91.2	58	0	83.7	41.0	75.0	19.4	231	55	3	1.99	0.66
	Spring	49.5	16.5	46.5	23.7	82.8	14	1	23.2	8.77	25.4	5.84	36.2	15	0	73.9	22.6	73.1	38.9	115	14	1	2.13	0.67
	Summer	40.5	19.6	47.6	13.0	68.2	11	2	18.8	7.49	19.6	6.40	27.7	13	0	60.4	26.8	67.2	19.4	95.9	11	2	2.15	0.67
	Fall	59.3	31.8	45.8	20.2	120	15	0	32.8	13.1	27.2	17.9	59.2	15	0	92.1	43.5	70.0	38.1	166	15	0	1.81	0.64
	Winter	66.5	33.7	57.8	27.8	140	15	0	34.9	20.6	29.8	13.1	91.2	15	0	101	51.8	97.0	45.4	231	15	0	1.91	0.66
Br	All	13.1	6.06	10.3	6.41	26.7	17	41														58		
	Spring							15														15		
	Summer	10.3					1	12														13		
	Fall	13.4	6.46	10.0	6.41	26.7	13	2														15		
	Winter	12.5	6.21	12.1	6.49	18.9	3	12														15		
Pb	All	62.6	33.0	57.0	19.2	164	49	9	35.9	18.0	34.4	16.3	91.9	24	34	114	45.3	98.7	49.8	212	24	34	1.74	0.55
	Spring	49.4	19.8	47.8	20.5	79.6	12	3	26.0	10.1	23.7	17.3	37.0	3	12	91.9	28.8	98.8	60.3	117	3	12	1.90	0.54
	Summer	67.8	39.0	61.3	19.2	124	7	6	36.3					1	12	160					1	12	1.87	0.42
	Fall	62.9	33.6	53.3	30.8	156	15	0	30.6	14.0	24.0	16.3	56.2	7	8	116	46.8	97.3	75.3	212	7	8	2.05	0.54
	Winter	70.6	37.6	64.4	25.9	164	15	0	41.1	20.9	37.5	16.7	91.9	13	2	114	49.0	102	49.8	191	13	2	1.72	0.62

3.2 The Distribution Characteristics of Elemental Components in the Study Area

In order to examine both absolute and relative contributions of elemental components contributing to PM composition, their magnitude was compared between the two particle fractions. According to our comparison based on the summarized results in Table 2, both similarities and dissimilarities coexist in their distribution patterns across particle sizes. In general, the elemental concentrations in the CP fraction appear to be significantly higher than their FP counterpart. In the CP fraction, their mean concentrations, expressed in ng m^{-3}, were found to decrease in the following order: Si (2596), Ca (1072), Al (1069), Fe (949), K (496), Cl (367), S (324), Na (265), Mg (231), Ti (98), Pb (36), Zn (28), Mn (21), V (13), Cu (8.3), Cr (7.0), and Ni (6.8). On the other hand, if the results are compared for the FP fraction, the relative patterns for most elements are quite compatible with a few exceptions such as: S (1136), Cl (459), Si (360), K (214), Al (183), Fe (146), Ca (99), Na (95), Mg (71), Pb (63), Zn (55), Ti (21), V (15), Cu, Br (13), Mn (11), Ni (8.7), and Cr (5.1). It is also worth noting that the changes in their concentration levels, in general, contrast starkly between major crustal and trace metal components. The former tends to exhibit a significant concentration drop from the CP to the FP fraction (Si, Ca, Al, Fe, K, Na, Mg, and Mn), while the latter tends to gain concentrations in the FP mode on many occasions (Pb, Zn, V, Cu, and Ni). If examined in terms of correlation analysis, the elements with similar source types generally exhibit significant correlations with each other. However, if changes in their relative ordering are concerned, an element like S appears to undergo the most significant changes of all. In the FP mode, S becomes the most dominant component of FP, as it alone can account for almost one half of the total elemental mass in the FP fraction.

As elements like Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe are known to be of crustal origin, they tend to be notably abundant in the CP rather than FP fraction (Chan et al. 1999, Chen et al. 1997, Chow et al. 1996, Lyons et al. 1993, Seinfeld 1986). Iron and manganese, however, are crustal elements that can also be emitted by industrial sources, in particular iron and steel operations (Chow 1996, Huang et al. 1994). However, in our study area, there are no known sources of iron and steel operations. Hence these elements are suspected to be of crustal origin. As previously mentioned, elemental sulfur was found to be the predominant component of FP elemental mass. The main sulfur sources in Chongju appear to come from the heavy and light oils used in industry and heating. Road salt, sea salt spray, automobile emissions, and coal combustion can act as sources of chlorine in the atmosphere (e.g., Spengler and Thurston 1983). However, there are also contrasting reports of Cl fractionation. For instance, Chow et al. (1996) reported that substantial amounts of Cl (and Na) were detected in the CP fraction at the coastal site. The correlation coefficients of Cl and Na in the CP and FP fractions were 0.7 and 0.3, respectively, suggesting that these components in the FP fraction did not originate from the same sources; Cl in the fine particles may have originated from anthropogenic sources. Elemental K in aerosols can come from either crustal matter or smoke. Therefore, non-soil K, rather than total K, has been usually used to indicate smoke emissions (Chan et al. 1999, Linda et al. 1997, Chow 1996, Huang et al. 1994).

Generally reduced $PM_{2.5}/PM_{10}$ ratios for potassium are consistently found from many sites such as those for Chongju, Los Angeles, Brisbane, and Helsinki (Table 4). Several metals including Pb, Zn, and Cu are found to be enriched in FP rather than CP mode. These metals are generally known to be emitted from combustion processes (Chan 1999, Chow 1996, Huang et al. 1994, Spengler and Thurston 1983). Lyons et al. (1993) also reported that particle size distributions of metals like Cu and Zn can be dominated by particle size ranges of less than 1 μm in diameter, indicating the possibly strong influence of anthropogenic sources. Pb has been considered as the traditional marker element for gasoline-powered vehicles. However, Pb does not appear to be an efficient marker in our study area or in S. Korea, as the use of leaded gasoline has been phased out since 1993 (e.g., Mishra et al. 2004). The comparative results summarized in Table 3 also indicate that those metals tend to be enriched in the FP fraction in most study sites including Los Angeles, Brisbane, and Helsinki (Table 4).

3.3 Temporal variation of PM compositions between elements

In order to more precisely understand the PM distribution characteristics in the study area, the concentrations of various elements measured in this study were further analyzed to assess factors affecting PM compositional changes across different seasons. It is worth noting that PM mass concentrations determined as both total (PM_{10}) and CP fraction ($PM_{2.5\text{-}10}$) complied well with general expectations, such as their relative depletions during the summer/fall period. As coarser particles can be more effectively removed by wet scavenging during the rainy summer season, they tend to exhibit more depletion during summer than their fine particle counterparts. By contrast, no such signal is apparent in fine-mode PM distribution; its distribution may be affected by different factors such as the chemistry of ionic components that are more abundant in the fine particle mode.

As seen in Fig. 3, the distribution patterns for the sum of elemental components contrast slightly with those of PM size distribution; they are consistently depleted in the summertime, regardless of particle size. However, if we compare the pattern after normalizing the elemental concentration by PM mass concentration, the coarse fraction does not exhibit any more depletion (Fig. 3, bottom). It is hence reasonable to suspect that summertime scavenging of elemental components in the coarse mode may proceed less efficiently than those of non-elemental components. When this type of seasonal pattern is examined across different elements, patterns do contrast among elements. Although most elemental components generally appear to comply well with the patterns of PM or the sum of elements, a few elements seem to exhibit their own unique patterns such as Na, Cu, and Pb.

4. CONCLUSIONS

In order to elucidate the relationship between size distribution and chemical characteristics of airborne particles, we investigated elemental constituents of aerosols between two size ranges across fine and coarse particle fractions in a moderately urbanized area in Korea. The results of our investigation generally indicated that the size distribution characteristics of PM can be accounted for by the complicated roles that exist between different particle fractions. It was found that the mass concentration of the CP mode was affected highly effectively by elemental components. If compared in terms of the summation of elements, the combined concen-

Table 4. The mean ratios of $PM_{2.5}$ to PM_{10} ($PM_{2.5}/PM_{10}$). Both mass and elemental concentrations of important species are compared with other studies.

Species	Chongju (this study)	Los Angeles[a] U.S.A.	Brisbane[b] Australia	Helsinki[c] Finland
Na	0.17	-[d]	-	0.36
Mg	0.15	0.19	-	0.16
Al	0.14	0.14	0.15	0.1
Si	0.12	0.09	0.11	-
S	0.78	-	0.76	-
Cl	0.52	-	0.16	-
K	0.3	0.23	0.42	0.3
Ca	0.08	0.10	0.11	0.13
Ti	0.07	0.09	0.15	-
Mn	0.27	0.50	0.50	0.28
Fe	0.13	0.18	0.20	0.16
Cu	0.58	-	-	0.33
Zn	0.65	0.60	0.75	0.64
Pb	0.8	-	0.82	0.74
Mass	0.58	0.59	0.41	0.48

a) January 1995 to February 1996 in downtown Los Angeles, USA (Kim et al. 2000).

b) December 1993 to November 1995 in Brisbane, a subtropical coastal city in Australia (Chan et al. 1999).

c) Aerosol samples of PM2.3 and PM2.3-15 collected from April 1996 to June 1997 in Helsinki, Finland (Pakkanen et al. 2001b).

d) Not available.

tration of CP [$\Sigma(\text{element})_c = 7.5\ \mu g\ m^{-3}$] exceeded its counterpart [$\Sigma(\text{element})_f = 2.8\ \mu g\ m^{-3}$]. The major elemental components of CP were found to be in the order of Si, Ca, Al, Fe, K, and Cl, while those of FP were S, Cl, Si, K, and Fe.

According to our study, clear seasonal patterns were observed consistent for both the different PM modes and different constituents. First of all, the CP mass data represented as ($PM_{2.5\text{-}10}$) showed rather strong seasonal variations, which can be described as enhancement

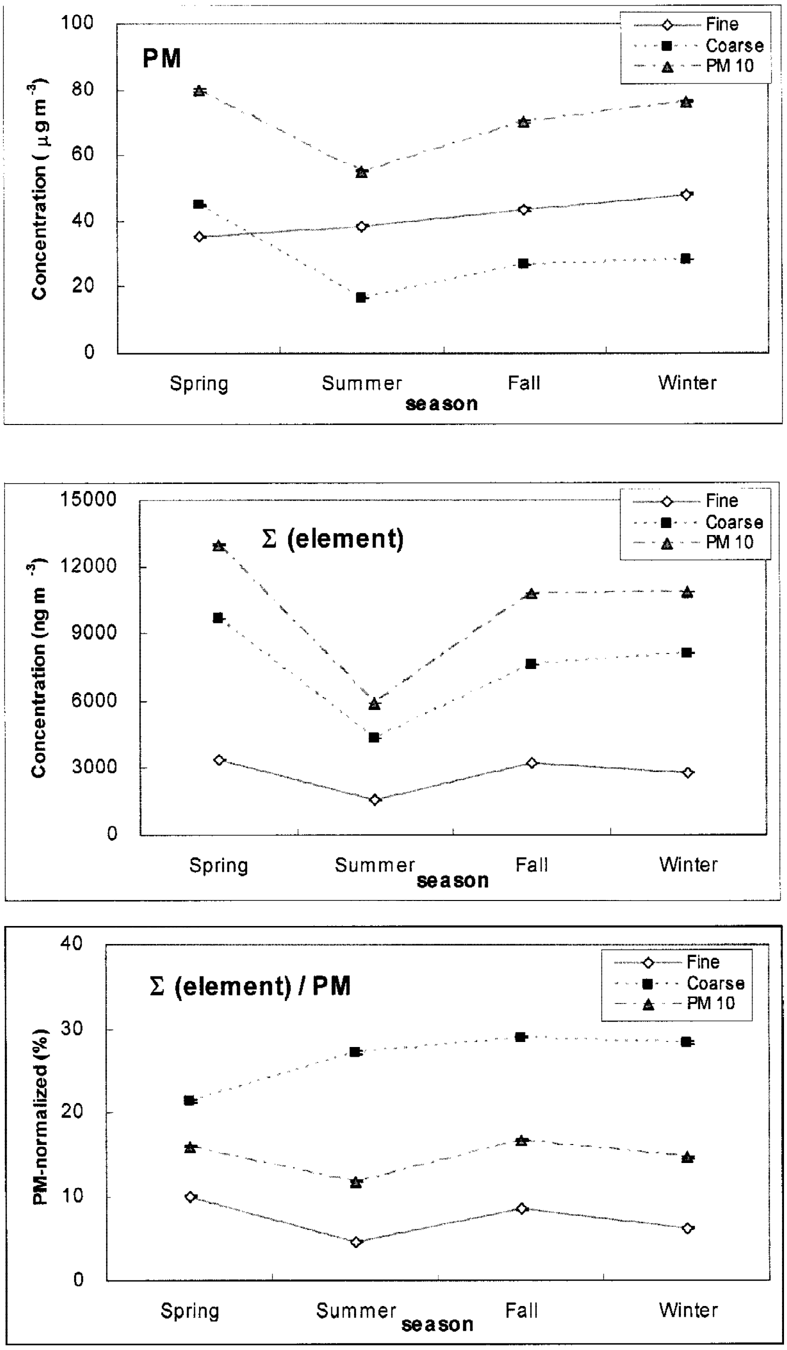

Fig. 3. Seasonal distribution patterns of PM and the associated elemental components determined from Chongju during 1995 - 1996.

in the winter/spring seasons relative to summer/fall seasons. Here mass and abundant species generally showed higher concentrations in the spring; this may reflect to some degree the influence of soil dust from China as a result of Asian dust storms. On the other hand, the results of the FP mass data were clearly distinguished from such patterns. The FP mode, in fact, tended to show moderately enhanced concentration levels during the summer relative to the spring or fall. If the mass ratio of $PM_{2.5}/PM_{10}$ is evaluated, its values are also higher in summer and than in the spring.

This detailed analysis of physical and chemical properties of airborne particles has been helpful in providing valuable insights into their geochemistry in a moderately urbanized area.

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