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RESEARCH ARTICLE

Natural and anthropogenic influences on heavy metals in airborne particles over the Korean Peninsula

Young Sung Ghim · Yongjoo Choi · Young-Soo Chang · Jeongsoo Kim

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Abstract Six monitoring stations were selected to characterize the variations in airborne concentrations of heavy metals in South Korea between 1999 and 2012. Three stations represented higher concentrations, and three represented lower concentrations. The heavy metals monitored at these stations include cadmium, chromium, copper, iron (Fe), lead, manganese (Mn), and nickel. During the study period, concentrations of heavy metals at many stations, including those around the Seoul metropolitan area, showed a decreasing trend. However, concentrations of Mn and Fe that are primarily of crustal origin increased at four of the six stations. Some stations were significantly affected by emissions from the local industrial complex (IC), and heavy metal concentrations at those stations were relatively high even in summer. Many heavy metal concentrations were higher in spring than in winter, but wintertime concentrations of Cr and Pb were higher at the stations representing lower concentrations due to the dominant influence of combustion emissions. At stations less affected by emissions from the IC, concentrations of Fe and Mn that are predominantly crustal in origin were higher in spring, when Asian dust (AD) events are most frequent. Although Mn concentrations were also high at stations within the steelmaking IC during AD periods, they were much higher during non-AD periods due to local emissions. Variations in heavy metal concentrations, which are heavily influenced by emissions from the IC, warrant individual analysis because their emission characteristics differ from those of typical cases.

Keywords Heavy metals · Industrial complex · Crustal origin · Combustion sources · Asian dust

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Y. S. Ghim (✉) · Y. Choi
Department of Environmental Science, Hankuk University of Foreign Studies, Yongin, Gyeonggi 449-791, South Korea
e-mail: ysghim@hufs.ac.kr

Y.-S. Chang
Environmental Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

J. Kim
Transportation Pollution Research Center, National Institute of Environmental Research, Incheon 404-708, South Korea

Introduction

The term "heavy metals" commonly refers to metals with a density above 4–5 g/cm^3, as the name implies. A major concern for heavy metals is their potential for detrimental effects on human health and the environment. Such effects have not been shown to be significantly affected by the density of the heavy metal. Although attempts have been made to explain the chemical toxicity of heavy metals based on their position in the periodic table or Lewis acid behavior, results have been inconclusive (Duffus 2002; Appenroth 2010).

Cadmium (Cd), lead (Pb), and mercury (Hg) are among the heavy metals that have received particular attention because of their potential for adverse health and environmental impacts. These three metals are targets of international agreements, including the Convention on Long-range Transboundary Air Pollution (UNECE 1998), and they are also the subject of extensive research (AMAP 2005; Ilyin et al. 2004; Pacyna et al. 2009). While some heavy metals such as copper (Cu), selenium (Se), and zinc (Zn) are biologically essential for enzyme structures or as catalytic co-factors (Dietz et al., 1998), Cd, Pb, and Hg do not appear to have any biological function in organisms and are thus termed nonessential metals. These metals could potentially constitute a risk to human health and the environment, even at doses slightly above background levels (Dietz et al. 1998). The European Monitoring and Evaluation Programme (EMEP) is monitoring arsenic (As), chromium (Cr), Cu, nickel (Ni), Se, and Zn

(Ilyin et al. 2011) in addition to Cd, Pb, and Hg. The World Health Organization (WHO 2000) suggested air quality guidelines for manganese (Mn) and vanadium (V) as well as Cd, Pb, and Hg. The European Union (EU 2012) has established annual average air quality standards for Pb, As, Cd, and Ni.

In Korea, Pb is designated as a criteria air pollutant, and a monitoring network for heavy metals such as Cd, Cr, Cu, iron (Fe), Pb, Mn, and Ni is in operation in the vicinity of metropolitan areas and industrial complexes (ICs). Sources of heavy metal emissions can be divided into two categories: anthropogenic and natural. Both Mn and Fe, which are included in the monitoring programs, are naturally occurring heavy metals of crustal origin, along with aluminum (Al), calcium (Ca), and silicon (Si) (Chow 1995; Nishikawa et al. 2000). Primary anthropogenic sources of heavy metals include fossil-fuel combustion, steelmaking, nonferrous metal production, waste incineration, and others (Pacyna et al. 2007, 2009). In Korea, the contributions of anthropogenic heavy metals to levels of air pollution are greater in the vicinity of ICs, while the effects of heavy metals of crustal origin are more pronounced during Asian dust (AD) periods (Kim et al. 2003; Kim 2007a, b).

In the present study, the levels of heavy metal concentrations collected during the 1999–2012 period were compared with those from other studies in Korea and other countries. For an in-depth analysis, three stations each were selected as being representative of higher- and lower-concentration characteristics, with the former located in industrial areas and the latter in residential areas, commercial areas, and open space. Characteristics of variations in concentrations from the stations representing lower and higher concentrations, respectively, were analyzed by station and season. The influence of AD on the variations in concentrations was examined in comparison with the influence of emissions from anthropogenic origins during the AD period.

Selection of stations for in-depth analysis

At each station in the heavy metal monitoring network in Korea, total suspended particles (TSP) are sampled using a high-volume sampler for 24 h beginning in the late morning. Samplings are made for 5 days during the second week of every month. The 24-h average concentration of each metal in the TSP is determined with the aid of atomic absorption spectrometry using an air-acetylene flame. Sample collection and analysis follow the standard procedures described by the Korean Ministry of Environment (KME) (2007). Table 1 shows selected parameters for determination of metals by atomic absorption spectrometry. The standard procedures are basically similar to the method of USEPA (1999). For detailed information and standard procedures on Mn (are not presented in Table 1), one can refer to USEPA (1999), Kim et al. (2004), or Duong and Lee (2009).

Table 1 Selected parameters for determination of heavy metals using flame atomic absorption spectrometry[a]

Metal	Analytical wavelength (nm)	Working range (mg/l)	Precision (% RSD)	Method detection limit (mg/l)
Cu	324.8	0.05–20	3–10	0.015
Pb	217.0/283.3	0.2–25	2–10	0.06
Ni	232.0	0.2–20	2–10	0.06
Fe	248.3	0.5–50	3–10	0.15
Cd	228.8	0.04–1.5	2–10	0.012
Cr	357.9	2–20	2–10	0.6

RSD relative standard deviation

[a] Standard test method ES 01450.1 (KME 2007). For Mn, see the text

As of 2012, there are 52 stations in the heavy metal monitoring network throughout Korea. Starting with 36 stations in 1999, the number of stations continued to increase during the study period. It is noteworthy that the number and locations of stations significantly changed at the beginning of the 2000s because of the devolution of management responsibility from the Ministry of Environment to local governments (KME 1999). As a result, the measurements for heavy metals have been carried out continuously at only 21 stations shown in Fig. 1 since 1999. Table 2 presents the means and standard deviations of the heavy metal concentration ratios at these 21 stations. On average, measurements were made 5 days per

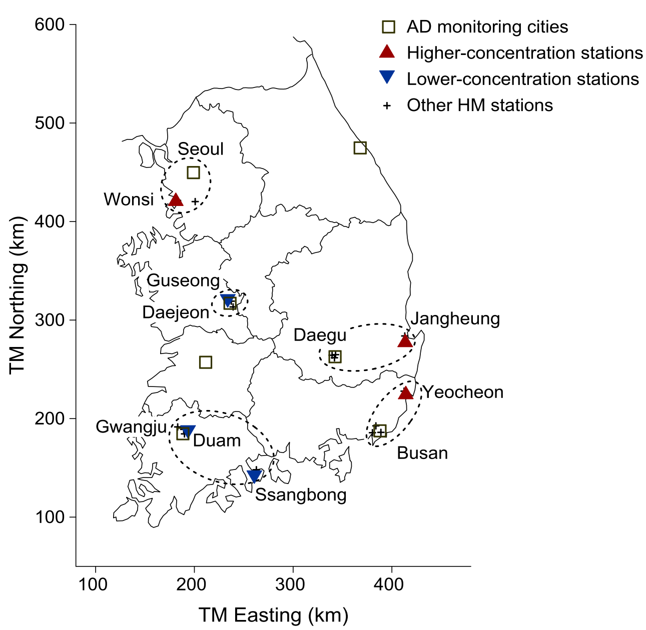


Fig. 1 Locations of six heavy metal monitoring stations for this study. Three stations each represent higher and lower concentrations, respectively. *Crosses* denote other heavy metal monitoring stations that continuously operated during the 1999–2012 study period. *Open squares* denote the cities where Asian dust (*AD*) is monitored. *Dashed ovals* show the region in Table 2 including the AD monitoring cities. *TM* Transverse Mercator

Table 2 Means and standard deviations of heavy metal concentration ratios at 21 stations during the study period (1999–2012)[a]

Region	Station	Zone[b]	Pb (58.1)[c]	Cd (2.09)	Cr (8.60)	Cu (159)	Mn (78.6)	Fe (1270)	Ni (9.03)
Northwest	Sinpung	R	0.94±0.83	0.68±0.80	0.39±0.63	0.97±1.19	0.42±0.36	0.63±0.71	0.39±0.66
	Wonsi	**I**	**3.13±3.36**	**2.07±2.59**	**1.58±2.56**	**2.57±2.54**	**0.77±0.58**	**1.17±1.53**	**1.69±2.40**
Midwest	Eumnae	I	1.95±1.98	0.58±0.59	1.09±1.10	0.47±0.81	0.78±0.60	1.15±0.94	1.31±4.92
	Munchang	C	0.76±0.63	0.51±0.55	0.28±0.32	0.29±0.30	0.34±0.35	0.55±0.57	0.40±0.47
	Guseong	***O***	***0.67±0.50***	***0.46±0.50***	***0.28±0.36***	***0.19±0.20***	***0.33±0.38***	***0.49±0.60***	***0.36±0.46***
Southwest	Nongseong	R	0.66±0.67	0.62±0.73	0.52±0.90	1.51±1.78	0.45±0.35	0.81±0.69	0.41±0.47
	Seo	O	0.56±0.51	0.55±0.57	0.47±0.99	1.23±1.42	0.45±0.60	0.60±0.42	0.39±0.55
	Ilgok	I	0.71±0.67	0.73±0.69	0.45±0.96	1.64±1.86	1.04±1.56	0.66±0.50	0.45±0.55
	Duam	***R***	***0.54±0.56***	***0.55±0.83***	***0.48±1.14***	***1.16±1.37***	***0.41±0.36***	***0.68±0.57***	***0.42±0.64***
	Samil	M	0.46±0.52	0.43±0.48	0.80±2.35	1.32±1.76	0.45±0.50	0.54±0.70	0.68±1.26
	Ssangbong	***C***	***0.48±0.61***	***0.45±0.51***	***1.05±2.84***	***0.85±1.31***	***0.43±0.46***	***0.59±0.64***	***0.78±1.84***
Southeast	Jeonpo	C	1.04±0.93	0.87±0.70	1.44±1.26	0.63±0.66	0.80±0.52	1.15±0.86	1.21±0.85
	Gamjeon	I	1.81±1.22	1.63±1.90	3.68±2.63	1.13±0.80	1.56±1.18	2.08±1.73	2.86±1.93
	Deokcheon	R	0.80±0.57	0.77±0.77	1.04±1.17	0.38±0.34	0.63±0.48	0.86±0.78	0.88±0.72
	Yeocheon	**I**	**1.19±1.18**	**4.70±9.06**	**1.26±1.69**	**1.02±1.12**	**1.38±1.49**	**1.55±1.31**	**1.65±1.57**
	Yaum	R	0.80±0.74	0.99±1.46	0.49±1.25	0.97±1.54	0.57±0.47	0.83±0.66	0.65±1.27
Mideast	Suchang	C	0.98±0.72	0.81±0.77	0.84±0.97	0.79±0.76	0.61±0.55	0.97±0.88	0.75±0.70
	Ihyeon	I	0.98±0.65	1.65±2.44	0.94±0.91	1.07±1.40	0.76±0.66	1.09±0.85	1.54±1.39
	Daemyeong	R	0.72±0.54	0.68±0.72	0.55±0.69	0.97±0.96	0.50±0.42	0.77±0.68	0.58±0.54
	Jangheung	**I**	**1.28±1.10**	**0.90±1.65**	**2.90±5.56**	**0.78±0.80**	**7.67±7.95**	**3.34±1.80**	**3.13±8.46**
	Jukdo	C	0.54±0.62	0.37±0.76	0.49±3.79	1.03±1.86	0.66±1.59	0.49±0.64	0.47±2.97

[a] Means ± standard deviations at each station are divided by the concentration averaged over all stations shown in the table. In-depth analysis was made for six selected stations, and their concentration data are shown in *bold* as being representative of lower (shown in *italic*) and higher (*underlined*) concentrations

[b] *C* commercial; *I* industrial; *M* mixed use (residential, commercial, and light industrial); *O* open space (all remaining areas except building lots and roadways); *R* residential

[c] Mean concentration (ng/m^3) of all monitoring stations shown in the table

month over 14 years; the total number of daily data by monitoring station ranges from 720 to 845.

To compare the differences in concentrations at each station (acknowledging a wide range of concentration values per heavy metal), the mean and standard deviation for each heavy metal was divided by the mean averaged over all 21 monitoring stations. Concentrations of Mn, Fe, and Ni are markedly high at Jangheung, which is located within the steelmaking IC in the Mideast. Similarly, the concentration of Cr is second highest at Jangheung. On the other hand, the concentrations are not that high at Jukdo, which is located in the commercial district about 3–4 km north of the same steelmaking IC. However, large variations in the concentrations of Cr, Mn, and Ni exist, as indicated by large standard deviations, although their mean concentrations are not high. In contrast, concentrations of Pb and Cu are the highest at Wonsi within the IC in the Northwest, Cd is the highest at Yeocheon, and Cr is the highest at Gamjeon within the IC in the Southeast. The lowest concentrations were reported at the following stations: Guseong in the Midwest for Cr, Cu, Mn, and Ni; and Jukdo in the Mideast for Cd and Fe. Concentrations of Pb were the lowest at Samil, even though that location is near the petrochemical IC in the Southwest.

To examine the variability in concentrations more closely, six stations were selected by region, with three each representing lower and higher concentrations. Jangheung in the Mideast (within the steelmaking IC), Wonsi in the Northwest (within the general IC), and Yeocheon in the Southeast (within the petrochemical IC) represent the higher-concentration stations. Guseong in the Midwest, and Duam and Ssangbong in the Southwest, represent the lower-concentration stations. The meaning of “by region” in this analysis is explained in the following examples. In the Midwest, although the concentrations are also low at Munchang, Guseong was selected as being the station representative of the characteristics of lower concentration areas because its concentrations are slightly lower than those at Munchang. In the Southeast, the concentration of Cd is the highest at Yeocheon while that of Cr is the highest at Gamjeon. However, Yeocheon was selected as the station to represent the characteristics of higher concentrations because it is within the petrochemical IC, while Gamjeon is also within the same general IC as Wonsi.

Levels of concentrations

Table 3 compares the concentration ranges among the stations listed in Table 2 with those from other studies in South Korea and other parts of the world. For reference, ambient air quality standards for heavy metals from the WHO and the EU as well as Korea are included, as available. Compared to Table 2, in which averages over the study period are presented by station, annual averages are listed in Table 3, when data from long-term monitoring (extending over more than 1 year) are available, for two reasons: (1) to compare with standards for annual average concentrations; and (2) to compare with annual averages by station, if available, due to differences in monitoring timing and period.

For Pb, the annual-average standard of 500 ng/m^3 is the same for the WHO, the EU, and Korea. From the data for Korea evaluated in this study, all annual-average concentrations are below the standard, although measurements were made at a variety of stations ranging from residential to heavy industrial areas over a relatively long period of time. The highest concentration of 409 ng/m^3 reported in this study was about 76 % higher than that of 232 ng/m^3 from the EMEP station. Note, however, that this study includes stations in industrial areas, whereas EMEP stations represent background measurements. The highest annual-average Pb concentration in this study occurred at the Wonsi station (see Fig. 1 for the location) in 2000. Among the EMEP stations, the highest Pb concentration was recorded at the Ispra station in northern Italy in 1989, assumed to result from high anthropogenic emissions; the annual-average Mn concentration was also the highest at the same station in the same year.

In contrast to the high annual-average concentrations, the mean Pb concentration of annual averages over all 21 stations in this study, 58 ng/m^3, is well below the standard. The mean Pb concentration at EMEP stations is 13 ng/m^3, about one-fifth of the mean concentration calculated in this study. For comparison, heavy metals were monitored in two US urban areas; the measurement periods fall in the later part of the first half of the EMEP monitoring period and are before the period covered in the current study. Except for Fe, the average concentrations for the study metals in the two US urban areas are slightly higher than those reported for EMEP. Considering that the concentrations of heavy metals in the USA. are likely following the same decreasing trend as observed in Europe (Pacyna et al. 2007, 2009), concentrations of heavy metals in the USA might be similar to those for EMEP.

For Ni, interestingly, the highest concentration of 971 ng/m^3 from an EMEP station is more than ten times the highest concentration in this study, 96 ng/m^3. This is because the concentration at East Ruston in southeast England was exceptionally high in 2000, and the second-highest concentration of 178 ng/m^3, recorded at Chopok in Slovakia in 1987, was also high. The highest concentration at East Ruston was elevated only in 2000, which is judged to be an outlier because typical concentrations ranged from 0.7 to 4.2 ng/m^3 in other years of the 1989–2002 period. However, because Ni concentrations at Chopok were 91 ng/m^3 until 1993 and because Thöni et al. (2011) reported that there is a difference in variability of concentrations of heavy metals between Eastern and Western Europe, these values are assumed to be statistically valid. Excluding the highest value of 971 ng/m^3 at East Ruston reduces the average Ni concentration calculated for EMEP stations to 3.6 ng/m^3.

More than a few annual averages for Cd, Mn, and Ni in this study exceeded the WHO or EU standards because of higher concentrations in industrial areas. Concentrations of heavy metals reported in Korea to date fall within the ranges presented in this study. Measured concentrations in industrial areas are high, but in the case of Fe, concentrations in Seoul approach the highest reported in this study because of particularly high levels caused by AD (Choi et al. 2001). However, the concentration at Jangheung, which is located within a steelmaking IC in the Mideast (see Fig. 1), was the highest in 2005; this was likely due to the influence of anthropogenic pollution.

Except for Pb and Cr, average concentrations of heavy metals in Japan are generally lower than those in Korea. Given that the study period in Japan is earlier than that evaluated for China or Korea, this trend is even more apparent. In contrast, average concentrations in China are mostly higher than those in Korea. The differences among China, Korea, and Japan are especially prominent for Mn, Fe, and Ni; mean concentrations are highest in China (mean of average concentrations given in Table 3) and lowest in Japan. Mean concentrations of Fe and Ni in Japan are even lower than those reported for US urban areas.

Variations in concentrations by station

Figure 2 shows the mean concentrations of heavy metals at the six stations selected for this study. The variation among stations as estimated by the coefficient of variation is large for Cd. The variation for Mn is larger but is reduced when Jangheung's highest concentration is excluded. Since the highest concentrations can be greatly influenced by local characteristics, variations are examined by excluding those values; they are higher for Cd, Cr, Mn and Ni and lower for Pb, Cu, and Fe. These findings are the same even when all monitoring stations listed in Table 2 are included. In other words, concentrations of Cd, Cr, Mn and Ni are generally

Table 3 Concentration of heavy metals in air for selected regions along with available air quality standards (ng/m^3)[a]

Organization or country	Region, period	Site characteristics	Sample	Pb	Cd	Cr	Cu	Mn	Fe	Ni	Source
WHO	Standards			500	5			150			WHO (2000)
EU	Standards			500	5					20	EU (2012)
Korea	Standard			500							KME and NIER (2009)
	Nationwide, 1999–2012	Various types[b]	TSP	1.4–409 (58.4)[c]	0.01–32 (2.09)	0.06–57 (8.65)	11–924 (159)	5.7–897 (78.8)	115–6,645 (1,274)	0.5–96 (9.11)	This study
	Ulsan, 2007	Residential, industrial areas[d]	TSP	46–151	2.0–4.0	4.1–8.3	140–178	55–174	1,310–2,860	4.4–15	Lee and Park (2010)
	Daejeon, 1998–1999	Industrial area	PM_{10}	195–259	2.7–5.1	16–39	32–41	42–47	1,530–1,580	39–43	Kim et al. (2002)
	Seoul, 1998[e]	Urban	PM_{10}	59–110	1.2–3.7	9.6–12	30–53	36–152	1,200–6,420	6.4–12	Choi et al. (2001)
EMEP	Regionwide, 1987–2010	Regional background	Aerosol[f]	0.3–232 (12.9)	0.01–10 (0.40)	0.03–26 (1.75)	0.05–552 (5.15)	0.1–36 (6.4)	13–1,040 (162)	0.05–971 (6.1)	NILU (2012)
USA	Philadelphia, 1994; Phoenix, 1995–1998[g]	Urban	PM_{10}	41, 11	–[h]	2.4, 3.2	22, 16	9.5, 35	486, 1,390	11, 2.4	USEPA (2004)
Japan	Cities, 1974–1996[g]	Urban	TSP	18–174 (74.7)	–	1.1–44 (11.6)	8.2–101 (22.8)	6.5–70 (30.2)	158–1,250 (565)	1.5–14 (5.7)	Var et al. (2000)
China	Beijing, 2001–2006, 2005–2008[g,i]	Urban	TSP	369, 443	5.5, 14	18, 22	100, 157	240, 381	5,110, 9,070	16, 16	Okuda et al. (2008), Schleicher et al. (2011)
	Nanjing, 2010[g]	Urban	TSP	236	4.2	47.1	151	147	–	28.4	Hu et al. (2012)
	Guangzhou, 2003–2005[g]	Suburban, urban	TSP	219, 269	5.7, 7.9	17, 21	65, 82	65, 85	2,090, 2,860	–	Lee et al. (2007)

[a] Annual averages unless otherwise indicated

[b] Residential area, commercial area, open space, mixed use, and industrial area (see Table 2 for detailed information)

[c] Mean concentrations of annual averages for the study period

[d] Means on clear days and misty days are separately calculated. The range indicates means between residential areas on clear days and industrial areas on misty days

[e] Means for nondust, dust, and heavy dust days

[f] In the EMEP data, samples are categorized as aerosol, PM_{10}, $PM_{2.5}$, and PM_1

[g] Period means

[h] Not available

[i] Median values

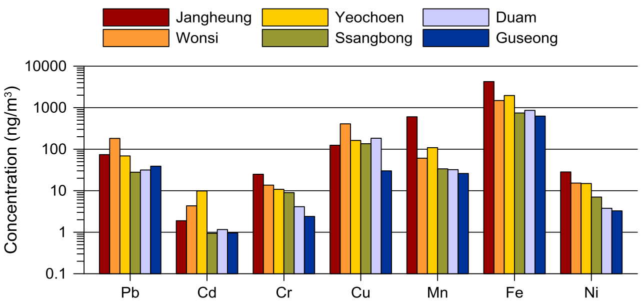


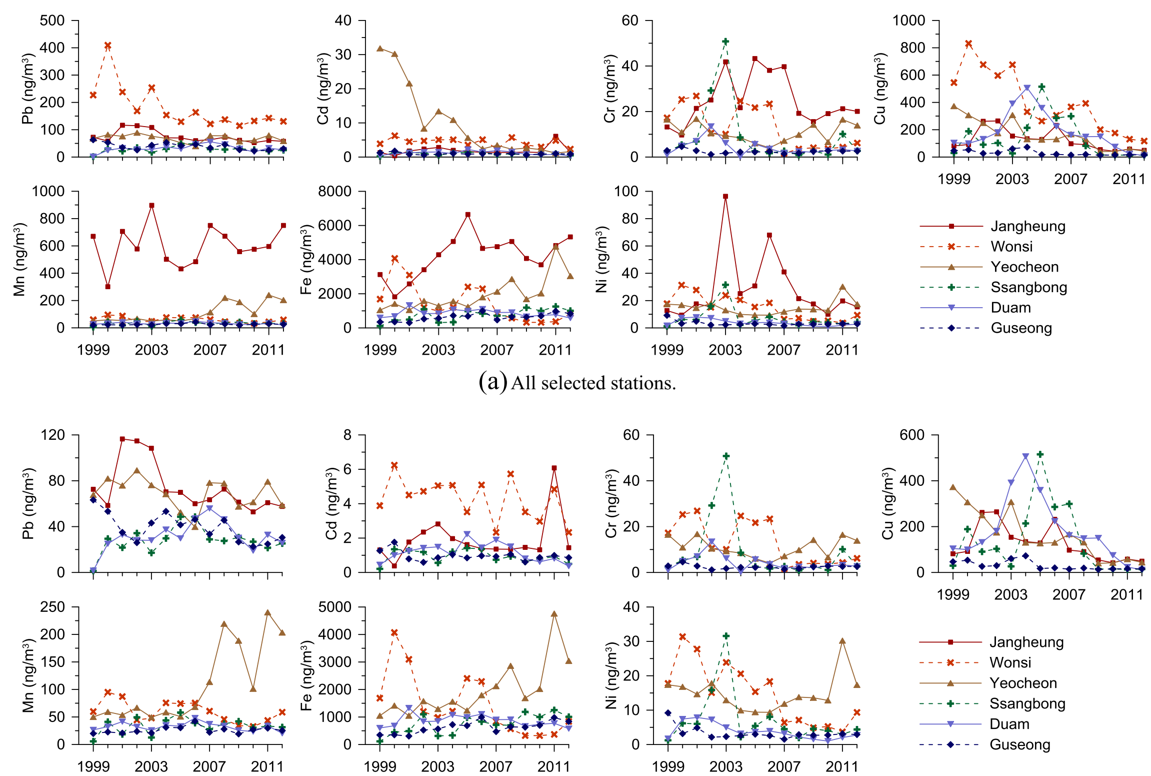
Fig. 2 Mean concentrations of heavy metals at selected stations for the period 1999–2012

determined by local characteristics, even when the highest concentrations are excluded.

Figure 3 shows variations of annual averages at the selected stations. Except for Cr and Cu, the concentrations at the station with the highest concentration are especially elevated; thus, the variability is noticeable (Fig. 3a). In Fig. 3b, the station with the highest concentration is excluded to highlight variations in concentrations at the other five stations. However, due to difficulties in understanding the year-to-year variability, estimates of the trends obtained using the Theil-Sen function — which is provided as a part of openair (open-source tools for analyzing air pollution data; Carslaw and Ropkins 2012) in the R package — are presented in Table 4. Since the Theil-Sen estimates are proportional to concentrations, they are divided by the mean concentrations of the six stations, considering a wide range of concentration values per heavy metal.

The variations in concentrations at stations with the highest concentrations were examined first, using the information shown in Fig. 3a and Table 4. Concentrations of Pb and Cu at Wonsi and Cd at Yeocheon decrease, with a significance level of $p<0.01$. In contrast, at Jangheung, all heavy metals show an increasing trend (with Cr, Mn, Fe, and Ni concentrations being the highest), although their significance levels are not high due to high variability (see Fig. 3a). In Table 4, concentrations of Cd and Cu decrease at all stations while Mn and Fe concentrations increase except at Wonsi and Duam. Concentrations of all heavy metals except Cd decrease at Wonsi, with a significance level of $p<0.05$.

Figure 4 shows the variations of monthly means at the six stations. Variations at stations with the highest concentrations are clearly evident in Fig. 4a as in Fig. 3a, but it is difficult to correlate monthly variations of the heavy metals. For Mn, seasonal variability is indicated by the higher concentrations in warmer months, a drop during the rainy period (July and August), and lower concentrations in colder months. However, the patterns for Mn at Jangheung in Fig. 4a are somewhat different from those at other stations in Fig. 4b



(a) All selected stations.

(b) Excluding the station with the highest mean concentration.

Fig. 3 Variability in annual average of heavy metal concentrations at selected stations for the period 1999–2012. **a** All selected stations. **b** Excluding the station with the highest mean concentration

Table 4 Theil-Sen estimates of the trends in annual-average concentrations (1999–2012)[a,b]

	Pb	Cd	Cr	Cu	Mn	Fe	Ni
Station	(70.5)[c]	(3.19)	(10.8)	(174)	(144)	(1655)	(12.1)
Jangheung	−0.025*	−0.003	0.009[d]	−0.065	0.069[d]	0.102[d]	0.005[d]
Wonsi	−0.134[d,]***	−0.038	−0.107*	−0.275[d,]**	−0.018*	−0.082**	−0.152***
Yeocheon	−0.016	−0.562[d,]***	−0.021	−0.126***	0.070***	0.088***	−0.004
Ssangbong	0.000	−0.014	−0.026	−0.011	0.003	0.039**	−0.015
Duam	0.009	−0.007	−0.021	−0.063	−0.002	−0.009	−0.040*
Guseong	−0.033*	−0.004	0.000	−0.010**	0.003	0.024*	−0.002

[a] Slopes are divided by the mean concentrations of the six stations shown in the table. *, **, and *** indicate p value less than 0.05, 0.01, and 0.005, respectively

[b] The first three stations represent higher concentrations, while the last three stations represent lower concentrations

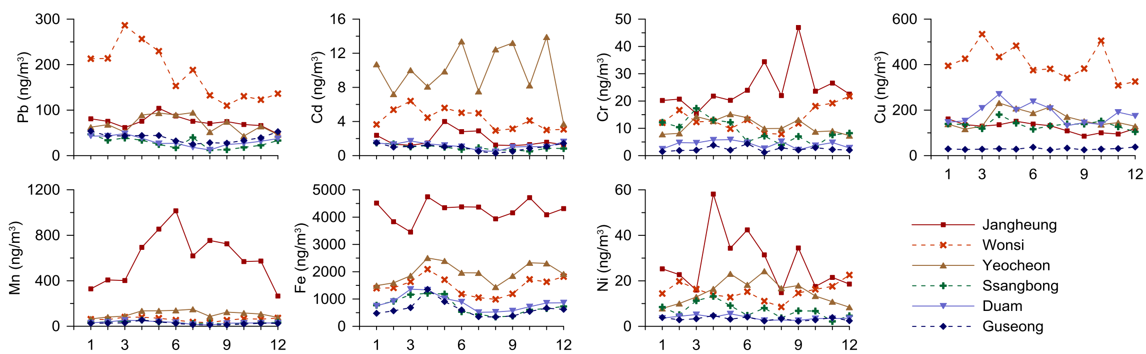
[c] Mean concentration (ng/m^3) of the six stations shown in the table

[d] Station with the highest mean concentration among the six stations.

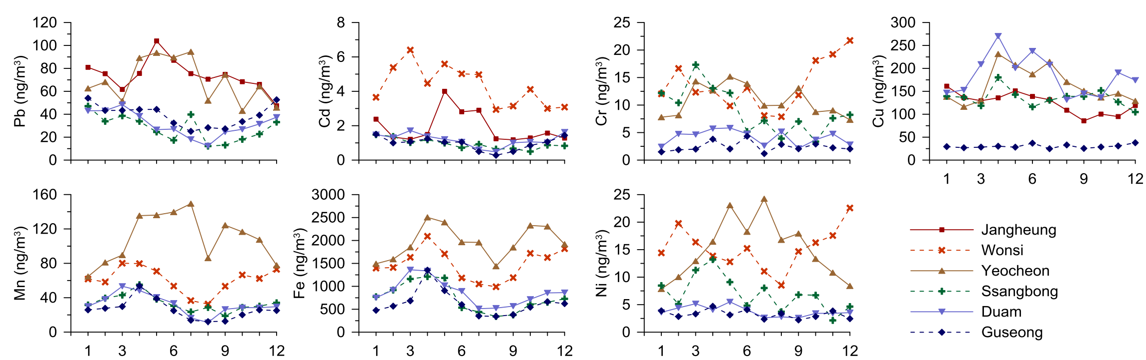
excluding Jangheung, the station with the highest mean concentration. Thus, the monthly variations of Mn at Jangheung are more likely due to local emissions than the season.

Kim (2007a, b) reported that concentrations of Pb and Cd were higher in spring and winter and lower in summer due to the influence of fuel use, meteorological conditions, and/or long-range transport from the Asian continent (primarily from China). In Korea, fugitive dust emissions are relatively high in spring due to low humidity and higher wind speeds along with the frequent occurrences of AD. In winter, when fuel use for heating is at its peak, the influence of anthropogenic emissions from fuel combustion is greater, irrespective of the effects of either other local emissions or long-range transport. In summer, concentrations of particulate matter are lower due to frequent rainfall and decreased inflow of air pollutants from the Asian continent.

Monthly means in Fig. 4 are grouped into seasonal means, and the ratios of mean concentrations for spring (March to



(a) All selected stations.



(b) Excluding the station with the highest mean concentration.

Fig. 4 Variability in monthly mean of heavy metal concentrations at selected stations for the period 1999–2012. **a** All selected stations. **b** Excluding the station with the highest mean concentration

May) to summer (June to August), and those for winter (December to February) to spring are presented in Table 5. The former ratio is assessed to examine the effect of fugitive dust, and the latter ratio is assessed to examine the effect of combustion emissions. Means of concentration ratios for the stations that represent higher and lower concentrations, respectively, are also presented for an overall comparison.

In assessing whether or not concentration ratios exceed one, it can be seen that ratios per heavy metal at stations representing the lower concentrations are mostly constant by station. This means that the influence of major sources by season is relatively uniform. Mean concentration ratios of spring to summer at stations representing lower concentrations are greater than those at stations representing higher concentrations. The ratios are higher, above two, for Mn and Fe in particular, which indicates the considerable influence of fugitive dust. All concentration ratios at stations representing the lower concentrations are above one except for those for Cr and Cu at Guseong. As shown in Fig. 4b, the concentrations of heavy metals at this station are markedly lower than at the other stations. The role of seasonal variations is unclear because the influence of sources near this station is minimal.

At all three stations representing lower concentrations, the concentration ratios for winter to spring exceed one for Pb and Cd, which suggests that combustion emissions have more influence than fugitive dust for these metals. However, the ratios of heavy metals at most stations are below one. Concentration ratios at the stations representing lower concentrations show smaller differences by heavy metal and by station, compared to those at stations representing higher concentrations. Stations representing higher concentrations are considered to be strongly affected by local emissions, which results in large variations among stations. In contrast, concentrations at the stations that represent lower concentrations, which are farther from anthropogenic emission sources of heavy metals, generally reflect patterns typical of background pollution. However, concentration ratios for Pb and Cd at these stations representing the lower concentrations are rather unusual. The relative effect of combustion emissions can be higher due to the lower concentrations in fugitive dusts that originate from soils, because lower levels of these metals have accumulated in those soils following deposition of similarly low airborne concentrations in the past. In fact, Cd and Pb in road dusts are more affected by emissions than Cu and Ni (Duong and Lee 2009). However, to elucidate the exact cause of this phenomenon, further investigation might be warranted.

Table 5 Concentration ratios of seasonal means[a]

Station	Pb	Cd	Cr	Cu	Mn	Fe	Ni
(a) Spring to summer							
Jangheung	1.03	0.96	0.72	1.10	0.82	0.99	1.22
Wonsi	1.63	1.27	1.20	1.32	1.88	1.68	1.24
Yeocheon	0.99	0.84	1.25	0.99	0.96	1.26	0.88
Mean	**1.22**	**1.02**	**1.06**	**1.14**	**1.22**	**1.31**	**1.11**
Ssangbong	1.40	1.40	2.62	1.14	1.65	2.70	2.03
Duam	1.97	2.00	1.29	1.18	2.32	1.92	1.56
Guseong	1.54	1.83	0.93	0.92	2.41	2.27	1.14
Mean	**1.64**	**1.74**	**1.61**	**1.08**	**2.13**	**2.30**	**1.58**
(b) Winter to spring							
Jangheung	0.84	0.75	1.10	1.00	0.51	1.01	0.61
Wonsi	0.73	0.74	1.45	0.79	0.84	0.85	1.32
Yeocheon	0.75	0.77	0.55	0.67	0.62	0.74	0.50
Mean	**0.77**	**0.75**	**1.03**	**0.82**	**0.66**	**0.87**	**0.81**
Ssangbong	1.18	1.15	0.72	0.86	0.77	0.68	0.54
Duam	1.09	1.03	0.62	0.70	0.69	0.68	0.78
Guseong	1.14	1.18	0.69	1.08	0.64	0.57	0.82
Mean	**1.14**	**1.12**	**0.68**	**0.88**	**0.70**	**0.64**	**0.71**

[a] The first three stations represent higher concentrations, while the last three stations represent lower concentrations. Means of concentration ratios for the three stations are provided at the bottom (in *bold*)

Typical features that signify local characteristics at the stations that represent higher concentrations are high summertime concentrations of some heavy metals, as illustrated by the data for Jangheung and Yeocheon in Table 5(a). Despite the dominant role of anthropogenic emissions, natural emissions of most heavy metals from soils are also substantial; however, these effects can be lessened by the scavenging effect of frequent precipitation in summer (Pacyna and Pacyna 2001; Vestreng et al. 2006). For comparison, the concentrations of Fe in Kawasaki, Japan, a steel industry area (similar to Jangheung), were higher in summer than in spring (Var et al. 2000); the authors noted that the higher summertime concentrations were due to the influence of the steel industry, although the reason for this influence was not provided. Hsu et al. (2005) reported that Zn concentrations, which were greatly influenced by vehicle emissions, were higher during daytime hours (from higher traffic volumes) and in summer. Kim (2007b) showed that seasonal means of Cd at Yeocheon (Table 5) were higher in fall and summer and explained that wet scavenging was difficult due to the high affinity of Cd to fine particles, along with emissions from surrounding areas. However, Table 5(a) shows that concentrations of several other heavy metals in addition to Cd are higher in summer at Jangheung as well as at Yeocheon. This study further concluded that higher summertime concentrations of heavy metals at Jangheung and Yeocheon are associated with activities at nearby ICs. However, the specific mechanisms underlying these phenomena have not yet been elucidated.

Variations in concentrations during the Asian dust period

The Ministry of Environment of Korea released information about AD days, i.e., those days in which AD was observed, for major cities by region (press release from Air Quality Management Division of KME, 2008.1.9). In Fig. 1, these cities are referred to as AD monitoring cities. During 1999–2012, the mean number of AD days is 9.0 per year, 5.6 of which fall in March and April (62 % of the total). For the six stations addressed in this study, the question of whether AD occurred was examined by using the data from AD monitoring cities within the same region shown, as shown in Fig. 1. The AD outbreaks are determined based on data from midnight to midnight, while heavy metal monitoring is done from late morning to the following morning for a 24-h period. Accordingly, measurement on an AD day is determined if either 1 or 2 days of heavy metal monitoring falls on an AD day.

Figure 5 shows the ratio of heavy metal concentrations during AD days relative to non-AD days at the six study stations. Figure 5a shows that for the whole year, relative concentrations of many heavy metals exceed one at most monitoring stations, which suggests that heavy metal concentrations are higher on AD days than non-AD days. In particular, relative concentrations of Mn and Fe are considerably elevated, and they are much higher at the stations that represent lower concentrations (including Guseong), which are less influenced by ICs. Albeit of anthropogenic origin, Cr concentrations at Yeocheon and Duam are higher for AD days. In contrast, relative concentrations of heavy metals other than Cu and Fe are less than one at Jangheung (i.e., lower on AD days). Compared with the mean concentrations in Fig. 2, the lower the mean concentration is (or the lower the effect from anthropogenic emissions, including from the IC), the larger the AD effect tends to be.

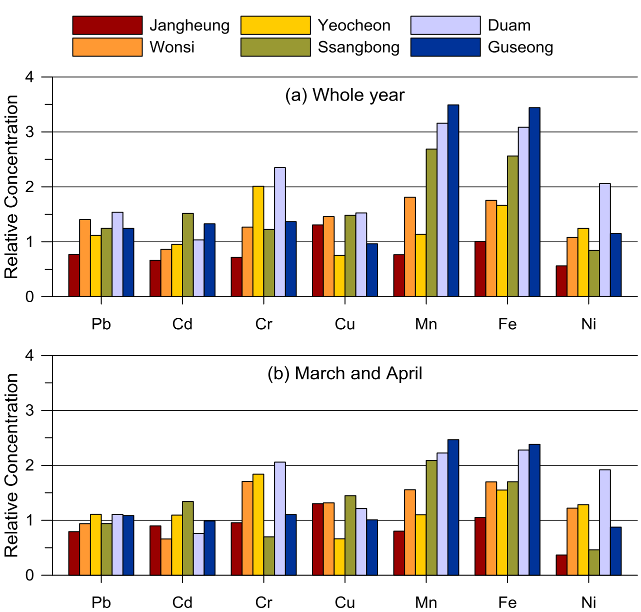


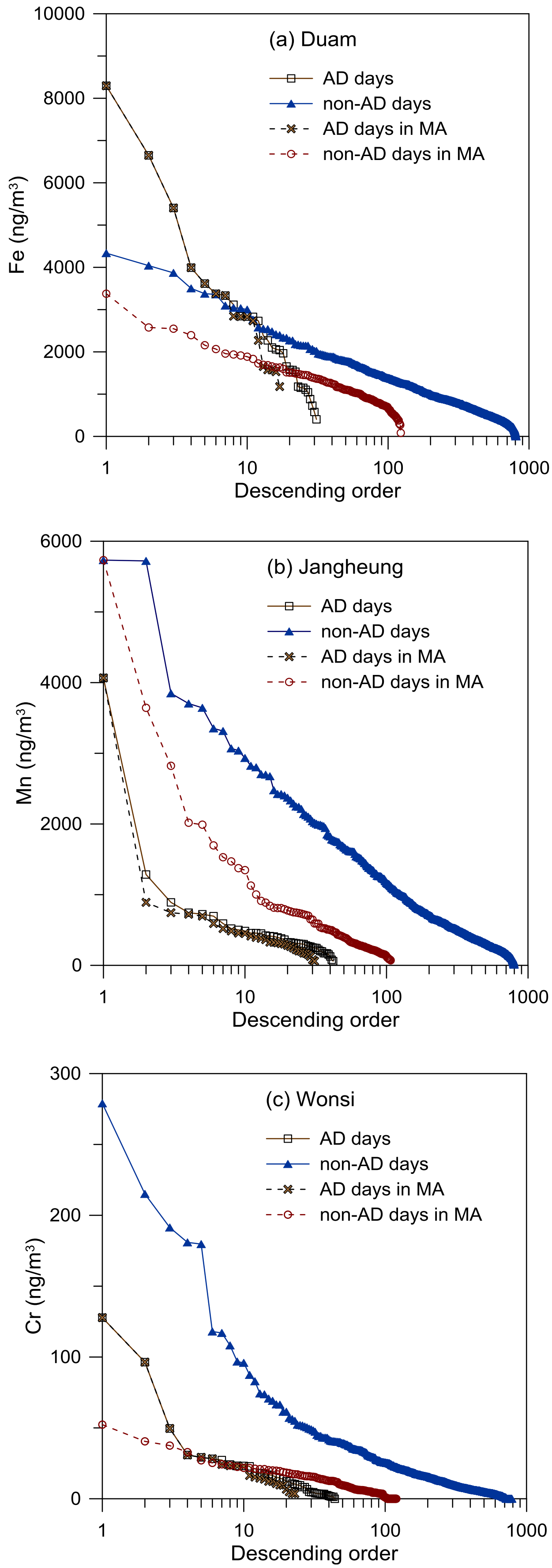
Fig. 5 Ratios of heavy metal concentrations on Asian dust days to those on non-Asian dust days over the whole year (**a**) and during March and April (**b**) for the period 1999–2012

If the data from March and April only (peak months for AD events) are considered, relative concentrations at the stations that represent lower concentrations generally decrease, particularly for Mn and Fe. As shown in Table 5, concentrations of Mn and Fe at these stations are higher in spring compared to summer and winter. When examining the variations of Mn and Fe as shown in Fig. 5a and b, it can be seen that concentrations of heavy metals are elevated in March and April even in the absence of AD. In contrast, low concentrations often occur over the whole year, with a main reason being frequent summer precipitation.

To examine the differences in mean concentrations between AD and non-AD days by heavy metal, concentration distributions for AD and non-AD days over the whole year and during April and March are compared in Fig. 6. For Fe, the concentrations at Duam are considerably higher on AD days, as shown in Fig. 5. Figure 6a shows that extremely high concentrations are observed on AD days; the three highest concentrations occur in March and April 2001, when severe AD events hit the Korean peninsula (Arimoto et al. 2006; Ghim 2011). A number of high concentrations are observed even on non-AD days, but the concentrations on AD days relative to non-AD days are higher, as shown in Fig. 5, due to the much larger number of low concentrations. The relative concentration for March and April is lower than that for the whole year, as shown in Fig. 5. As noted in the previous paragraph, this is because for non-AD days, the proportion of low concentrations in March and April is lower than that over the whole year.

During AD events, which typically involve elevated concentrations of crustal materials, relative concentrations are slightly above one for Fe and below one for Mn at Jangheung, as shown in Fig. 5. The latter is not because concentrations for the AD days are lower than those at other stations, but because concentrations for the non-AD days are higher than those for the AD days (see Fig. 6)). As shown in Fig. 2, Mn concentrations at Jangheung are markedly higher than those at other stations. The high concentration of Mn from nearby ICs is dispersed by strong winds accompanied by AD (Wu et al. 2009), mixed with a lower concentration of Mn from crustal materials for the AD days, which makes the relative concentration less than one.

In Fig. 5, the relative concentration of Cr at Wonsi is somewhat higher during March and April than that over the whole year. Concentration distributions for the AD days are similar for the whole year and for March and April, but concentrations for the non-AD days are very low in March and April (Fig. 6c). As seen at Duam, mean concentrations for the non-AD days over the whole year are generally lower than those during the non-AD days in March and April because of



◀ **Fig. 6** Comparison of selected heavy metal concentration distributions during Asian dust (AD) days and non-Asian dust days for the period 1999–2012. MA denotes March and April, when AD events are most frequent

the large proportion of lower concentrations. However, at Wonsi, a larger number of higher concentrations were observed during non-AD days over the whole year rather than in March and April (Fig. 6c). This is because of higher wintertime concentrations, as shown in Table 5(b), and the relative concentration over the whole year is lower than that of March and April.

Summary and conclusions

Six stations were selected to examine variations in heavy metal concentrations from 1999 to 2012 in Korea. Three stations located within ICs were selected to represent areas with higher concentration: Jangheung in the Mideast, Wonsi in the Northwest, and Yeocheon in the Southeast. Three were selected to represent stations with lower concentrations: Ssangbong in the Southwest, which is located near a large-scale petrochemical IC, and Duam in the Southwest and Guseong in the Midwest, which are not directly influenced by industrial sources.

Although industrial areas are included in this study, the annual-average concentrations for Pb at all stations are below the air quality standard, which is the same for WHO, EU, and Korea. However, concentrations for Cd, Mn, and Ni at some stations exceed the WHO and/or EU standards. On average, concentrations by station are higher than EMEP's background levels, and they are also higher than those reported for the USA and Japan — noting that those comparison data reflect the 1990s and 1970–1990s, respectively, when concentrations were likely to be higher than current levels. In Northeast Asia, which is located in the prevailing westerly regime, concentrations of heavy metals are generally higher in China and lower in Japan. These trends are apparent for Mn, Fe, and Ni, which are primarily of crustal origin.

During the study period, concentrations of all heavy metals except Cd decreased at Wonsi, at a significance level of $p<0.05$. By comparison, at Jangheung, all heavy metals, including Mn and Fe whose concentrations are highest, show an increasing trend although their significance levels are lower due to high variability. In addition to decreasing concentrations of Cd and Cu at all stations, as well as generally decreasing concentrations for other heavy metals, the concentrations of Mn and Fe — which are primarily of crustal origin — tend to increase except at Wonsi and Duam.

These findings can be interpreted as follows: higher concentrations in spring compared to summer can be attributed to the effects of crustal materials via fugitive dust, while higher concentrations in winter compared to spring are related to the effects of fuel combustion. Mean concentration ratios of spring to summer at the stations representing lower concentrations are greater than those at stations representing higher concentrations, especially those stations with a mean concentration ratio above two for Mn and Fe. Concentrations of many heavy metals are higher in spring than in winter. However, the concentrations of Pb and Cd at the three stations representing lower concentrations are higher in winter. This indicates that the effects of combustion emissions are higher due to lower concentrations of these two metals in fugitive dusts that originate from soils, due to the lower levels of those metals that have accumulated in soils following past deposition of similarly lower airborne concentrations. At Jangheung and Yeocheon, concentrations of heavy metals are higher in summer, which is presumed to reflect the influence of nearby ICs.

At most stations, the concentrations of many heavy metals are higher on AD days than on non-AD days. At the stations representing lower concentrations, the concentrations of Mn and Fe are particularly high on AD days; the Mn concentrations at Jangheung are especially high. During the non-AD period, the metal concentrations are frequently high due to the influence of the nearby ICs, and mean concentrations are usually higher than during the AD period. At Wonsi, the concentration ratio of AD periods to non-AD periods for Cr is higher in March and April than over the whole year. This is attributed to frequently high Cr concentrations in winter due to fuel combustion, and mean concentration increases during non-AD periods over the whole year.

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