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Pollution of airborne metallic species in Seoul, Korea from 1998 to 2010

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HIGHLIGHTS

- Long-term variations of metals are investigated using the data from urban areas of Seoul in Korea.
- The pollution status of seven metals is explored in association with changes in environmental conditions.
- The long-term reductions of metals reflect the effects of implementation of administrative efforts.

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ABSTRACT

A comprehensive analysis was made to characterize the long-term changes in concentration of seven key heavy metal species (iron (Fe), Copper (Cu), lead (Pb), manganese (Mn), chromium (Cr), nickel (Ni), and cadmium (Cd)) bound to total suspended particles (TSP) in Seoul, Korea, from 1998 to 2010. Their mean values over this period were: 1579 ± 652, 174 ± 54.3, 63.6 ± 8.60, 46.0 ± 15.2, 11.7 ± 9.58, 9.34 ± 8.87, and 1.78 ± 0.64 ng m^{-3}, respectively. Most of the metals exhibited a strong seasonality with maxima in spring (Mn, Fe, and Ni), winter (Pb and Cd), or fall (Cr and Cu) but minima in summer. The most prominent reductions of 71.5% (Pb) and 91.1% (Cu) were seen from early in the study period (1999–2002) to the most recent year (2010). Despite many advances in air quality, these latest concentration values were still higher than in many Western cities. It is thus still desirable to reduce their levels even further to ensure air quality improvement in the coming years.

1. Introduction

The emission of trace amounts of heavy metals to the atmosphere can have severe adverse effects on the quality of ambient air, surface and sub-surface water resources, and arable soils (Pacyna and Pacyna, 2001; Li et al., 2015). If not properly controlled, such emissions can impose a long-term burden on the biogeochemical cycling of entire ecosystems (Nriagu, 1988; Bai et al., 2011). Human exposure to airborne heavy metals has been linked to various diseases (e.g. cancer, developmental retardation, and kidney damage) (Ariane et al., 2001; Cheng, 2003; Zhang et al., 2015) and can even be fatal in cases of extreme exposure (Shi et al., 2011).

An overview of the current situation regarding heavy metal pollution in air was recently provided in a report by the European Monitoring and Evaluation Programme (EMEP) (Ilyin et al., 2011). Sources were noted to be primarily anthropogenic, typically as a result of traffic and industrial emissions (Park et al., 2008; Fang et al., 2010; Keshavarzi et al., 2015). Accelerated industrialization

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has resulted in heavy metal air pollution increasing largely unchecked around the world, especially in many developing countries (Wei and Yang, 2010; Thevenon et al., 2011; Yaylalı-Abanuz, 2011). The suite of airborne heavy metals commonly designated as targets for environmental monitoring and control include: Pb, Cd, Cr, Cu, Mn, Fe, and Ni (MSC-W, 2002).

Our research group has been involved in numerous projects to characterize the concentrations of key airborne heavy metal species in major urban areas on the Korean peninsula (e.g. Cu (Kim, 2014); Cr (Nguyen and Kim, 2008); Pb (Kim, 2007b); and Cd (Kim, 2007a)). This study simultaneously focused on the environmental behavior of seven species of atmospheric heavy metal pollutants (Pb, Cd, Cr, Cu, Mn, Fe, and Ni) using data acquired from the Seoul air quality monitoring network, operated by the Korean Ministry of the Environment (KMOE). The primary aim of this study is to provide valuable insights into the diverse factors and processes regulating the distribution of key heavy metal species in urban air.

2. Materials and methods

2.1. Site characteristics of the study area

Seoul, located on the Han River (37°34′0″N; 126°58′41″E), is the capital of South Korea. Designated as the world's third largest metropolitan area, it has a population of over 25.6 million (http://www.index.go.kr/potal/main/EachDtlPageDetail.do?idx_cd=2729), and contains almost 3 million registered vehicles. Since it is considered to have been one of the greatest beneficiaries of 'The Miracle on the Han River' (an economic boom), Seoul is also responsible for considerably large anthropogenic emissions. Recognizing the critical need to improve poor air quality in South Korea, the Korean government implemented new strategies for the management of urban air quality, including creation of an Air Quality Index (AQI) in the Seoul metropolitan area to track the distribution of key pollutants (Nguyen and Kim, 2008). Moreover, measures to reduce air pollution have been introduced in several forms such as regulations on factory emissions, incentives for low-pollution vehicles, introduction of compressed natural gas buses, improved traffic design to reduce congestion, and creation of additional green spaces. To characterize the airborne metal pollution of the Seoul area, we analyzed concentrations of seven key metal species (Pb, Cd, Cr, Cu, Mn, Fe, and Ni) measured as a part of routine KMOE air quality monitoring.

2.2. Data processing

The KMOE has established a number of heavy metal monitoring stations at major locations on the Korean peninsula. Information regarding the basic management and data acquisition systems of these stations has been described elsewhere (Kim et al., 2003; Nguyen and Kim, 2006; Kim, 2007b). For comparative analysis of heavy metal concentrations, daily-integrated TSP samples were collected and analyzed on a monthly basis from each monitoring station.

TSP samples for this study were obtained from 13 monitoring stations in Seoul (Fig. 1) over the period 1998 to 2010. Results were analyzed to evaluate the fundamental factors and processes regulating their behavior in the Seoul urban environment. To this end, heavy metal concentration data from all stations were pooled together to derive values representative of the citywide pollution at monthly intervals.

Aerosol sampling at each station was performed according to the KMOE standard air quality measurement protocol. Accordingly, TSP samples were collected by high volume samplers, and the heavy metals extracted from these samples were analyzed with the aid of atomic absorption spectrometry (AAS) (Kim et al., 2004). Samples were collected at a flow rate of 1.5 m^3 min^{-1} (a total volume of ~2100 m^3) using Whatman PM2000 glass fiber filters (0.1 μm pore-size and 99.9% collection efficiency). The collected samples were then pre-treated by immersing 23% of the filter cut into several pieces in 35 ml of acid solution, 6(HNO_3): 1(H_2O_2). Concentrations of the target metals were then analyzed using AAS. The detection limit of all the metals was found in different ranges: (1) 0.5 μg (in absolute mass (AM) or 0.25 ng m^{-3} (Cd); (2) 2–10 μg (in AM) or 1–5 ng m^{-3} (Pb, Cr, Mn, and Ni); and (3) 0.2 μg (in AM) or 0.1 ng m^{-3} (Cu and Fe). The measured concentrations were then quality controlled according to the KMOE procedures and stored in its data management network system.

3. Results and discussion

3.1. Basic features of airborne metallic species

Annual mean concentrations of each metallic species derived from monthly mean values from each station, averaged across the whole city, are summarized in Table 1. Based on means derived over the whole 13-year period, the highest concentrations were observed for Fe (1579 ng m^{-3}), followed by Cu (174), Pb (63.6), Mn (46.0), Cr (11.7), Ni (9.34), and Cd (1.78 ng m^{-3}) (Fig. 2). The relative mean concentrations of the seven metals was the same for each year of the study period, which has been reported in many previous studies (Var et al., 2000; Fang, 2006). The concentrations of atmospheric heavy metals (in ng m^{-3}) in 44 cities in China monitored over a 10-year period also showed a similar relative ordering: Pb (195) > Mn (75.0) > Cu (60.0) > Cr (45.0) > Ni (20.0) (Duan and Tan, 2013).

Annual mean concentrations of most metals observed showed maximum values early in the study period (e.g. during 2001 for Mn and Fe; and 2002 for Cd, Cr, and Ni; Fig. 3). By contrast, the lowest concentrations for all metals were consistently encountered in the most recent year of the study (2010). Consistent, gradual decreases in atmospheric heavy metal concentrations of this kind are not uncommon, as evident in the results of a comparable study from 16 Japanese cities during the period from 1974 to 1996 (Var et al., 2000).

3.2. Seasonality of airborne metallic species

Changing meteorology and source/sink patterns can result in a pronounced seasonality in observed TSP heavy metal concentrations (Duan and Tan, 2013). In order to characterize the seasonal variability of airborne metals in Seoul, the monthly concentration data were subdivided by season according to: spring (March to May), summer (June to August), fall (September to November), and winter (December to February).

The seasonal cycles of heavy metals were characterized by minimum concentrations in summer, and maximum concentrations in: winter (Pb and Cd), fall (Cr and Cu), or spring (Mn, Fe, and Ni) (Table 2). Pb and Cd exhibited a similar seasonality a winter maximum, followed by spring, fall, and summer (Fig. 1S). The seasonality of Mn and Fe were also similar, with spring > winter > fall > summer. In contrast, Cr and Cu exhibited maximum values in fall. The enhanced metallic concentrations in spring and winter may be due to the Asian dust particles to reflect

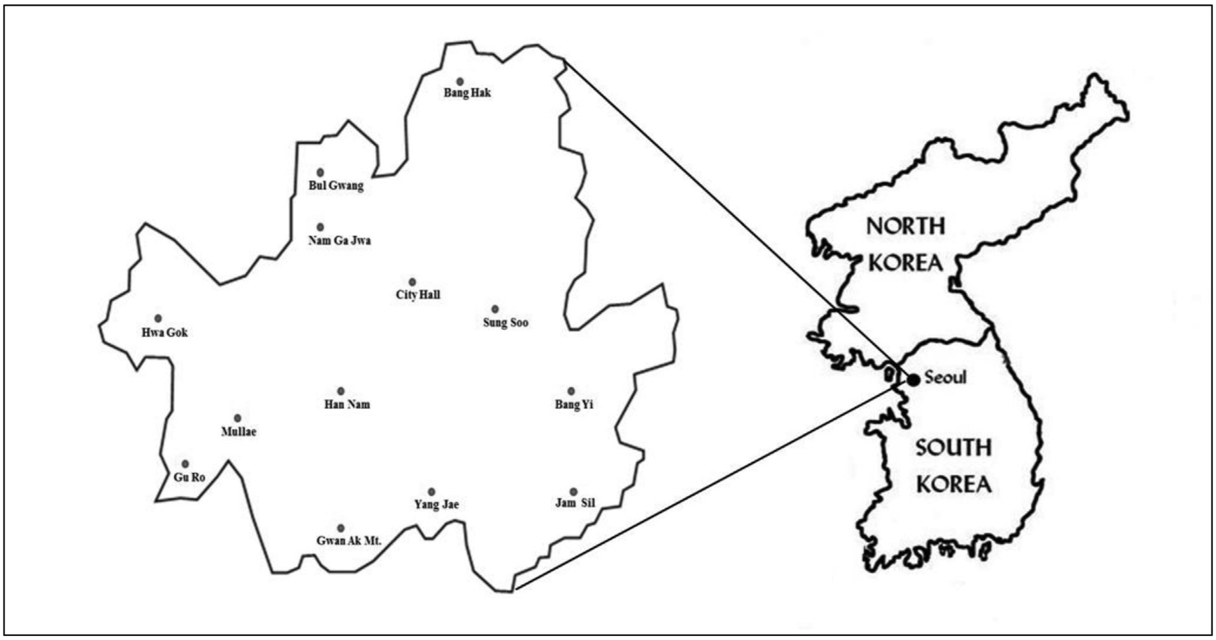

Fig. 1. Geographical locations of 13 individual stations selected for the monitoring of airborne metals in Seoul, Korea (1998–2010).

the considerable contribution of the Chinese continent (Zhuang et al., 2002; Lee et al., 2004). Conversely, their reduced values in summer should possibly reflect the combined effects of decreased Asian dust effect, increased precipitation and dilution, and mixing effects of the marine air mass from the south (Yang et al., 2003; Lee and Hieu, 2011). A winter maximum of Cd was also reported from Beijing, China, and attributed to the enhancement of combustion activities (Yang et al., 2003). Similarly, the winter dominance of many metals (Pb, Cd, Ni, Mn, and Fe) has been commonly observed elsewhere, e.g., Kolkata, India from November 2003 to November 2004 (Karar and Gupta, 2006).

As a simple means to check the statistical significance of the observed seasonality, a *t*-test for each metallic pollutant was conducted by examining the difference between the maximum and the second highest seasonal mean values. In Table 1Sa, the results of all metals were statistically significant ($p < 0.001$), showing that their seasonality was strong enough except for Cd ($p = 0.293$). However, such strong seasonality can be explained due to the influence of meteorological conditions. Little vegetation and relatively strong wind in winter can contribute to an increase in airborne metal concentration levels (Hao et al., 2007). The analysis of principal component analysis (PCA) (presented in Table 3S) also indicate a noticeable effect of such variations with temperature and precipitation. Analysis of the Mann–Kendall (hereafter MK) test can also be used to assess seasonal trends in other respects. The MK non-parametric method is an efficient statistical tool for analyzing long-term trends of a given pollutant (Yue et al., 2002). For the MK test, a monotonically increasing or decreasing trend is evaluated along with the non-parametric Sen's method for estimating the slope of a linear trend; the presence of a trend and its qualitative result can then be developed into a quantitative metric by calculation of a slope using Sen's method (Gilbert, 1987; Hamed, 2009). The MK test for seasonal trends (presented in Fig. 2S) demonstrated a random distribution, as they were plotted using their monthly mean values over the entire study period. However, seasonal MK trends indicated negative slope (Q) values for all pollutant species, while the confidence level for almost all cases was above 95% (with an exception for Fe ($p = 0.283$) only).

3.3. Long-term trends of airborne heavy metal species

Analyzing long-term variations in pollutant concentrations is an important tool in understanding long-term changes in the source processes of airborne metallic pollutants (Brox and Malik, 2010). To assess the long-term (inter-annual) trends of metallic pollutants at our study site, an MK test was conducted using annual mean values collected over the entire study period. Based on the MK test results (Table 1Sb), the slope for each metallic pollutant confirmed that the reduction occurred constantly throughout the period. The magnitude of reduction, however, appears to differ greatly between metals (Fig. 4). Among all the metals analyzed, Cu showed the maximum slope (-21.2 ng m^{-3} yr^{-1}, with a statistical significance of $p = 0.000$). Fe also indicated a high slope (-16.9 ng m^{-3} yr^{-1}), although its confidence level only slightly exceeded 95% (i.e., $p = 0.510$). By contrast, Cd exhibited the lowest slope (-0.068 ng m^{-3} yr^{-1}, $p = 0.042$). In line with the general patterns of most metals, the results of PM_{10} also exhibited a moderate reduction, with a slope of -1.45 μg m^{-3} yr^{-1} ($p = 0.015$).

To learn more about the temporal variations in Seoul's heavy metal pollution, we compared the percentage reduction in mean annual concentrations of airborne heavy metals from the first (1998) to the last year (2010) of our study. Accordingly, reductions in concentration were found in the following order: Cu (91.1%) > Cr (88.2%) > Ni (82.2%) > Cd (72.4%) > Pb (71.5%) > Mn (62%) > Fe (61.1%). Although there is noticeable concentration peaks between 2000 and 2005, the considerable reductions of metals seen consistently across the latest years (from 2005 to onwards) may reflect the effect of mitigation efforts for heavy metal emissions

Table 1
Summary of the annual mean concentrations of seven airborne metal species (Pb, Cd, Cr, Cu, Mn, Fe, and Ni: ng m^{-3}) along with PM_{10} (μg m^{-3}) data measured in Seoul, Korea between 1998 and 2010 (the annual mean values of each metal were derived using their monthly data).

Pollutant species	1998	1999	2000	2001	2002	2003	2004
Pb	93.6 ± 36.4[a] (101)[b] 48.4–160[c] (12)[d]	98.4 ± 37.2 (107) 43.8–148 (12)	82.5 ± 33.0 (84.1) 3.80–126 (12)	75.4 ± 39.7 (67.3) 25.9–153 (12)	83.2 ± 20.9 (84.3) 40.5–116 (12)	58.4 ± 28.1 (57.5) 26.8–105 (12)	78.7 ± 33.3 (79.2) 37.4–141 (12)
Cd	1.68 ± 0.59 (1.70) 0.50–2.70 (12)	1.73 ± 1.04 (2.10) 0.30–3.10 (12)	1.81 ± 2.08 (1.30) 0.00–7.80 (12)	2.98 ± 1.41 (3.00) 0.20–5.10 (12)	3.55 ± 1.63 (3.30) 1.40–6.20 (12)	2.55 ± 2.23 (1.65) 0.10–6.90 (12)	1.68 ± 1.88 (1.30) 0.00–6.80 (12)
Cr	7.59 ± 3.59 (8.35) 0.20–13.7 (12)	10.9 ± 7.14 (9.35) 2.00–25.7 (12)	10.6 ± 3.90 (10.2) 3.90–17.3 (12)	17.4 ± 7.22 (15.9) 5.00–29.5 (12)	35.4 ± 34.3 (25.9) 9.40–136 (12)	7.65 ± 2.98 (6.30) 4.30–12.9 (12)	11.5 ± 4.61 (10.8) 4.30–21.1 (12)
Cu	239 ± 61.4 (239) 144–352 (12)	241 ± 112 (280) 53.0–443 (12)	340 ± 188 (266) 144–691 (12)	211 ± 42.0 (205) 155–294 (12)	266 ± 82.0 (246) 169–435 (12)	312 ± 141 (283) 122–610 (12)	146 ± 73.7 (134) 58.2–308 (12)
Mn	38.6 ± 10.2 (36.9) 15.6–52.8 (12)	42.5 ± 19.5 (38.6) 17.8–76.2 (12)	49.6 ± 16.8 (52.0) 25.5–73.9 (12)	80.0 ± 67.5 (57.0) 22.2–255 (12)	58.6 ± 20.9 (56.5) 32.2–104 (12)	39.4 ± 10.3 (38.3) 28.4–58.0 (12)	61.1 ± 31.0 (59.0) 26.2–142 (12)
Fe	1209 ± 430 (1178) 534–2442 (12)	1284 ± 602 (1378) 375–2138 (12)	1731 ± 586 (1833) 937–2594 (12)	2833 ± 2811 (1838) 763–10,790 (12)	1941 ± 977 (1422) 921–3757 (12)	1225 ± 360 (1179) 658–1959 (12)	2145 ± 1332 (2096) 736–5772 (12)
Ni	8.13 ± 3.79 (6.55) 4.40–17.8 (12)	7.10 ± 4.24 (6.10) 1.10–14.2 (12)	7.58 ± 3.94 (7.00) 1.70–14.6 (12)	15.8 ± 12.5 (15.3) 1.00–38.8 (12)	19.8 ± 34.5 (10.6) 1.30–126 (12)	15.1 ± 6.42 (14.9) 3.90–27.4 (12)	8.38 ± 2.89 (8.90) 3.60–14.1 (12)
PM_{10}[f]	59.3 ± 12.4 (59.0) 36.0–80.0 (12)	68.4 ± 12.8 (72.5) 39.0–81.0 (12)	65.0 ± 13.7 (67.0) 37.0–80.0 (12)	72.5 ± 20.4 (77.0) 37.0–104 (12)	75.8 ± 32.7 (67.5) 41.0–149 (12)	69.8 ± 15.6 (73.0) 47.0–93.0 (12)	60.7 ± 14.0 (65.0) 35.0–81.0 (12)

[a] Mean ± Standard Deviation (SD).
[b] Numbers in parenthesis denote the median value.
[c] Range = Minimum-Maximum.
[d] N = Number of monthly data; and.
[e] N = Number of total data (from 1998 to 2010).
[f] Computation of PM_{10} was made using its monthly data.

(Barrett et al., 2013; Steinle et al., 2013). Another factor contributing to the constant decrease in heavy metal concentrations in the recent years is the intensive efforts to control PM emissions in Korea (Kim and Shon, 2011). However, a large reduction observed in the case of Cu, compared to the smaller changes in Fe and Mn, indicates that the mitigation efforts can only have large impact on metals of primarily anthropogenic origin compared to those with also natural sources (Nguyen and Kim, 2008; Shon and Kim, 2011; Kim, 2014).

The trend of airborne heavy metal concentrations in the Northwestern Mediterranean (between 1986 and 2008) indicated a remarkable reduction (for instance, Pb and Cd concentrations decreased from 29.3 to 3.33 ng m^{-3} and 0.27 to 0.09 ng m^{-3}, respectively). These findings demonstrate the response of the atmospheric environment to the implementation of an antipollution policy in that region (Heimbürger et al., 2010). Brown et al. (2008) also observed significant downward trends for Pb, Ni, and Cd in ambient particulates (PM_{10}) in the UK from a nationwide air quality management network over a 25 year period (1980–2005). In our previous study, long-term changes in airborne toxic metals were also evaluated using the data sets collected from South Korea's two largest cities (Seoul and Busan) from 1991 to 2004 (Kim et al., 2009). The results generally showed strong reductions in metal concentrations (e.g., Pb, Cd, Mn, and Ni) throughout the period.

3.4. *Factors affecting the behavior of airborne heavy metal pollutants*

To account for the factors and processes controlling the behavior of airborne metals in our model city, our measurement data were evaluated in a number of ways. As the first step, a correlation analysis was carried out using the monthly data sets of each metal species and other parameters (Table 2S). Accordingly, Pb indicated strong correlations (high Pearson correlation (r) values) with Cd (0.533), Mn (0.577), and Fe (0.492). In contrast, the results of Fe and Mn (r = 0.897) were more noticeable (at the p = 0.01 level) throughout the entire study period (Table 2Sa).

Correlations were also analyzed for different time periods. Similarly strong correlations (r = 0.833, 0.773, 0.619, and 0.719) were observed for the pairs (Pb and Cd), (Pb and Mn), (Cd and Mn), and (Fe and Mn), respectively, in the earliest year (1998) (Table 2Sb). In contrast, the number of highly correlated pairs was high for most pollutant species in the latest year (2010) (Table 2Sc). The presence of this type of strong correlation among the metals (Pb, Cd, Mn, and Fe) reflects the fact that the pollution levels of these metals are maintained by similar anthropogenic sources (Li et al., 2009).

As a means to assess the source characteristics of the atmospheric heavy metal species, we carried out a principal component analysis (PCA) (Table 3S). Accordingly, the results for the seven heavy metals (Pb, Cd, Cr, Cu, Mn, Fe, and Ni) can be grouped into four component factors (Table 3Sa), which accounted for 65% of the total variability. Factor 1 had high loadings for Pb, Cd, Mn, and Fe, which explained 29% of the total variance. This factor was likely associated with such source processes as steel, plastics, and pigments production (Pb, Cd, and Fe), and gasoline/coal combustion (Mn) (Kauppinen and Pakkanen, 1990; Loranger et al., 1995; Tian et al., 2010; Li et al., 2012). Factor 2 explained 15% of the total variance, suggesting the potent role of high loadings of road dust (Fe) and petroleum/coal combustion (Mn and Ni) (Manoli et al., 2002; Tian et al., 2012). Factors 3 and 4 explained 12 and 8% of the total variance, respectively, indicating significant roles played by vehicle emissions (Cu and PM_{10}) and fuel combustion (Cr) (Tian et al., 2010; Xia and Gao, 2011). In addition, natural soil dust (i.e., Asian dust) is also likely to have high loadings with high correlations of Fe, Mn, Cr, and PM_{10} (Lee et al., 2004; Zhao et al., 2011). Our findings indicate that most metals investigated in this study (Pb, Cd, Cu, Mn, Fe, and Ni) are emitted from similar sources such as traffic and industrial activities (Chen et al., 2005; Chang et al., 2009).

To investigate the potential impact of the time factor in these

2005	2006	2007	2008	2009	2010	All (1998–2010)
44.2 ± 19.2 (45.3)	42.1 ± 21.2 (36.4)	54.2 ± 36.2 (43.2)	45.3 ± 24.0 (39.7)	43.2 ± 22.0 (35.2)	28.0 ± 12.2 (28.7)	63.6 ± 22.7 (58.4)
16.0–81.3 (12)	13.1–77.1 (12)	6.00–106 (12)	17.8–87.7 (12)	7.10–74.9 (12)	10.1–45.6 (12)	28.0–98.4 (156)[e]
1.19 ± 0.71 (1.10)	1.14 ± 0.57 (1.00)	1.23 ± 0.98 (1.00)	1.28 ± 0.56 (1.40)	1.35 ± 0.60 (1.35)	0.98 ± 0.39 (1.10)	1.78 ± 0.78 (1.68)
0.40–3.11 (12)	0.40–2.20 (12)	0.20–3.40 (12)	0.50–2.00 (12)	0.50–2.70 (12)	0.40–1.50 (12)	0.98–3.55 (156)
20.1 ± 21.2 (8.65)	11.2 ± 8.84 (7.20)	4.85 ± 1.81 (4.70)	4.98 ± 1.73 (4.60)	5.19 ± 1.38 (5.40)	4.17 ± 1.59 (4.40)	11.7 ± 8.61 (10.6)
4.70–58.4 (12)	3.00–29.4 (12)	2.00–7.70 (12)	2.60–7.50 (12)	3.00–7.30 (12)	1.70–6.30 (12)	4.17–35.4 (156)
124 ± 25.4 (134)	143 ± 31.9 (140)	120 ± 28.0 (109)	55.0 ± 21.6 (50.4)	36.3 ± 12.7 (34.2)	30.3 ± 12.3 (31.4)	174 ± 103 (146)
74.6–152 (12)	97.6–205 (12)	95.3–191 (12)	33.8–107 (12)	18.7–57.8 (12)	13.0–49.1 (12)	30.3–340 (156)
41.4 ± 32.5 (36.8)	34.7 ± 12.9 (35.4)	37.7 ± 19.8 (41.7)	45.5 ± 20.4 (41.1)	38.6 ± 13.3 (40.3)	30.6 ± 14.6 (29.2)	46.0 ± 13.4 (41.4)
14.3–137 (12)	13.4–58.1 (12)	4.70–60.4 (12)	22.4–82.4 (12)	12.6–61.5 (12)	10.9–60.4 (12)	30.6–80.6 (156)
1410 ± 728 (1279)	1174 ± 504 (1148)	1497 ± 632 (1491)	1644 ± 701 (1528)	1333 ± 416 (1258)	1102 ± 548 (1079)	1579 ± 491 (1410)
545–3371 (12)	359–2251 (12)	268–2286 (12)	856–3370 (12)	574–2123 (12)	336–2156 (12)	1102–2833 (156)
11.9 ± 11.0 (5.75)	7.77 ± 6.53 (5.30)	4.23 ± 1.64 (3.85)	7.45 ± 4.58 (5.70)	4.73 ± 1.43 (4.60)	3.53 ± 1.40 (3.45)	9.34 ± 4.91 (7.77)
3.40–36.4 (12)	2.10–22.0 (12)	1.90–6.80 (12)	3.30–18.3 (11)	2.10–7.20 (12)	1.60–5.60 (12)	3.53–19.8 (155)
57.7 ± 13.0 (58.0)	59.9 ± 20.5 (62.0)	61.3 ± 18.6 (69.0)	55.4 ± 12.9 (61.0)	54.2 ± 14.0 (54.0)	49.2 ± 14.0 (50.5)	62.2 ± 7.72 (60.7)
36.0–83.0 (12)	33.0–106 (12)	31.0–86.0 (12)	32–73.0 (12)	31.0–81.0 (12)	25.0–71.0 (12)	49.2–75.8 (155)

source processes, we carried out a PCA for the first (1998) and last (2010) years, alongside an analysis for the entire period (1998–2010). The results derived for each period indicate some distinctions in the source processes for each of the three selected time periods. It shows that five main component factors are apparent in the latest period (2010: Table 3Sb), whereas four main component factors were apparent in the earliest year (1998: Table 3Sc). The sum values of these factors were found to account for 87% and 91% of total variability, respectively. In a previous study, the principal components for heavy metals in air in a residential area of Ulsan, Korea were identified to assess their industrial emissions and road air sources (like Fe, Zn, Cd, Mn, Pb, Cu, Cr, and Ni) (Lee and Hieu, 2011). Combustion emissions, crust related sources, and traffic related activities were also indicated as major sources of metal pollution in Beijing, China (Duan et al., 2012). A principal component analysis in Shenyang, China also revealed heavy metal contamination originating from traffic and industrial activities (Sun et al., 2010).

3.5. Status of heavy metal pollution between different studies

In Table 3, concentrations (ng m^{-3}) of airborne heavy metals from this study are compared with those measured from other places around the world. If concentrations from different sites are compared over a similar temporal band, a certain degree of spatial gradients can easily be observed. However, it is quite striking to find that there had been noticeable reductions across the study period, showing the lowest values in the latest years. For example, in Tokyo, Japan, Var et al. (2000) observed enhanced metal concentrations of Pb, Cr, Cu, Mn, and Fe (i.e., 124.7, 6.09, 30.2, 40.1, and 676.9 ng m^{-3}), respectively, during the period 1974–1996. In contrast, Furuta et al. (2005) reported noticeable reductions in concentration levels (39.2, 2.58, 11.9, 16.3, and 229 ng m^{-3}, respectively) in the later period (1995–2004). We observe similar reductions in metal levels after 2000 in the current study. Nevertheless, comparing our concentrations with those measured in many Western countries, a relatively large difference remains. Most of the Asian cities indicate enhanced levels of metallic pollution compared to Western cities. For instance, the lowest concentrations of almost all metallic species were observed in Helsinki, Finland (Pakkanen et al., 2001). Richard et al. (2011) also measured very low metallic concentrations (3.60, 0.90, 8.80, 1.60, 121, and 0.40 ng m^{-3} for Pb, Cr, Cu, Mn, Fe, and Ni, respectively) in Zurich and Kaseme, Switzerland between 2008 and 2009.

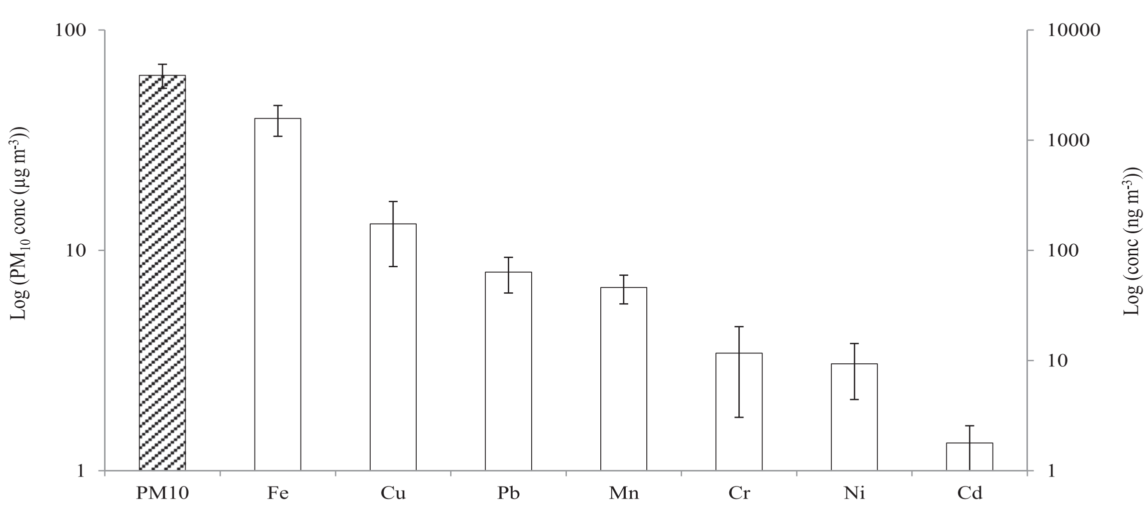

Fig. 2. Comparison of the mean concentrations of PM_{10} and airborne metals (M (in a secondary vertical axis) = Fe, Cu, Pb, Mn, Cr, Ni, and Cd) measured in Seoul, Korea between 1998 and 2010 (error bar denotes SD).

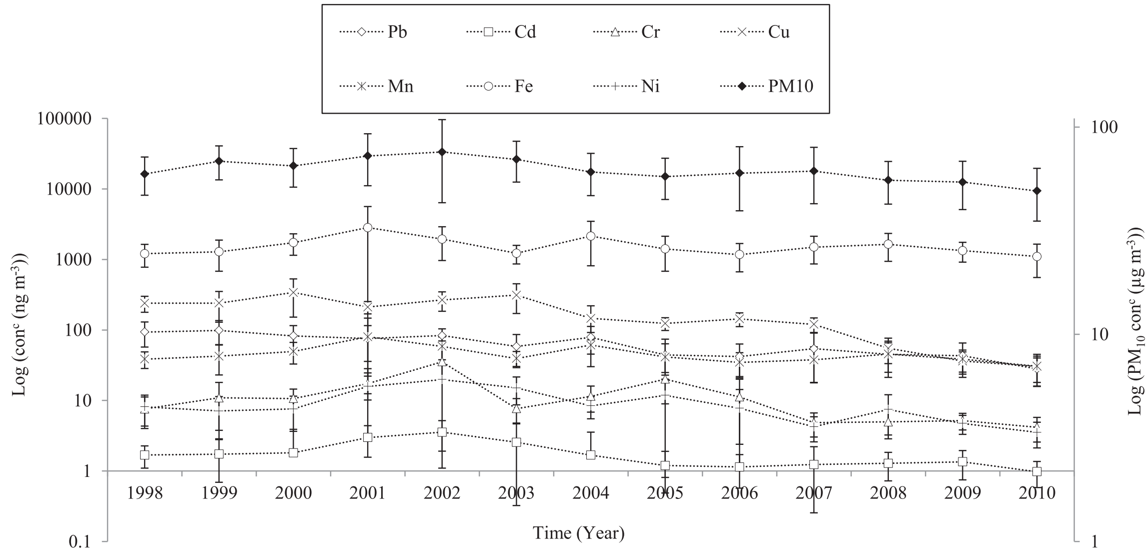

Fig. 3. Comparison of the annual mean concentrations of airborne metal pollutants (M = Pb, Cd, Cr, Cu, Mn, Fe, and Ni) and PM_{10} measured in Seoul, Korea between 1998 and 2010 (error bar denotes SD for each year).

Yang et al. (2002) reported very low concentrations of five metallic components (Pb, Cu, Fe, Mn, and Ni) at 3.00, 26.0, 177, 8.00, and 0.90 ng m^{-3}, respectively, in New York, USA in 1999. Likewise, similarly reduced concentrations of Pb, Cd, Cr, Mn, and Ni were also seen: 2.75, 0.10, 1.89, 12.78, and 0.74 ng m^{-3}, respectively, in more recent years (2008–2009) from Tuscon, Arizona, USA (Foley et al., 2012). As such, the concentrations of atmospheric heavy metals in Seoul, when compared with other cities, are generally higher than those of Western countries (such as the United States and the European Union). Nevertheless, if the concentration data of metallic species in Seoul are compared with other Asian cities, differences are not that significant. A comparison between results of the current study and those from a study in Taejon city, Korea conducted by Alastuey et al. (2006) also reflects the improved air quality conditions in Seoul. As such, our comparison of airborne metallic species over a long time period indicates that the reductions observed in Seoul were primarily attributable to the consistent efforts to control PM (Thi Nguyen et al., 2010; Shon and Kim, 2011).

4. Conclusion

In this study, the concentrations of seven airborne heavy metal species (Pb, Cd, Cr, Cu, Mn, Fe, and Ni) were measured from Seoul, Korea, over a 13-year period (1998–2010). Results were analyzed to describe their spatiotemporal distribution characteristics. A long-term trend analysis indicated consistently decreasing concentrations throughout the entire study period, demonstrating the success of efforts to control PM and associated metallic species on the Korean peninsula. Examination of the seasonal patterns of airborne metals indicated a strong seasonality for winter and/or spring. The strong correlations among most metals suggest the effect of similar anthropogenic sources.

The results of our analysis indicate that air quality in one of the major urban areas in East Asia has been considerably improved through the years in terms of key heavy metal species. Likewise, if the status of heavy metal pollution in Seoul is assessed against the guidance level of the Korean Ministry of Environment (KMOE), the results indicate that air quality has improved prominently in recent years. It is obvious that such a reduction in recent years is a positive outcome of efforts to control PM on the Korean peninsula. However, their concentrations still remain fairly higher than those commonly observed in many Western countries. Hence, future studies are needed to help develop, and assess the efficacy of, effective control methods so that regulations on individual sources can be further tightened. Such efforts will eventually help us find a basis for

Table 2
Comparison of the seasonal mean values of seven airborne metals (Pb, Cd, Cr, Cu, Mn, Fe, and Ni: ng m^{-3}) and PM_{10} (μg m^{-3}) in Seoul, Korea from 1998 to 2010.

Season	Pb	Cd	Cr	Cu	Mn	Fe	Ni	PM_{10}
Spring	73.3 ± 34.5[a] (74.4)[b]	1.86 ± 1.28 (1.50)	10.7 ± 7.68 (8.30)	185 ± 135 (155)	64.0 ± 42.3 (50.9)	2201 ± 1688 (1896)	13.1 ± 20.3 (6.70)	76.6 ± 19.8 (72.0)
	16.5–153[c] (39)[d]	0.10–6.20 (39)	1.70–35.7 (39)	13.6–691 (39)	27.4–255 (39)	658–10,790 (39)	1.70–126 (39)	49.0–149 (39)
Summer	47.2 ± 33.3 (35.9)	1.37 ± 1.17 (1.00)	9.05 ± 8.77 (6.80)	173 ± 118 (163)	34.2 ± 21.2 (30.4)	1150 ± 582 (1075)	7.25 ± 5.90 (5.00)	49.7 ± 14.8 (47.0)
	3.80–126 (39)	0.00–5.10 (39)	0.20–49.5 (39)	13.0–443 (39)	4.70–124 (39)	268–3424 (39)	1.10–24.8 (39)	31.0–82.0 (38)
Fall	57.7 ± 36.0 (44.8)	1.67 ± 1.45 (1.20)	14.0 ± 14.9 (7.50)	186 ± 148 (145)	40.6 ± 18.1 (38.8)	1463 ± 683 (1254)	8.76 ± 7.39 (5.90)	55.0 ± 13.9 (58.0)
	7.10–136 (39)	0.20–6.90 (39)	2.30–58.4 (39)	16.8–610 (39)	11.5–84.2 (39)	454–3757 (39)	1.80–36.4 (38)	25.0–80.0 (39)
Winter	76.3 ± 31.3 (71.3)	2.22 ± 1.76 (1.70)	12.8 ± 21.3 (7.40)	152 ± 105 (144)	45.4 ± 17.3 (44.4)	1502 ± 812 (1304)	8.30 ± 6.58 (5.90)	67.1 ± 10.1 (68)
	21.3–160 (39)	0.00–7.80 (39)	2.00–136 (39)	21.9–552 (39)	16.1–82.4 (39)	375–4768 (39)	1.00–33.5 (39)	45.0–85.0 (39)

[a] Mean ± Standard Deviation (SD).
[b] Numbers in parenthesis denote median value.
[c] Range = Minimum–Maximum; and.
[d] N = number of seasonal data.

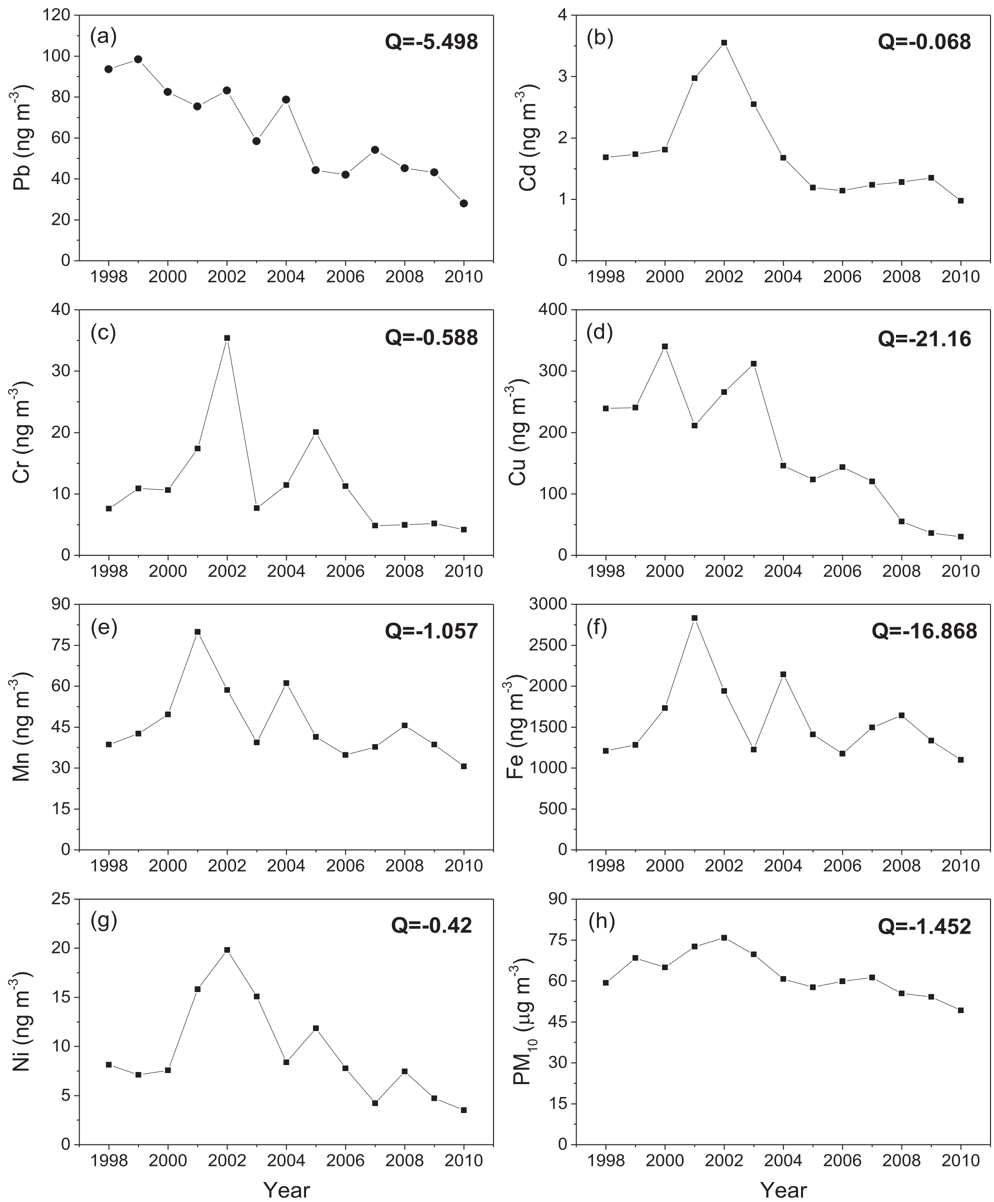

Fig. 4. Long-term trends of airborne metals and PM_{10} in Seoul, Korea: MK test done using annual mean values (1998–2010).

Table 3
Comparison of airborne metal concentration levels (ng m^{-3}) in different locations around the world.

Order	Study area	Period	Pb	Cd	Cr	Cu	Mn	Fe	Ni	Reference
(A) Europe										
1	Helsinki, Finland	April, 1996–June, 1997	2.00	0.01	-[a]	6.20	8.60	520	0.79	(Pakkanen et al., 2001)
2	Cadrezzate, Italy	1998	98.0	0.51	7.00	11.0	14.0	511	10.0	(Gallorini et al., 1999)
3	Brownfield, UK	1999	30.0	0.62	–	13.0	6.20	260	1.80	(Allen et al., 2001)
4	Barcelona, Spain	June, 1999–June, 2000	149	–	6.00	74.0	24.0	890	7.00	(Querol et al., 2001)
5	Uludag, Turkey	May, 2000–March, 2001	7.00	2.00	3.00	–	14.0	486	4.00	(Samura et al., 2003)
6	Frankfurt, Germany	August, 2001–July, 2002	11.6	0.20	3.80	12.4	9.70	–	2.60	(Zereini et al., 2005)
7	L'Alcora, Spain	2002–2006	156	1.40	5.00	5.00	6.00	–	3.00	(Querol et al., 2008)
8	Dunkrik, France	June, 2003–March, 2005	37.5	1.32	7.50	12.6	147	977	12.4	(Alleman et al., 2010)
9	Puertellano, Spain	2003–2006	12.0	0.14	3.46	26.5	11.3	–	4.40	(Moreno et al., 2010)
10	Zurich Kaserne, Switzerland	November, 2008–January, 2009	3.60	–	0.90	8.80	1.60	121	0.40	(Richard et al., 2011)
(B) Americas										
11	New York, USA	1999	3.00	–	–	26.0	8.00	177	0.90	(Yang et al., 2002)
12	Florida, USA	2002	5.30	–	–	2.40	1.90	79.0	1.30	(Olson et al., 2008)
13	Los Angels, CA, USA	September, 2000–January 2001	12.5	–	6.09	–	12.81	–	4.98	(Singh et al., 2002)
14	Tuscon, AZ, USA	June, 2008–September, 2009	2.75	0.10	1.89	–	12.78	–	0.74	(Foley et al., 2012)
15	Tampico, Mexico	2003	18.0	1.00	3.00	–	154	–	6.00	(Flores-Rangel et al., 2007)
16	La Plata, Argentina	1993	64.0	0.41	4.30	30.0	26.0	1183	3.20	(Bilos et al., 2001)
(C) Asia										
17	Tokyo, Japan	1974–1996	125	–	6.09	30.2	40.1	677	5.63	(Var et al., 2000)
18	Tehran, Iran	March, 1994–February, 1995	1020	–	48.0	–	78.0	2230	37.0	(Sohrabpour et al., 1999)
19	Tokyo, Japan	May, 1995–December, 2004	39.2	1.17	2.58	11.9	16.3	229	3.19	(Furuta et al., 2005)
20	Ho Chi Minh City, Vietnam	August, 1996–May, 1998	146	–	8.63	1.28	38.0	2904	–	(Hien et al., 2001)
21	Taejon City, Korea	1997–1999	243	3.24	25.1	41.1	50.3	1633	37.9	(Alastuey et al., 2006)
22	Beijing, China	March, 2001–August, 2003	430	6.80	19.0	110	240	5500	22.0	(Okuda et al., 2004)
23	Beijing, China	March, 2001–March, 2006	327	4.82	15.7	87.4	212	4580	14.0	(Okuda et al., 2008)
24	Taichung, Taiwan	July, 2001–April, 2002	574	8.50	29.3	199	–	1183	15.8	(Fang et al., 2003)
25	Islamabad, Pakistan	November, 2002–April, 2003	163	3.00	36.0	–	56.0	667	8.00	(Shah et al., 2006)
26	Delhi, Inida	September, 2003–August, 2004	441	11.0	351	3691	745	16,435	148	(Shridhar et al., 2010)
27	Kolkata, India	November, 2003–November, 2004	119	5.20	6.30	–	2.10	123	8.30	(Karar and Gupta, 2006)
28	Hong Kong, China	December, 2003–January, 2005	56.5	1.61	15.3	70.8	–	–	–	(Lee et al., 2007)
29	Guangzhou, China	December, 2003–January, 2005	269	7.85	20.9	82.3	–	–	–	(Lee et al., 2007)
30	Agra, Inida	May, 2006–March, 2008	1100	–	300	100	900	2900	200	(Kulshrestha et al., 2009)
31	Seoul, Korea	1998–2010	63.6	1.78	11.7	174	46.0	1579	9.34	Present study

[a] Denotes data not detected/found.

further reductions of metallic concentrations in urban atmospheres.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.11.001.

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