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Airborne iron across major urban centers in South Korea between 1991 and 2012

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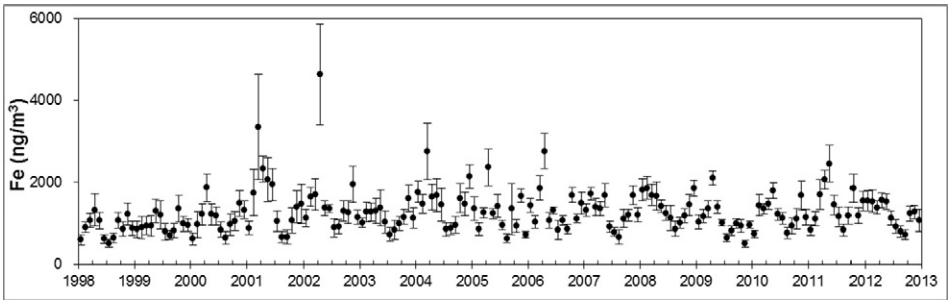
HIGHLIGHTS

- The atmospheric metal levels reflect the intensity of industrial activities.
- Anthropogenic processes substantially increased emission of Fe.
- The atmospheric behavior of Fe is yet poorly known.
- The impact of various sources on Fe distribution was evaluated.
- The man-made sources influenced Fe more evidently than PM.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the distribution of airborne iron (Fe), one of the most abundant heavy metals in the Earth's crust was investigated to describe the basic features of i'ts pollution in various urban locations. The spatiotemporal distribution of Fe concentrations in seven major South Korean cities exhibited unique patterns to reflect differences as to Fe sources reflected in the relative enrichment in coastal relative to inland areas. In addition, the analysis of long-term trends of different metal species indicated that Fe levels maintained a fairly constant trend, while there had been a noticeable decline in concentrations of other metals (Cd, Cr, Cu, Mn, and Ni). The relative robustness of our correlation analysis was assessed by comparing (1) the Fe concentrations among cities, and (2) Fe with other metals at a given city. Fe concentrations were also partly explainable by the frequency of Asian dust events in most cities, with the observed spatial gradients in such relationships.

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1. Introduction

Trace amounts of some metals are essential for life, playing a part in various metabolic processes (e.g., Fe in hemoglobin; Puntarulo, 2005). However, many types of heavy metals are toxic to human health and ecological systems. When released into the atmosphere, heavy metals are easily bound to fine particles (particulate matter, PM) and can remain suspended in the atmosphere for extended periods. Human exposure to heavy metals typically occurs as a result of respiratory deposition via inhalation. These metals can then act as carcinogens or toxins by binding to biomolecules. High-risk groups, such as children and the elderly, are particularly vulnerable (Berggren et al., 1990; Lippmann et al., 2006; Lippmann and Chen, 2009; Bollati et al., 2010). Consequently, considerable research effort has been directed toward identifying the sources and distribution of atmospheric heavy metals and assessing the degree of their ingestion by biota (including humans).

Natural sources of airborne metals include the emission of crustal material (e.g. Fe and Al) to the atmosphere via volcanic eruptions and the weathering of rocks or as a result of microbial activity. Anthropogenic sources of atmospheric heavy metals (e.g., As, Cd, Cr, Ni, and Pb) are primarily a result of particulate matter deriving from industrial activities (Dockery et al., 1993). The analysis of metallic component levels, when evaluated in relation to the presence/absence of a major source event (e.g., Asian dust (AD)) and PM sizes, indicated that such events are prominent sources for major crustal components like Al and Fe in both fine and coarse particle fractions (Kim et al., 2003; Wang et al., 2015). Consequently, many studies have tried to estimate heavy metal contamination levels in relation to PM size and to assess the extent of correlations between different metals (Samara and Voutsa, 2005; Ragosta et al., 2006). Globally, about 95% of the airborne Fe in PM is attributable to arid region dust emissions (in particular the Sahara and Gobi deserts), with the remaining 5% attributable to the combustion of biomass and fuels (Luo et al., 2008; Mahowald et al., 2009). As such, the airborne Fe concentration measured from eight U.S. states (CA, AZ, MN, KY, FL, TX, PA, and NY), showed that its levels in an arid area of AZ recorded the highest of all sites (e.g., 17 times) (Han et al., 2012).

It is generally known that Asian PM_{10} mainly consists of silica, feldspar, aluminum, iron, calcium, etc. (Donaldson et al., 2001). Record of Asian dust demonstrated that windblown dust storms originating in the deserts of Mongolia and China should travel to populated cities in East Asia (including Korea, Japan, and Taiwan) in spring (Kang et al., 2012; Kwon et al., 2002). In Korea, Asian dust particles of around 5 μm are typically observed between March and May (Choi et al., 2000). According to observations in Taean-gun Chungnam, South Korea, heavy metal concentrations were more than three times higher during Asian dust periods than in all other periods (Bae et al., 2005). Especially, it

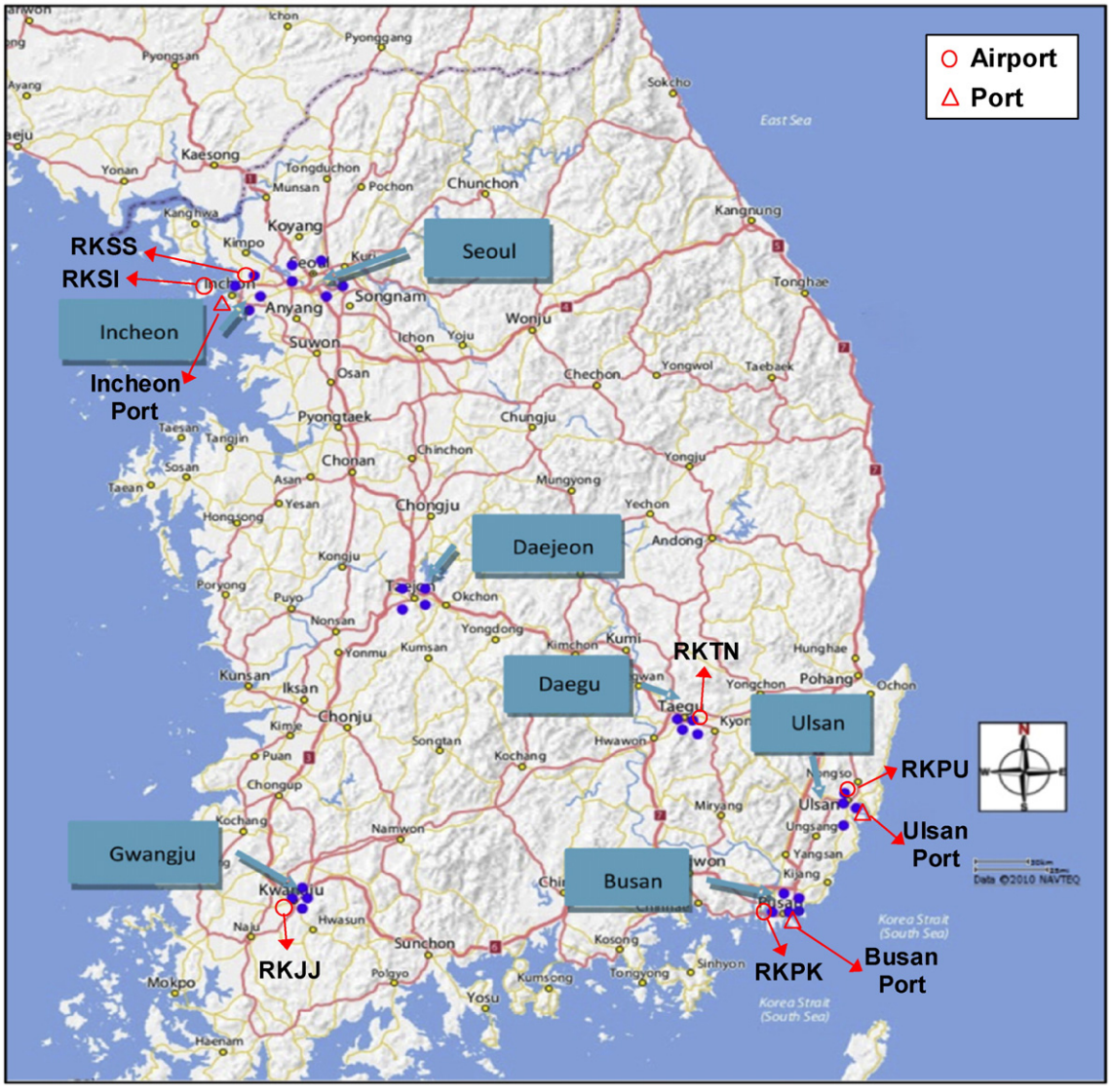

Fig. 1. Map showing the seven major Korean cities where airborne Fe concentration levels were monitored (Source: Ray and Kim, 2014).

was noticed that Mn exhibited a high correlation with the Asian dust periods, while Fe was subtly influenced (Myeong et al., 2009).

Iron is a very common element in nature (with the fourth highest abundance among the elements), accounting for 5.4% by weight of the Earth's crust. However, anthropogenic industrial processes over the last 200 years have significantly contributed to the increase in the global budget of the most trace metals (Querol et al., 2004; Garimella and Deo, 2008). When inhaled, Fe can lead to chronic medical conditions such as coughing, bronchitis, dyspnea, and phlegm (Banks et al., 1999; Chen et al., 2006; Driscoll et al., 2005; Kuo et al., 1998). Workers who inhale iron oxides may develop pneumoconiosis, and lung inflammation in mice is also known to result from exposure to iron particles emitted from iron mills (Billings and Howard, 1993; Hutchison et al., 2005). Due to its relatively high toxicity, airborne iron is currently the only heavy metal that is regulated by the 2014 Clean Air Conservation Act of the Republic of Korea. Monitoring the iron concentration of suspended PM can serve as an important indicator for overall urban air quality.

In this study, the spatial and temporal distribution of airborne Fe was investigated based on PM measurements in seven major Korean cities with contrasting levels of urbanization to describe the basic features of heavy metal pollution in urban air. Previous studies have found statistically significant correlations between PM/metal (e.g., Fe and Pb) and Asian dust periods (Kim et al., 2003, 2005, 2006; Myeong et al., 2009). Despite the fact that Fe is a dominant metallic component of aerosols, our knowledge regarding the atmospheric behavior of Fe is yet poor relative to that of many other toxic metallic components in general (e.g., Pb, Cd, Hg, Ni, As, V, and Mn). An aim of this study is hence set to evaluate the environmental fate of atmospheric Fe through careful examination of its temporal trends across cities in relation to the levels of Fe or

Table 1
Statistical summary of Fe and other metals measured in air at seven major cities in Korea (units: ng/m^3)[a].

		SL	BS	DG	IC	GJ	DJ	UL
		Avg ± SD (med)	Avg ± SD (med)	Avg ± SD (med)	Avg ± SD (med)	Avg ± SD (med)	Avg ± SD (med)	Avg ± SD (med)
		Min–max (N)	Min–max (N)	Min–max (N)	Min–max (N)	Min–max (N)	Min–max (N)	Min–max (N)
Fe	All[b]	1515 ± 1059 (1279)	1433 ± 780 (1245)	1088 ± 782 (1017)	1879 ± 1015 (1634)	851 ± 451 (739)	825 ± 518 (701)	1319 ± 649 (1231)
		138–10790 (180)	312–7564 (180)	40.6–7388 (180)	333–9003 (179)	167–2493 (180)	229–4481 (180)	220–3288 (180)
	1998[c]	1209 ± 449 (1178)	1045 ± 299 (1055)	364 ± 108 (355)	1461 ± 771 (1251)	619 ± 255 (550)	534 ± 159 (526)	1027 ± 438 (1073)
		534–2442 (12)	551–1553 (12)	134–506 (12)	669–3580 (12)	313–1131 (12)	305–773 (12)	300–1696 (12)
	2012[c]	1039 ± 471 (1070)	1736 ± 698 (1603)	992 ± 196 (1,003)	1,510 ± 437 (1482)	564 ± 251 (483)	1334 ± 493 (1363)	1386 ± 326 (1417)
		259–1683 (12)	802–2912 (12)	696–1272 (12)	573–2048 (12)	302–1091 (12)	553–2033 (12)	827–2052 (12)
Pb	All	60.4 ± 34.5 (51.2)	65.8 ± 34.7 (57)	47.4 ± 24.7 (41.6)	100.9 ± 48.3 (96.5)	34.1 ± 24.7 (28.7)	61.1 ± 32.2 (54.6)	62.6 ± 33.1 (58.6)
		3.8–160 (180)	16.8–263 (180)	10.7–177 (180)	12.3–279 (179)	0.2–123 (179)	11.–151 (180)	4.53–167 (179)
	1998	93.6 ± 36.4 (101)	110 ± 60.3 (98.6)	35.8 ± 7.29 (36.7)	126 ± 59.8 (116)	8.94 ± 8.32 (7.05)	88.5 ± 32.2 (85)	70.3 ± 37.8 (60.9)
		48.4–160 (12)	38.7–263 (12)	21.6–47.7 (12)	33.8–262 (12)	0.2–24.3 (12)	50.3–148 (12)	23.8–134 (12)
	2012	40.9 ± 15.7 (45.2)	58.2 ± 15.5 (59.1)	39.7 ± 16.7 (38.8)	82.7 ± 39.1 (75.5)	26.9 ± 14.1 (24.5)	44.8 ± 26.6 (35.5)	60.3 ± 26.3 (55.1)
		19.8–66.3 (12)	37.3–77.6 (12)	18.9–75.8 (12)	27.8–152 (12)	6.8–48.2 (12)	14.9–104 (12)	28.7–108 (12)
Cd	All	1.77 ± 1.37 (1.4)	2.06 ± 1.01 (1.89)	1.97 ± 1.49 (1.5)	4.96 ± 6.15 (3.9)	1.33 ± 1.06 (1)	1.17 ± 0.83 (1)	6.54 ± 7.55 (3.28)
		0.1–7.8 (177)	0.1–5.6 (180)	0.1–10.1 (176)	0.1–68.8 (179)	0.1–10.4 (162)	0.1–3.9 (168)	0.1–37.3 (175)
	1998	1.68 ± 0.61 (1.7)	2.33 ± 1.08 (2.15)	2.74 ± 2.72 (1.6)	4.29 ± 2.31 (4.75)	0.58 ± 0.28 (0.7)	1.22 ± 0.84 (1)	15.2 ± 8.38 (15.5)
		0.5–2.7 (12)	0.8–4.3 (12)	0.8–9.8 (11)	0.9–8.6 (12)	0.1–0.8 (5)	0.3–3 (10)	3.8–28.2 (12)
	2012	1.71 ± 0.74 (1.62)	1.25 ± 0.45 (1.21)	1.23 ± 1.32 (0.81)	1.99 ± 1.11 (1.71)	0.79 ± 0.39 (0.7)	1.32 ± 1.2 (0.75)	2.37 ± 1.45 (2.06)
		0.52–2.8 (12)	0.68–1.9 (12)	0.23–5.25 (12)	0.95–4.5 (12)	0.43–1.6 (8)	0.15–3.25 (11)	0.53–5.13 (12)
Cr	All	10.7 ± 13.5 (6.85)	14.36 ± 7.36 (13.4)	5.82 ± 5.03 (5)	12.3 ± 10 (9.8)	4.25 ± 5.16 (2.8)	4.12 ± 2.79 (3.65)	7.13 ± 7.16 (4.9)
		0.2–136 (180)	1.3–43.1 (178)	0.3–42.6 (177)	2.7–99 (178)	0.1–35.3 (163)	0.1–15.4 (176)	0.6–59.6 (178)
	1998	7.59 ± 3.75 (8.35)	11.9 ± 7.59 (10.5)	4.13 ± 1.61 (3.75)	11.5 ± 6.89 (10.1)	0.64 ± 0.48 (0.5)	2.68 ± 2.06 (1.8)	13.9 ± 8.44 (11.1)
		0.2–13.7 (12)	3.3–25.5 (12)	1.1–7.4 (12)	2.7–23.2 (12)	0.2–1.2 (5)	0.7–6.6 (12)	4.1–34.7 (12)
	2012	5.14 ± 2.19 (5.56)	15.2 ± 3.45 (15.5)	4.78 ± 2.03 (4.85)	8.29 ± 1.98 (8.75)	2.73 ± 1 (2.9)	7.03 ± 3.2 (6.1)	7.73 ± 3.03 (7.15)
		1.86–9.46 (12)	9.82–20.2 (12)	2.25–9.75 (12)	3.45–10.7 (12)	0.8–3.8 (12)	2.88–13 (12)	3.75–12.5 (12)
Cu	All	155 ± 128 (133)	126 ± 83 (111)	152 ± 127 (127)	156 ± 96.7 (140)	212 ± 207 (161)	51.6 ± 50 (36.7)	180 ± 179 (128)
		3.8–691 (180)	18.9–524 (180)	37.4–1451 (180)	21.9–652 (179)	7.65–1447 (180)	8.1–371 (180)	11.2–1151 (180)
	1998	239 ± 64.2 (239)	145 ± 52.2 (131)	127 ± 63.2 (110)	169 ± 75.1 (145)	229 ± 177 (171)	100 ± 87.4 (73)	440 ± 300 (417)
		144–352 (12)	75.2–260 (12)	47.3–227 (12)	85.7–361 (12)	103–732 (12)	47.9–371 (12)	90.3–1,151 (12)
	2012	29.3 ± 11.9 (32.9)	39.1 ± 5.35 (37.9)	51.1 ± 11 (48.1)	52.5 ± 12.6 (53)	14.8 ± 4.8 (15.2)	21.5 ± 7.32 (22.9)	41.4 ± 19.1 (44.1)
		3.8–47.9 (12)	29.3–46.8 (12)	37.4–65.8 (12)	21.9–72.5 (12)	7.65–26.5 (12)	10.8–33.2 (12)	15–67.2 (12)
Mn	All	44.7 ± 27.8 (40.2)	65.2 ± 30.6 (60.6)	43.8 ± 29.1 (39.9)	87 ± 37.7 (80.3)	45.5 ± 29.1 (39.6)	33.7 ± 18.8 (29.8)	63.1 ± 35 (54.8)
		4.66–255 (180)	14.8–206 (180)	6.1–280 (180)	19.9–341 (179)	3.5–246 (179)	5.4–120 (180)	10.2–237 (180)
	1998	38.6 ± 10.6 (36.9)	51.6 ± 20.1 (46.6)	19.9 ± 4.55 (19.6)	73.9 ± 33.7 (66.8)	54.3 ± 33 (41.8)	25.8 ± 9.1 (25.1)	46.3 ± 18.9 (46.2)
		15.6–52.8 (12)	22.9–84.9 (12)	12.3–30.7 (12)	28.2–139 (12)	11.5–128 (12)	13.9–40.7 (12)	19–85.2 (12)
	2012	33.3 ± 18.7 (27.9)	85.7 ± 43.9 (74)	38.3 ± 8.1 (40.5)	76.5 ± 23.2 (77.1)	24.8 ± 14.3 (24.4)	39.1 ± 16.5 (42.9)	81.4 ± 32.1 (75.9)
		4.66–65.9 (12)	31.9–175 (12)	25.4–51.2 (12)	30.5–111 (12)	10–59.1 (12)	12.9–63.4 (12)	35–139 (12)
Ni	All	8.64 ± 11.2 (5.5)	11.9 ± 4.88 (11.5)	7.19 ± 4.91 (6)	12.6 ± 6.07 (11.5)	3.66 ± 3.04 (2.6)	5.78 ± 5.72 (4.3)	9.01 ± 6.85 (7.4)
		1–126 (179)	0.9–27.8 (180)	0.4–23.7 (180)	0.3–40 (179)	0.1–18.1 (177)	0.2–60.7 (178)	1–68.9 (179)
	1998	8.13 ± 3.96 (6.55)	8.51 ± 2.52 (9.35)	7.6 ± 4.38 (6.7)	10.7 ± 6 (9.2)	1.46 ± 1.63 (0.8)	8.51 ± 3.14 (7.25)	11.4 ± 4.53 (9.95)
		4.4–17.8 (12)	4.1–12.3 (12)	1.2–16.9 (12)	3.8–23.1 (12)	0.1–5.2 (12)	3.9–13.6 (12)	5.5–22 (12)
	2012	4.11 ± 2.29 (3.99)	12.6 ± 4.84 (12.7)	2.87 ± 1.72 (2.54)	10.4 ± 4.82 (8.98)	3.71 ± 2.01 (3.74)	4.43 ± 1.54 (4.11)	9.16 ± 4.59 (7.5)
		1.42–8.66 (12)	7.1–24.8 (12)	1–8.03 (12)	2.63–20.3 (12)	0.55–6.7 (12)	2.5–7.75 (12)	4.18 – 18.38 (12)
PM_{10}[d]	All	59.7 ± 18.8 (61.0)	56.8 ± 14.1 (55.0)	57.5 ± 16.1 (57.0)	57.6 ± 14.5 (56.0)	48.5 ± 14.39 (48.5)	47.7 ± 14.6 (48.0)	46.9 ± 14.6 (45.0)
		22.0–149 (179)	33.0–122(180)	27.0–117 (177)	28.0–110 (180)	22.0–98.0 (178)	19.0–100 (177)	17.0–104(174)
	1998	59.3 ± 12.41(59.0)	66.7 ± 12.9 (68.0)	72.0 ± 16.2(71.5)	57.3 ± 13.4 (55.5)	48.8 ± 11.7 (49.5)	57.6 ± 19.0(64.0)	28.5 ± 5.44 (29.0)
		36.0–80.0 (12)	48.0–91.0 (12)	48.0–102(12)	34.0–78.0 (12)	28.00–66.00 (12)	35.0–81.0(9)	20.0–39.0 (12.0)
	2012	41.0 ± 11.6(41.5)	43.4 ± 7.37 (43.5)	42.5 ± 8.25 (45.5)	47.3 ± 12.2 (47.5)	38.1 ± 9.76 (39.5)	39.2 ± 10.7 (41.0)	45.6 ± 8.4 (46.0)
		22.0–60.0 (12)	34.0–58.0 (12)	27.0–51.0 (12)	28.0–64.0 (12)	22.0–56.0(12)	19.0–53.0 (12)	34.0–60.0 (12.0)

[a] Unit: ng/m^3.
[b] Statistical values for all periods (1998–2012) were derived using the monthly mean values of each city.
[c] All statistics are derived using the monthly values of each city.
[d] Unit: μg/m^3.

PM pollution. It is also evaluated using the results of correlation analysis between Fe and other parameters measured concurrently. Moreover, we also explored the relationship between Fe concentrations and Asian dust events because most Asian dust events occurring in spring affect the dust budgets in the study area most sensitively. The impact and influence of large dust events, such as Asian dust events, on the airborne Fe levels was hence evaluated in detail.

2. Methods

2.1. Data acquisition and processing

Daily integrated (midnight-to-midnight) PM_{10} aerosol samples were collected from 30 sites in South Korea over 15 years (1998–2012) using high-volume samplers with intakes situated at about 10 m above ground level (see Kim et al., 2004 for details). The 30 observation sites were distributed between 7 major South Korean cities: Seoul (SL), Incheon (IC), Busan (BS), Ulsan (UL), Daegu (DG), Gwangju (GJ), and Daejeon (DJ) (see Fig. 1).

The concentration of select metal species (Fe, Cd, Ni, Cr, Cu, Mn, and Pb) in each daily PM_{10} sample was assayed by standard Korean Ministry of Environment (KMOE) atomic absorbance methods and reported as ng m^{-3} of air. The basic QA procedures for the measurement of these metal species follow the protocol established by the KMOE and have been described elsewhere (e.g., Kim et al., 2004). The samples collected using Whatman PM2000 glass fiber filters were pre-treated by immersing 23% of the filter (cut into several pieces) in 35 ml of acid solution prepared by mixing 6:1 ratio of concentrated HNO_3 (after 50% dilution) and H_2O_2 solution. This procedure was completed by repetitive treatments of heating, filtering, and resolubilization of this mixture. The concentrations of seven metals were then analyzed using Atomic Absorption Spectrometry (AAS: Polarized AAS, Z-8100 Model, Hitachi, Japan). Detection limits (DL) of all metals were typically found in three 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, Cu, Cr, Mn, and Ni), and (3) 50 μg (in AM) or 25 ng m^{-3} (Fe). Performance testing via regular submission of standards, blank analysis, and replicate analysis was used to estimate precision. The precision, if expressed in terms of relative standard error (RSE), was typically over 3%, but less than 10%, for all metals analyzed.

Monthly means of the PM_{10} observations and metal concentrations were generated from each site and stored in a KMOE database that is available from the Environmental Statistics portal (http://stat.me.co.kr). As well as the 15-year dataset outlined above, annual mean PM_{10} and metal concentration information was also acquired for the period 1991–1997. Other environmental parameters including gaseous pollutants (CO, NO_2, SO_2, and O_3) and basic climatological parameters measured from each station on an hourly-mean basis were also processed to derive the values at monthly intervals.

2.2. Study sites

Detailed sampling site information about each of all seven cities investigated in this study has been provided elsewhere (e.g., Ray and Kim, 2014). Briefly, SL is the capital city with the largest metropolitan area in South Korea. BS is the second largest city, serving as the country's main port for international cargo on the southeasternmost tip of the Korean peninsula. IC is a port city designated as Korea's first free economic zone in 2003. UL is a highly industrialized coastal city located on the southeastern part of Korea. Of the less Fe polluted cities, all are located

Table 2
Comparison of Fe concentration levels between different sites on the globe (unit: ng/m^{-3}).

Order	City	Site info	PM fraction[a]	Study period	Mean	SD	Min	Max	Methods[b]	Extraction	Reference
(A) This study (seven Korean cities)											
1	Seoul, Korea	Urban (near-coastal)		98.01–12.12	1515	1059	138	10,790			This study
2	Busan, Korea	Urban (coastal)		98.01–12.12	1433	780	312	7564			This study
3	Daegu, Korea	Urban (inland)	PM_{10}	98.01–12.12	1088	782	40.6	7388	AAS	HNO_3/H_2O_2	This study
4	Incheon, Korea	Urban (coastal)		98.01–12.12	1879	1015	333	9003			This study
5	Gwangju, Korea	Urban (inland)		98.01–12.12	851	451	167	2493			This study
6	Daejeon, Korea	Urban (inland)		98.01–12.12	825	518	229	4481			This study
7	Ulsan, Korea	Urban (coastal)		98.01–12.12	1319	649	220	3288			This study
(B) Other locations											
8	Santa Cruz, Brazil	Industrial	TSP	01.03–02.02	38903		77.4	290,000	ICP/AES	$HNO_3/HCl/H_2O$	Quiterio et al. (2004)
9	Beijing, China	Urban (university)	PM_{10}	01.03–03.08	5500	3900			LA-ICP/MS	N/A	Okuda et al. (2004)
10	Yokohama, Japan	Urban (metropolitan)	PM_{10}	01.03–03.08	1300	400			LA-ICP/MS	N/A	Okuda et al. (2004)
11	Oporto (SF), Portugal	Urban (university)	TSP	91.07–91.09	505	95	150	960	AAS	HNO_3/H_2O	Vasconcelos and Tavares (1998)
12	Central LA (USC), USA	Various sites (rural/polluted)	Coarse	08.04–09.03	487	584			ICP/MS	HNO_3/HF/HCl	Cheung et al. (2011)
13	Debrecen, Hungary	Urban	Fine/coarse	1991–1996	120/478				PIXE	N/A	Borbély-Kiss et al. (1999)
14	Hortobagy-Nagyivan, Hungary	Rural	Fine/coarse	1991–1996	92.5/256				PIXE	N/A	Borbély-Kiss et al. (1999)
15	Tito Scalo, Italy	Industrial (rural)	PM_{10}	2001.03–07	589	524	123	3695	AAS	HNO_3/HF	Ragosta et al. (2006)
16	EROS, West Midlands, UK	Urban (background)	$PM_{2.5}$	07.05–08.04	102		23.2	310	XRF	N/A	Harrison and Yin (2010)
17	CPSS, West Midlands, UK	Rural	$PM_{2.5}$	07.05–08.04	87.1		15.5	390	XRF	N/A	Harrison and Yin (2010)
18	Zaragoza, Spain	Urban (traffic area)	PM_{10}	01.07–02.06	666	396	46	1820	ICP-OES	HNO_3	López et al. (2005)
19	Bonsucesso (Fiocruz), Brazil	Suburban	PM_{10}	04.09–05.08	775		156	2392	ICP-OES	$HNO_3/HCl/H_2O$	Toledo et al. (2008)

[a] Fine and coarse implies particles less than 2 or 2.5 and between 2.5 and 10 μm, respectively.
[b] LA-ICP/MS (inductively coupled plasma mass spectrometry equipped with a laser ablation sample introduction); PIXE (proton-induced X-ray emission); XRF (X-ray fluorescence spectrometer); ICP-OES (inductively coupled plasma optical emission spectroscopy); and NA (extraction is not applicable).

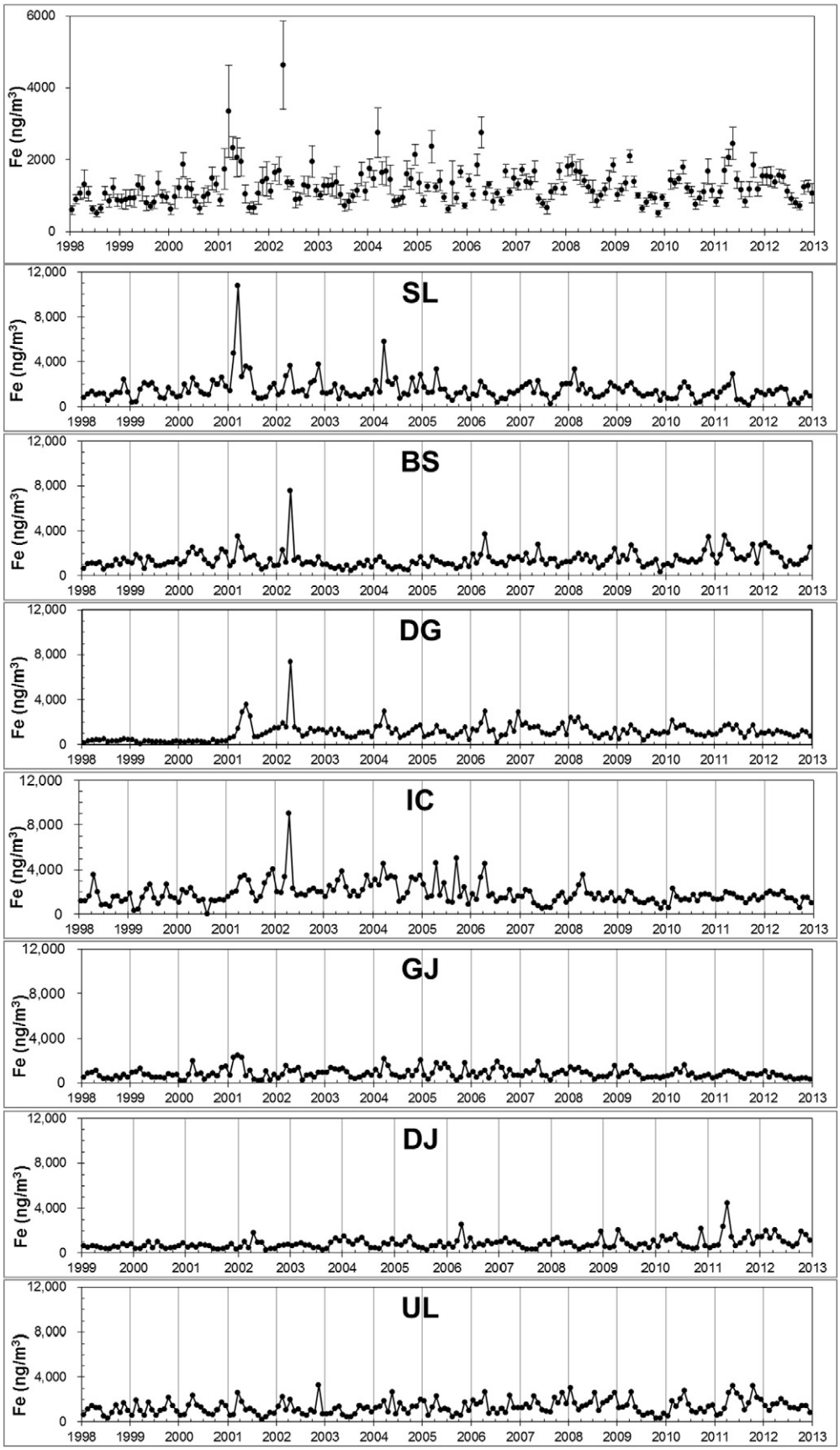

Fig. 2. Plots of monthly concentration data of Fe in air measured at seven major cities in Korea (1998–2012): Top panel shows the mean Fe values for all cities ((a) on top), while the lower ones of (b) through (h) correspond to SL, BS, DG, IC, GJ, DJ, and UL, respectively.

inland well away from the coast. GJ is located in southwestern Korea, and is one of the cleanest urban areas. DJ is primarily a transport hub, where many major transport routes meet. The third largest city, DG, is located in the southeastern part of Korea near the Nakdong River.

2.3. Data analysis — enrichment factors and modified enrichment factors

When trying to distinguish between anthropogenic and natural sources, the enrichment factor (EF) of metal (M) is sometimes used as a means to evaluate relative source contributions (Yaroshevsky, 2006).

$$EF = ([M]/[Fe])_{PM}/([M]/[Fe])_{cr}$$

where [M] and [Fe] are their respective concentrations in PM and the crust (cr) (e.g., Samara and Voutsa, 2005). In general, the ubiquitous and abundant Fe (or Al) is used as the reference species for computing EF values (e.g., Samara and Voutsa, 2005). An EF value of >5 for a given element indicates that it probably has an anthropogenic source (Samara and Voutsa, 2005). In addition a modified enrichment factor (MEF) is defined as,

$$MEF = \frac{\text{metal fraction in the PM}}{\text{metal fraction in the crust}}$$

Our MEF definition differs from the more conventional definition. This is so to calculate an MEF for Fe as data for PM-Al concentrations are not available.

3. Results and discussion

3.1. Spatial distribution of airborne Fe

The mean concentration data of Fe measured over a 15 year period are compared for the seven cities in Table 1 along with means of the PM_{10} and the other metal species. Also shown are the concentration ranges (based on monthly mean values), and the trend across the study period (1998 cf. 2012). The spatial distribution of Fe and PM_{10}, if assessed from the results summarized in Table 1, indicates that their patterns are comparable to each other at first glance. However, their results are also distinguishable on both temporal and spatial basis. The mean PM_{10} concentrations over the entire period were generally differentiated by the size (or population) of cities; its values were noticeably higher at the four largest cities (SL, BS, DG, and IC: >50 μg m^{-3}) than the rest (UL, GJ, and DJ: <50 μg m^{-3}). In contrast, the Fe concentration data were readily distinguishable between coastal (IC, BS, and UL)/near-coastal (SL) relative to inland cities (DG, DJ, and GJ). The mean Fe levels at the former were generally 1319 (UL) to 1879 ng m^{-3} (IC), while those of the latter were 825 (DJ) to 1088 ng m^{-3} (DG). Although considerable increase in Fe levels at DJ in recent years led to the dilution of such trend, it was observed consistently over the years.

It may be meaningful to assess the causes of observed differences in spatial distribution (or concentration gradients) existing in PM or Fe levels between cities to assess the relative importance of different source processes affecting each of them. The extent of anthropogenic activities should exert a dominant effect on Fe and PM distributions manifested in many different ways. In the case of Fe, it may be meaningful to consider the relative significance of two possible processes. Firstly, if the distribution of Fe was affected primarily by advected mineral dust,

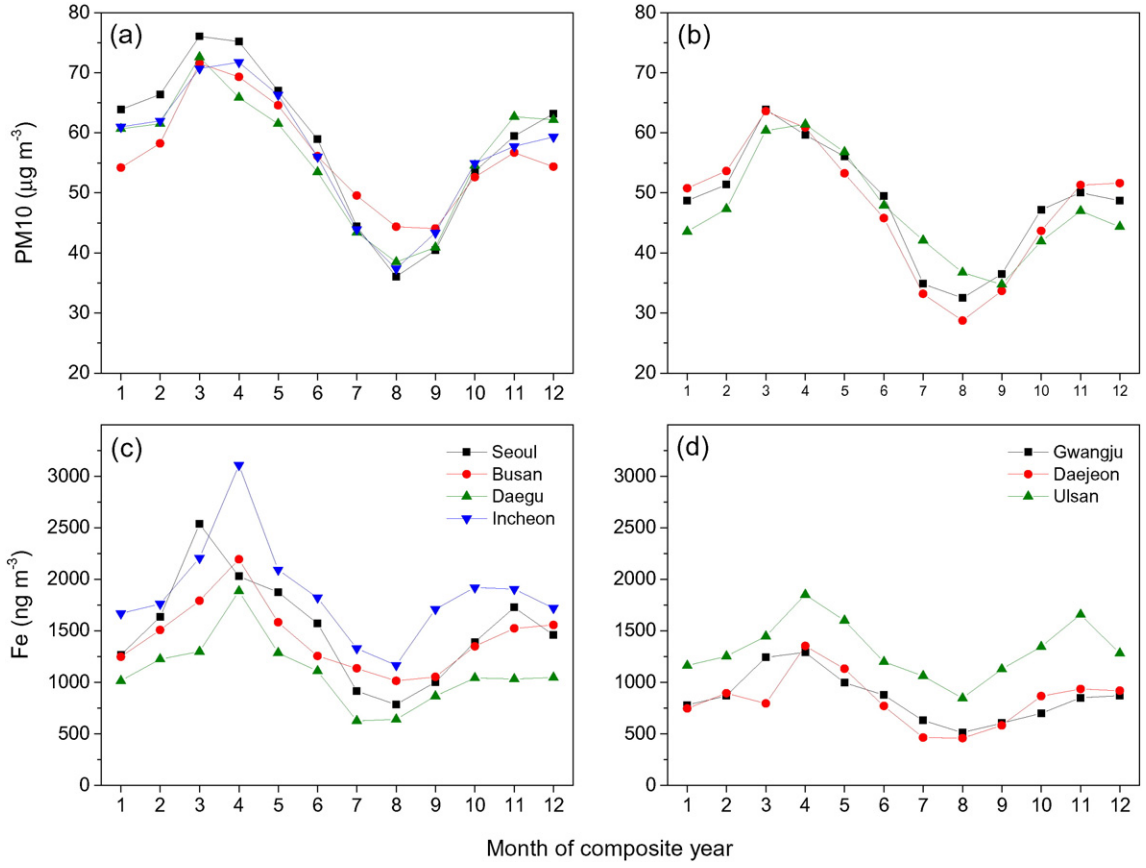

Fig. 3. Temporal variation of PM_{10} ((a) and (b)) and Fe data ((c) and (d)) measured from seven cities using their monthly mean values for all periods. (A) Annual concentration of Fe in each city. (B) Mean annual concentration of Fe and PM_{10} in all cities (error bar denotes standard error).

there should be no significant differences across the city (either upwind or downwind). Secondly, on the other hand, if Fe is predominately from anthropogenic emissions, there would likely be a significant difference in Fe levels depending on the wind direction (assuming that enough of the anthropogenic signature is captured in the PM_{10} size fraction). The results of comparison in this respect suggest the possibly important role of the latter factor. As there are large anthropogenic sources in the big port cities (relative to inland cities), their effects seem to be reflected more prominently on the distribution of Fe in PM. It should be noted that the spatial distinction in Fe levels between inland and coastal cities, which was apparent by the mean values of all study period, are more apparent in the earlier period of the study (results of 1998 in Table 1: 1027–1461 (coastal) vs. 364–619 ng m^{-3} (inland)). However, such pattern became less significant in recent years (results of 2012 in Table 1: 1039–1736 (coastal) vs. 564–1334 ng m^{-3} (inland). As such, the observed spatial distinctions tend to disappear in recent years; only the results of GJ (564 ng m^{-3}) are significantly different from the remaining cities. This noticeable reduction in spatial distinction in 2012 is likely to reflect the result of population expansion (anthropogenic effects) across all cities.

The overall spatiotemporal trend of PM and Fe observed in this study may thus agree well with the findings of other researchers in which the distribution of soluble iron in a region was strongly correlated to anthropogenic activity rather than mineral dust wind events (Chuang et al., 2005; Takahashi et al., 2013). As such, the decoupling of major source signals (e.g., Asian dust periods) should have been more noticeable between Fe and PM_{10} levels in both spatial (multiple samplers per city and across multiple cities) and temporal scales (monthly, annual, and decadal) (Jiang et al., 2015).

3.2. Comparison of airborne Fe levels between different studies and computation of EF values

In Table 2, the mean concentrations of Fe measured from the seven main S. Korean cities over the study period are compared with those observed from diverse land use types from several other countries. Note that the interpretation of the Fe concentration data between different studies should be made cautiously due to differences in its measurement approaches. As explained in Table 2, several studies were carried out to measure "total" Fe in PM (using digestions with hydrofluoric acid (HF) or non-destructive techniques like XRF), whereas "selective" acid leaching (without HF) was applied in others including our work. In the case of the latter, the extent of extraction from PM samples can be limited to release a certain fraction of Fe such as those bound to silicates and other crystalline materials. This difference is important to consider as the "selective" acid leaching might not fully capture the crustal

Table 3
Comparison of annual mean concentrations of airborne Fe and related information from the seven cities throughout the entire study period (1991–2012, units: ng/m^3).

Year	Target city							Statistical parameter				
	SL	BS	DG	IC	GJ	DJ	UL	Mean	SD	Med	Min	Max
A. Annual mean values of Fe from seven cities in Korea												
1991	2196	1187	705	2149	890	161	904	1170	752	904	161	2196
1992	2462	1302	885	2816	651	374	1182	1382	919	1182	374	2816
1993	1639	484	395	1547	722	1911	353	1007	666	722	353	1911
1994	1666	1105	586	1720	879	1555	761	1182	464	1105	586	1720
1995	1842	1049	205	1926	638	1590	744	1142	659	1049	205	1926
1996	1347	1407	359	1640	567	862	1273	1065	476	1273	359	1640
1997	1206	1288	279	1677	520	750	1194	988	489	1194	279	1677
1998	1209	1045	364	1461	619	534	1027	894	398	1027	364	1461
1999	1284	1228	251	1559	751	572	1175	974	461	1175	251	1559
2000	1731	1692	272	1389	841	598	1203	1104	555	1203	272	1731
2001	2833	1475	1474	2547	1034	544	964	1553	844	1474	544	2833
2002	1941	1837	1852	2690	874	714	1325	1605	685	1837	714	2690
2003	1225	818	969	2432	902	714	908	1138	592	908	714	2432
2004	2145	1022	1437	2885	1090	895	1410	1555	717	1410	895	2885
2005	1410	1081	977	2262	1003	702	1152	1227	503	1081	702	2262
2006	1174	1619	1483	1950	993	965	1453	1377	356	1453	965	1950
2007	1497	1421	1365	1257	895	741	1582	1251	316	1365	741	1582
2008	1644	1504	1357	1847	925	881	1848	1429	400	1504	881	1848
2009	1333	1355	1013	1253	720	811	1030	1074	251	1030	720	1355
2010	1102	1604	1240	1490	796	963	1391	1227	291	1240	796	1604
2011	1165	2063	1279	1503	767	1414	1929	1446	445	1414	767	2063
2012	1039	1736	992	1510	564	1334	1386	1223	389	1334	564	1736
B. Comparison of basic statistics for Fe and PM_{10} both before and after grouping periods of I and II[a]												
Fe	Period I	1737 ± 515 (1666)	1224 ± 353 (1228)	661 ± 513 (395)	1975 ± 490 (1720)	761 ± 155 (751)	837 ± 520 (714)	1001 ± 271 (1027)	1171 ± 218 (1138)	Avg ± SD (Med)		
		1206 – 2833 (13)	484 – 1837 (13)	205 – 1852 (13)	1463 – 2816 (13)	520 – 1034 (13)	161 – 1911 (13)	353 – 1325 (13)	894 – 1605 (13)	Min – Max (N)		
	Period II	1390 ± 345 (1333)	1490 ± 322 (1540)	1238 ± 179 (1279)	1773 ± 533 (1510)	861 ± 165 (895)	967 ± 248 (895)	1465 ± 291 (1410)	1312 ± 149 (1251)	Avg ± SD (Med)		
		1039 – 2145 (9)	1022 – 2063 (9)	977 – 1483 (9)	1253 – 2885 (9)	564 – 1090 (9)	702 – 1414 (9)	1030 – 1929 (9)	1074 – 1555 (9)	Min – Max (N)		
PM_{10}	Period I	68.5 ± 5.82 (69.1)	62.9 ± 5.33 (63.4)	66.7 ± 4.21 (67.0)	55.5 ± 3.53 (55.1)	50.6 ± 3.53 (52.6)	51.3 ± 5.34 (52.2)	42.8 ± 12.2 (45.4)	56.9 ± 3.19 (56.8)	Avg ± SD (Med)		
		59.3 – 75.8 (6)	54.9 – 69.8 (6)	61.1 – 72.0 (6)	52.0 – 60.9 (6)	35.9 – 57.5 (6)	42.5 – 57.6 (6)	28.5 – 55.0 (6)	52.1 – 67.1 (6)	Min – Max (N)		
	Period II	54.0 ± 6.95 (55.4)	52.8 ± 5.99 (51.3)	50.7 ± 5.64 (51.1)	59.0 ± 5.89 (60.6)	47.2 ± 5.08 (46.4)	45.6 ± 3.42 (45.3)	50.0 ± 2.54 (49.5)	51.3 ± 4.53 (52.9)	Avg ± SD (Med)		
		41.0 – 61.3 (9)	43.4 – 60.3 (9)	42.5 – 57.7 (9)	47.3 – 66.9 (9)	38.1 – 54.9 (9)	39.2 – 49.3 (9)	45.6 – 53.7 (9)	42.4 – 56.5 (9)	Min – Max (N)		

[a] Information of coverage time for each period (P): all (1991–2012), Fe PI(1991–2003), Fe PII (2003–2012), PM_{10} PI (1998–2003), and PM_{10} PII (2003–2012).

source component of Fe. As such, Samara and Voutsa (2005) noted much reduced recoveries of Fe (70%) relative to other metals (90–110% recovery) from a standard reference material (NIST SRM 1648: urban particulate matter). This lower recovery of Fe using a 'selective' acid leaching (incomplete digestion) could lead to bias in computing EF by excluding a portion of the crustal Fe component. Moreover, the strong influence of mineralogy on iron solubility (leachability) from dust samples was also recognized (e.g., Journet et al., 2008).

Considering that the Fe data obtained between different studies are distinguished by both spatiotemporal factors and differences in pretreatment approaches (as aforementioned selective leaching that can lead to underestimation of the results), the Fe data collected from all different studies can be compared with caution. The Fe concentrations in Korean cities were significantly low compared to those in Beijing, China (5500 ng/m^3: Okuda et al., 2004) or Santa Cruz, Brazil (38,903 ng/m^3: Quiterio et al., 2004). Our values were however comparable to those in Yokohama, Japan (1300 ng/m^3: Okuda et al., 2004) or Bonsucesso, Brazil (775 ng/m^3: Toledo et al., 2008). In addition, they were relatively high when compared to those in Zaragoza, Spain (666 ng/m^3: López et al., 2005), Oporto, Portugal (505 ng/m^3: Vasconcelos and Tavares, 1998), Central Los Angeles, California, U.S. (487 ng/m^3: Cheung et al., 2011) or West Midlands, U.K. (102 ng/m^3: Harrison and Yin, 2010).

Using the monthly mean concentrations for each individual city, the temporal changes in Fe were assessed. In Fig. 2(A), the highest monthly Fe concentration were observed in SL in March 2001 (10,790 ng/m^3), IC in April 2002 (9003 ng/m^3), and BS in April 2002 (7564 ng/m^3). Based on all cities in this study, the mean monthly Fe concentration was at its highest in March 2002 at 4638 ng/m^3 (Fig. 2 (B)). The PM_{10} concentration was at its lowest during the monsoon season (July and August) and highest in spring during Asian dust periods, e.g., particularly in March/April of 2002 (Fig. 1S). This may be related to changes in the prevailing wind direction from north and west (winter and spring) to south and east (monsoon season) (Zahorowski et al., 2005).

Using Fe as the chosen reference element, the EF values of Cr and Mn were all <5, while EF values of all other metals exceeded 5. Here we expect that elements with significant natural sources (e.g. Fe, Cr, and Mn) will have MEF values that are relatively stable in time. Our results [for non-crustal metals] are consistent with previously reported trends. It was reported that concentrations of Pb, Ni, and Cd tended to decrease to a constant level over time (Kim, 2007a, 2007b; Kim et al., 2014; Myeong et al., 2009). By contrast, Cr concentrations did not decrease much over time and were subjected significantly to changing environmental influences (Nguyen and Kim, 2008). The MEF values for selected metals averaged over the entire study period (based on monthly MEF data) are shown in Table 1S in Supplementary information (SI).

As discussed earlier, the highest Fe concentrations and MEF values were found in coastal areas such that IC, a comparatively highly industrialized city (1879 ± 1015 ng/m^3, 0.66 ± 0.30) recorded the highest value followed by SL, a megacity (1515 ± 1059 ng/m^3, 0.50 ± 0.24), BS (1433 ± 780 ng/m^3, 0.52 ± 0.25), and UL (1319 ± 649 ng/m^3, 0.58 ± 0.28). Fe concentrations and MEFs were lower in inland areas such as DG (1088 ± 782 ng/m^3, 0.39 ± 0.23), GJ (851 ± 451 ng/m^3, 0.35 ± 0.18), and DJ (825 ± 518 ng/m^3, 0.39 ± 0.23) on account of the relatively low industrial emissions at those cities. The findings of relatively low MEF values for Fe, Mn, and Ni (Table 1S) suggest that these metals are crustal in origin; these results are consistent with $PM_{2.5}$ EF data for Milan, Italy (Lonati et al., 2005). On the other hand, the metal concentrations and MEFs, respectively, are as follows: Cu (52 ± 50 ng/m^3, 15 ± 15 (DJ)), Pb (34.1 ± 24.7 ng/m^3, 47 ± 31 (GJ)), and Cd (6.54 ± 7.55 ng/m^3, 1126 ± 1575 (UL)) suggest that these metals are anthropogenic in origin.

The Cd MEF (up to 9000) was particularly very high in UL in the early 1990s and as a 1-time occurrence in IC (Cd MEF = 8494) in November 2009 not reported by Mutlu et al. (2012) (Fig. 2S). UL has a nearby zinc smelter which has an annual Cd production capacity of 2100 t (Shi, 2012). A very high Cd EF of >1000 and [Cd] of 8.3 ± 1.5 ng/m^3 were also reported for $PM_{2.5}$ samples collected in Milan, Italy in August–November 2003 (Lonati et al., 2005). In the period of March 2004 to November 2010, Cd levels were highest in UL, GJ, and IC (up to 12 ng/m^3) and much lower in BS, DG, DJ, and SL (the lowest) (Mutlu et al., 2012). Cd MEF in PM_{10} at Sejong University, Seoul, South Korea in spring 2001 was the lowest during Asian dust periods (MEF = 358) vs. non-Asian dust periods (MEF = 702) (Kim et al., 2003).

3.3. Seasonal trends in airborne Fe and other metal concentrations

Because Fe concentrations showed less spatiotemporal variability between cities than other heavy metals, the temporal variations of Fe concentration in these cities were assessed on a seasonal basis (using monthly mean values); as seen in Fig. 3, the monthly means of Fe and PM_{10} were compared. Analysis showed substantial similarity and regular trends. In spite of differences between cities for the entire study period, SL recorded its highest mean monthly Fe concentration in March (2537 ng/m^3); IC and BS in April, i.e., 3107 ng/m^3 and 2193 ng/m^3, respectively. In March and April for all cities, the mean monthly Fe levels were relatively high at 1493 ng/m^3 and 1931 ng/m^3, respectively. Fe concentrations were thus higher in spring (Asian dust periods, minimal rain) than in July and August (monsoonal rainy season causing wet deposition). As such, the monthly mean Fe concentrations in July and August were at their lowest levels in most cities. The mean April/August [Fe] ratio was 2.55 ± 0.32 for all seven cities for the entire study period. The high airborne Fe concentrations in March/April (for most years) may be related to Asian dust periods. Globally, dry arid regions (e.g., the Gobi Desert) are the major source of atmospheric dust Fe emissions (~95%, 54.8 Tg Fe/year), whereas anthropogenic emissions contribute ~5% (Luo et al., 2008; Mahowald et al., 2009). In South Korea, it is also assumed that natural dust and anthropogenic (from combustion)

Table 4
Results of linear regression analysis for assessment of the long-term trend of Fe, PM_{10} and other metals using the respective annual mean values.

(A) Fe: 1991–2012

City	Regression eqn		R^2	P	N
SL	Y = −34.457	x + 70560	0.2200	0.028	22
BS	Y = 30.958	x − 60629	0.3149	0.007	22
DG	Y = 47.372	x − 93918	0.3794	2.28×10^{-3}	22
IC	Y = −19.194	x + 40310	0.0607	0.269	22
GJ	Y = 5.7735	x + 735.39	0.0528	0.303	22
DJ	Y = 6.6816	x − 12483	0.0103	0.654	22
UL	Y = 38.164	x − 75195	0.477	3.72×10^{-4}	22

(B) PM_{10}: 1998–2012

City	Regression eqn		R^2	P	N
SL	Y = −1.739	x + 3534.4	0.6491	2.04×10^{-3}	14
BS	Y = −1.5182	x + 3100.7	0.8071	6.01×10^{-5}	14
DG	Y = −1.928	x + 3922.7	0.8236	2.52×10^{-5}	14
IC	Y = 0.0101	x + 37.295	0.0001	0.272	14
GJ	Y = −0.7426	x + 1537.4	0.2806	0.142	14
DJ	Y = −0.9344	x + 1914.9	0.6975	5.32×10^{-4}	14
UL	Y = 0.8174	x − 1591.8	0.19	0.059	14

(C) Using the mean concentration of all seven cities

City	Regression eqn		R^2	P	N
Fe	Y = 10.757	x = 20301	0.1201	0.114	22
Pb	Y = −6.4946	x + 13088	0.7679	9.37×10^{-8}	22
Cd	Y = −0.2108	x + 425.52	0.8162	2.57×10^{-8}	22
Cr	Y = −0.2182	x + 445.87	0.3293	3.47×10^{-3}	22
Cu	Y = −6.6663	x + 13501	0.5074	2.00×10^{-4}	22
Mn	Y = −0.3735	x + 804.68	0.1051	0.138	22
Ni	Y = −1.000	x + 2014.2	0.3735	2.55×10^{-3}	22
PM_{10}	Y = −0.862	x + 1782	0.6378	3.04×10^{-4}	15

deposition rates of Fe should be comparable at around 1–5 ng/m^2/s (Luo et al., 2008).

The concentrations of Fe are summarized in terms of the annual mean and two representative periods between P1 and P2 (along with that of PM_{10}) in Table 3. Temporal variations in PM metal fractions (MF, the mass fraction of a metal in PM) at all seven study cities are also shown in Fig. 3S for the entire study period. As evident in the figure, the spatiotemporal MF pattern varied considerably; e.g., short-lived elevated MF values were observed for Cr in SL, IC, GJ, and UL. In DG, the PM Fe fraction abruptly increased from 0.46% (in 1998–2000) to 2.3% (in 2001–2012) for unknown reasons. In contrast, in BS, it steadily increased and doubled from 2.1% (1998–2001) to 4.2% (2011–2012), although airborne Fe levels changed little. We have not made any attempt to find official reports on industrial metal emission incidents to explain these PM MF or EF spikes.

In spring, when Asian dust occurred most frequently, Fe and PM_{10} concentrations (in SL) recorded their highest levels in March such as 2537 ng/m^3 and 77 μg/m^3, respectively (Fig. 3). In contrast during the heavy summer monsoonal rainy season (August), both Fe and PM_{10} levels were at their lowest, 783 ng/m^3 and 36 μg/m^3, respectively. As a result, the low Summer Fe concentrations had a coefficient of variation (CV) of 29.6%, whereas the CV was 40.3% in the spring with the highest Fe. Likewise, there were large Fe concentration differences across the seasons. Consequently, the summer monsoonal rains reduced Fe concentrations relatively evenly in all cities whereas in spring, the effects of iron sources were reflected in the Fe concentration at each city by varying degrees.

3.4. Long-term changes in airborne Fe concentration over the study period: 1991–2012

The spatial characteristics of Fe levels in each city were compared using the annual mean data. No significant change in the long-term trend of Fe was noted based on annual mean values (Table 3). The highest concentrations by city were in SL (2001), BS (2011), DG (2002), IC (2004), GJ (2004), DJ (1994), and UL (2014). Specifically, the long-term trends of Fe were examined using the annual data for each city with the aid of linear regression analysis (Table 4(A)). Among the cities with the highest concentration (excluding SL), Fe concentrations marginally increased over time, e.g., BS ($P < 0.007$), DG ($P <$

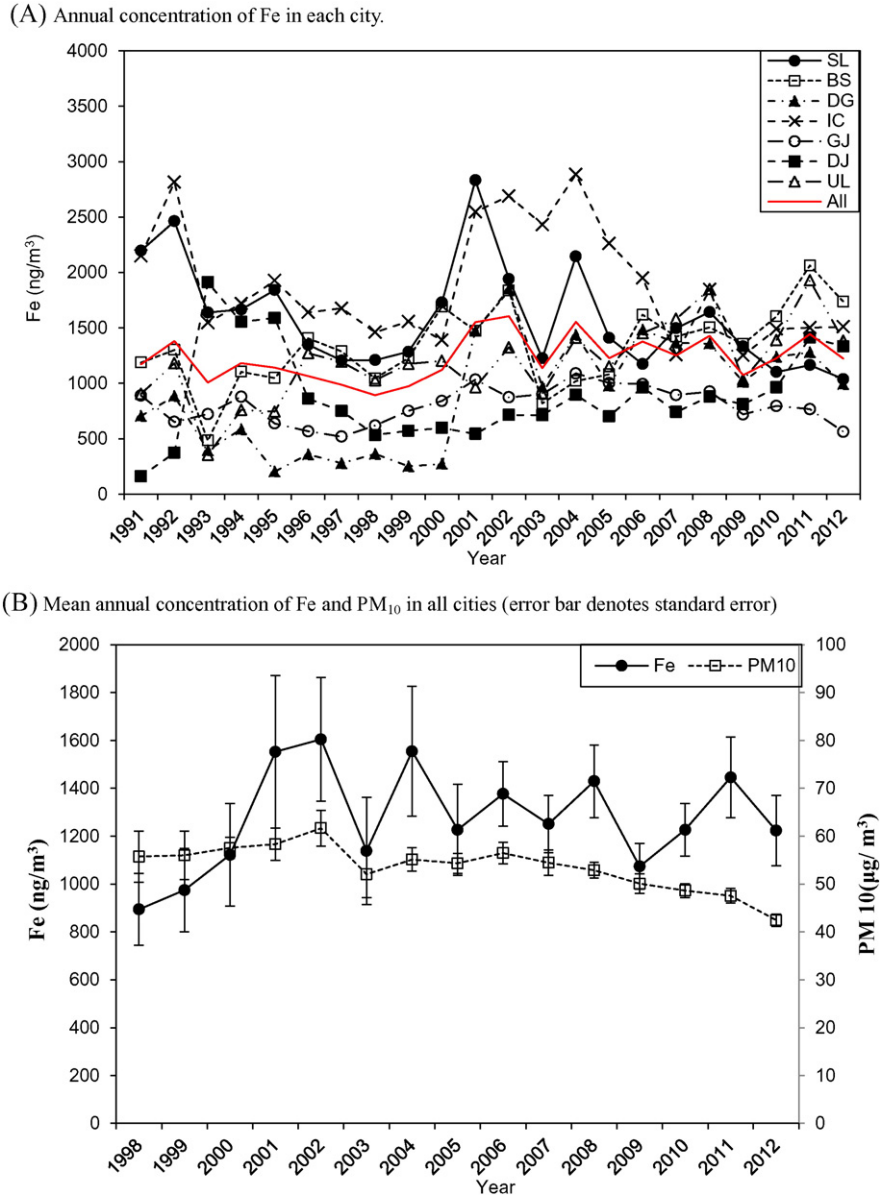

Fig. 4. Plot of annual mean concentration data of Fe across the entire study period.

0.002) and UL ($P < 0.0001$). However, if the tendency is compared on a yearly basis by taking the national means of the seven cities, the changes in the concentration were rather insignificant (Fig. 4). In contrast, PM_{10} concentration had a clearly downward trend in most cities except UL ($P < 0.157$) (Table 4 (B)). Thus, there was a small and definite long-term trend in Fe concentrations.

Regression analysis was carried out on the annual data of metals to compare the long-term trends between Fe and other heavy metals (Table 4 (C)). It was observed that the concentrations of most airborne metals (except Fe) tended to decrease slowly over time. The exact reasons for this small overall decrease over time are unknown. However, the temporal trends for Cr ($P < 3.47 \times 10^{-3}$) and Mn ($P < 1.38 \times 10^{-1}$) were not statistically significant.

To meaningfully explore the long-term distribution characteristics of Fe, the data were arbitrarily divided into two temporal sets as follows: (a) a period when the annual mean concentrations in all seven cities were at their highest in 2002 and 2004 at 1605 ng/m^3 and 1555 ng/m^3, respectively and (b) assigning 2003 (1138 ng/m^3) as the arbitrary reference point; the Fe concentration data were then compared in two periods, i.e., Period I (1991–2003) and Period II (2004–2012) (Table 3). If the means are compared between the two major periods, the concentration in many cities exhibited a moderately decreasing tendency such as SL (1737 to 1390 ng/m^3) and IC (1975 to 1773 ng/m^3). In some cases, however, an opposing trend was also apparent, as its values at DG exhibited a two-fold increase from 661 ng/m^3 to 1238 ng/m^3. The trends in PM_{10} concentration changes were also compared similarly to Fe by dividing into Period I (1998–2003) and Period II (2004–2012). (In the case of PM_{10}, the data was only measured since 1998; Period I is thus shorter by seven years). PM_{10} concentrations were higher in March to May

Table 5
Results of correlation analysis using the monthly concentration data of Fe (1998–2012).

(A) Correlation analysis of Fe data between cities.

		SL	BS	DG	IC	GJ	DJ	UL
	r	1	0.321	0.354	0.401	0.548	0.141	0.324
SL	P		1.11×10^{-5}	1.09×10^{-6}	2.66×10^{-8}	1.59×10^{-15}	0.059	9.41×10^{-6}
	N		180	180	179	180	180	180
	r		1	0.553	0.333	0.287	0.486	0.451
BS	P			8.90×10^{-16}	5.12×10^{-6}	9.17×10^{-5}	4.48×10^{-12}	2.21×10^{-10}
	N			180	179	180	180	180
	r			1	0.623	0.325	0.409	0.35
DG	P				1.19×10^{-20}	8.66×10^{-6}	1.20×10^{-8}	1.44×10^{-6}
	N				179	180	180	180
	r				1	0.303	0.229	0.152
IC	P					2.65×10^{-5}	2.01×10^{-3}	0.042
	N					179	179	179
	r					1	0.244	0.369
GJ	P						9.57×10^{-4}	3.38×10^{-7}
	N						180	180
	r						1	0.559
DJ	P							3.54×10^{-16}
	N							180
	r							1
UL	P							
	N							

(B) Correlation analysis between Fe and other concurrently measured parameters (results derived for each city).

	(ng/m^3)						(μg/m^3)	(ppb)	(ppb)	(ppb)	(ppb)
	Pb	Cd	Cr	Cu	Mn	Ni	PM_{10}	SO_2	NO_2	O_3	CO
SL	0.514[a]	0.286	0.209	0.211	0.894[a]	0.353	0.522[a]	0.158	0.396	0.006	0.183
BS	0.227	0.155	0.211	0.007	0.881[a]	0.423	0.324	0.036	0.211	0.192	0.037
DG	0.473	0.264	0.574[a]	0.674[a]	0.953[a]	0.532[a]	0.227	0.199	0.068	0.201	0.146
IC	0.404	0.246	0.359	0.363	0.819[a]	0.503[a]	0.402	0.013	0.187	0.096	0.064
GJ	0.381	0.259	0.304	0.251	0.394	0.351	0.445	0.083	0.333	0.143	0.097
DJ	0.165	0.308	0.466	0.158	0.778[a]	0.038	0.290	0.108	0.168	0.183	0.236
UL	0.423	0.235	0.361	0.173	0.541[a]	0.544[a]	0.167	0.331	0.052	0.231	0.035

(C) Comparison of r^2 value between PM_{10} and all relevant parameters

	SL	BS	DG	IC	GJ	DJ	UL	Avg
Fe	0.544**	0.324**	0.227	0.402**	0.445**	0.286**	0.167	0.343
Pb		0.406**	0.249	0.283**	0.370**	0.496**	0.392*	0.366
Cd	0.333**	0.449**	0.399**	0.100	0.193	0.313**	−0.235	0.222
Cr	0.262*	0.054	0.302**	0.100	0.091	−0.063	−0.207	0.077
Cu	0.319**	0.442**	0.339**	0.090	0.092	0.214	−0.309**	0.170
Mn	0.567**	0.295**	0.202	0.478	0.467**	0.485**	0.337**	0.404
Ni	0.518**	0.197	0.425**	0.124	0.200	0.180	−0.006	0.234
SO_2	0.434**	0.427**	0.639**	0.525	0.368**	0.586**	−0.1890	0.399
NO_2	0.639**	0.527**	0.618**	0.608	0.548**	0.407**	0.479**	0.547
O_3	−0.128	0.131	−0.102	0.134	0.096	0.071	0.499*	0.100
CO	0.466**	0.468**	0.563**	0.324	0.382*	0.445**	0.015	0.380
Avg	0.395	0.338	0.351	0.288	0.296	0.311	0.086	

[a] Correlation is significant at the 1.00×10^{-12} level (2-tailed).
* $P < 0.0005$.
** $P < 0.0001$.

and lower in July and August. Consequently, in the two periods, the mean PM_{10} concentrations in all cities decreased by 6 to 21% (except for IC and UL); there was clearly a significant decreasing trend in PM_{10} unlike the relatively insignificant trend of Fe. It was interesting to note that PM_{10} levels were considerably elevated in SL, BS, and to a lesser extent in DG in the spring of 2002 compared to other years.

3.5. Factors influencing the distribution of airborne Fe and heavy metal levels

Using the monthly Fe data collected from seven major cities, spatial correlations were investigated among the seven cities (Table 5). In this study, the number of monthly data points was 180, and most correlations are high based on P value. Thus, to assess the connection among the cities, r value 0.5 ($P < 1 \times 10^{-12}$) was arbitrarily selected to distinguish the relative correlations trends among the cities. As a result, the highest correlations were observed in several city pairs such as between SL and GJ, BS and DG, DG and IC, and DJ and UL ($r > 0.5$). In most cities, the Fe concentrations had a significantly high spatial correlation. However, there were differences in such trends in some areas possibly due to differences in local Fe emission sources (e.g., geological and industrial).

The heterogeneity of the Fe fraction in $PM_{2.5}$ collected from eight U.S. counties in eight states (mainly from residential sites) varied considerably, e.g., from 0.40% in Florida (limestone rocks) to 5.6% in Arizona (arid region rich in Fe) (Han et al., 2012). The average Fe fraction (%) in PM_{10} (this work, all years) is as follows: SL (2.5), BS (2.6), DG (2.0), IC (3.3), GJ (1.8), DJ (1.8), and UL (2.9). The PM_{10} Fe fraction was high in SL, BS, IC, and UL and low in DG, GJ, and DJ. The observed differences in Fe fraction between cities are still consistent with those seen from our grouping of data by differences in source strengths between coastal and inland cities. The Fe fraction in PM_{10} collected in Spring 2001 on the roof of a 5-story building at Sejong Univeristy, SL, was slightly higher during Asian dust periods (2.8% in 144 μg/m^3 PM) vs. non-Asian dust periods (2.1% in 72.5 μg/m^3 PM) (Kim et al., 2003). For example, DJ (low Fe concentration) had a weak correlation ($P > 0.05$) with SL (high Fe concentration). Similarly, IC (an industrial city) had a relatively low correlation ($0.05 > P > 0.01$) with UL. In the latter case, Fe concentration in UL could be the result of high and gradually increasing Fe emissions over time due to major source processes (e.g., large steel making plants). In contrast, there were slight variations at IC that consistently maintained a high airborne Fe concentration. It should be noted that the correlations are weak and may in fact be spurious in nature.

The correlation trends between Fe and other metal concentrations were also compared using an arbitrarily chosen r value of 0.5 ($P < 1 \times 10^{-12}$) (Table 5). As a result, Mn and Ni showed relatively modest correlations with Fe. By locality, in DG, there were strong correlations with all heavy metals except Cd. In GJ (an exception), there was a much weaker correlation of Fe with most other heavy metals. In all areas except GJ, Fe had a relatively very strong correlation with Mn concentration. In BS, IC, and UL (including DG), Fe maintained a high correlation with Ni as well. Furthermore, the Fe concentration had low correlations with all gaseous air pollutants (Table 5). This result was similar to that of a correlation analysis made previously on fine dust components in some areas in SL, Korea in 2005 (Kim et al., 2005). In fact, these trends and correlations have been observed globally in many other countries, e.g., a study of fine dust and airborne heavy metals in industrial areas in Brazil (Loyola et al., 2006). Therefore, it was noted that a high correlation of Fe with other metals (like Mn) was seen globally in many metropolitan cities of the world.

In this study, we also attempted to explore the possible connection between Fe concentration and the frequency of Asian dust events. Monthly frequency data on Asian dust events provided by the Meteorological Agency were used for the period of our Fe observation from Jan. 1998 to Dec. 2012 (Fig. 5). As a result of this comparison in each city, Fe concentrations observed in SL, BS, IC, DG, and GJ were moderately correlated to the frequency of Asian dust events. As discussed above, the factors controlling

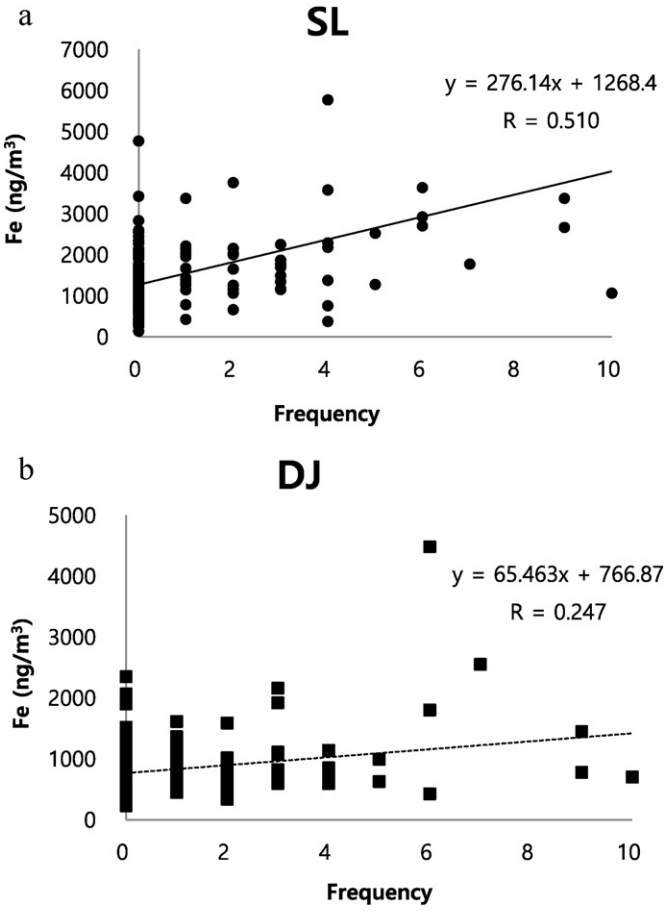

Fig. 5. Plot of monthly Fe concentration (ng/m^{-3}) vs. frequency of Asian dust events for the entire study period: (a) upper (Seoul) and (b) lower (Daejeon).

the distribution of airborne Fe are to be distinguished from those of PM_{10} in a number of respects. However, both of them should also share the similar source signals to a certain extent at the same time. As seen from this frequency analysis, it can be inferred that the intensity of Asian dust events is likely to exert a modest effect on the spatial distribution of Fe as frequently noted in elevated PM_{10} concentrations in spring.

4. Conclusions

This study characterized the spatiotemporal distribution of Fe in South Korea over a 22 year span based on a detailed analysis of data collected from seven major cities. The results clearly indicated the existence of constantly decreasing trends of PM_{10} and most heavy metals. However, unlike those, airborne Fe concentration was essentially invariant over the study period. In addition, comparison of airborne Fe concentrations showed that its highest mean annual concentrations occurred from coastal areas with large-scale anthropogenic activities. The analysis of Fe data was made with other concurrently measured airborne heavy metals and air pollutants at each monitoring station. Especially, Fe showed the same relative concentration profile as Mn with a high correlation ($P < 1 \times 10^{-12}$), while there were relatively low correlations with the gaseous pollutants.

To understand the factors governing airborne Fe concentrations, correlation with Asian dust events was undertaken. When the Fe concentration was compared with the frequency of Asian dust events, only moderate correlations were observed in most cities. Thus, it can be concluded that Asian dust events can have less significant impacts on observed Fe levels, although the spatial gradient of Fe was maintained to a certain degree. If the spatio-temporal distribution characteristics of different airborne metals are considered, that of

Fe is highly unique from other common metallic species. As such, the long-term trends of Fe were also distinguished quite significantly from PM_{10} or other metal species measured concurrently. This unique feature of Fe distribution is likely to reflect differences in their source processes (relative to PM or other metals) despite the fact that most metals are the essential components of airborne PM_{10}.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.11.109.

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