Journal of Hazardous Materials 184 (2010) 406–416

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Characteristics of heavy metals in airborne particulate matter on misty and clear days

Byeong-Kyu Lee [a,*], Gee-Hyeong Park [b]

[a] Department of Civil and Environmental Engineering, University of Ulsan, Ulsan 680-749, Republic of Korea
[b] Busan Institute of Health and Environmental Research, Busan, Republic of Korea

ARTICLE INFO

Article history:
Received 16 July 2010
Received in revised form 13 August 2010
Accepted 13 August 2010
Available online 26 August 2010

Keywords:
TSP
Heavy metal
Correlation
Air pollution
Misty days

ABSTRACT

This study identified characteristics of heavy metals in ambient total suspended particulates (TSP) and air pollutants (PM_{10}, CO, NO_x, SO_2 and O_3) collected on clear and misty days at an urban-residential area and an industrial area in the largest industrial city, Korea, for one-year study period. Average concentrations of TSP at the urban-residential (130 $\mu g/m^3$) and industrial (141 $\mu g/m^3$) areas on misty days were 1.9–2.1 ($p < 0.05$) times higher than those on clear days. Concentrations of heavy metals in the TSP from both areas on misty days were significantly ($p < 0.05$) higher than those on clear days. In particular, Pb and Mn concentrations on misty days were 2.4–2.6 ($p < 0.05$) and 1.7–1.8 ($p < 0.05$) times, respectively, higher at both areas as compared to clear days. Clear days showed higher correlations between TSP and heavy metal concentrations than on misty days at both areas. Average concentrations of PM_{10}, CO and NO_2 simultaneously measured at/near the sampling sites on misty days were significantly ($p < 0.05$) higher than on clear days at both areas. Average O_3 and SO_2 concentrations showed a similar increase pattern at only one area.

1. Introduction

A lot of studies have reported that long term exposure to high concentrations of particulate matter (PM) in urban ambient air can lead to increases in hospital admissions, respiratory disease, cancer risk, cardiovascular mortality, and morbidity of human beings [1–8]. PM can carry toxic or hazardous pollutants such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), elemental and organic carbons (EC/OC), etc [9–13]. Numerous studies have dealt with toxicity, adverse pulmonary and cardiovascular disease, and mortality associated with specific PM constituents such as heavy metals [6,14–16].

Characteristics of the components and concentrations of PM in ambient air easily vary with changes in meteorological conditions [17,18]. Deteriorated urban air quality (UAQ) on hazy days may be associated with atmospheric chemistry and aerosols or PM [19,20]. For example, PM formation or size increase mechanisms, including gas-to-particle conversion or particle coagulation, are affected by changes in ambient temperature or humidity [21]. Concentrations of heavy metals in ambient air would also be affected by changes in meteorological conditions [22,23].

According to the Indian Ocean Experiment (INDOEX) and the United Nations Environment Program (UNEP) report [24], haze can have "profound effects on human health, crop yield and rainfall patterns in the region". Schichtel et al. [25] reported haze trends in the USA and Okada et al. [26] also reported individual aerosol particles in Indonesian haze episode. Air pollution levels on hazy or mist days which have reduced visibility and increased humidity can be worse than those on normal days [27–31]. For example, haze episode days showed 10 times higher concentrations of water soluble ions [27], 3.0 and 1.6 times higher ones of OC and EC, respectively [28], and more acidic ions [29] as compared normal days. Only a few studies of urban air quality on haze or mist days have been conducted in Korea [29,32]. In particular, there has been no scientific study on ambient levels of PM and heavy metals associated with haze or mist episode available for a typical industrial city in Korea. The purpose of this study is to investigate different characteristics between on clear and misty days on the ambient levels of TSP and heavy metals collected from urban-residential and industrial areas during the sampling period of a year. Also, this study compared the ambient levels of air pollutants (PM_{10}, CO, NO_x, SO_2 and O_3) between on clear and misty days.

2. Materials and methods

2.1. Study area description

The metropolitan city of Ulsan is the largest industrial city in Korea with a population over 1.1 million. Ulsan has three national-scale industrial complexes (ICs), including a non-ferrous metal IC,

* Corresponding author. Tel.: +82 52 259 2864; fax: +82 52 259 2629.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.08.050

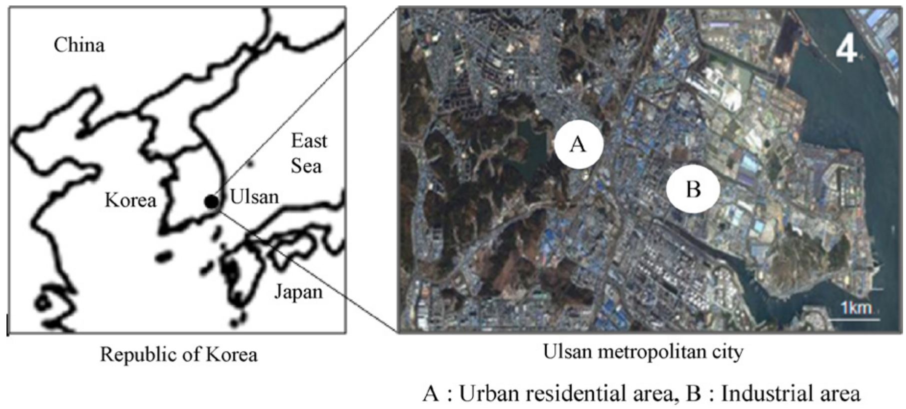

Fig. 1. A map and a satellite photo of the investigated areas in Ulsan, Korea.

petrochemical IC, and mechanical/shipbuilding IC. Fig. 1 shows the location of Ulsan in Korea and a satellite photo of the investigated areas. The urban-residential site was located at a center of a typical residential area, Yaum-dong, in Ulsan. The site was located 4 km from the center of a petrochemical IC to the north. Because prevailing winds at the site are the north-western and northern series from spring, fall, and winter periods, the urban-residential site may not be greatly influenced by industrial emissions. The industrial site was located at a center of a petrochemical IC which has many fine chemical and petrochemical production facilities such as propylene and epoxy resin, dye and pigment, and petrochemical fiber production facilities. The air quality at the industrial site is influenced by industrial emissions and located in a central area of the PC-IC, and thus the site can play a role in a representative sampling place for an industrial area. The distance between the urban-residential site and the industrial site was approximately 3.8 km.

2.2. Sampling protocol

TSP samples were collected from an urban-residential area and an industrial area in Ulsan from January to December 2007. Continuous five daily (24 h) air samples during the selected week periods every month were obtained using a high-volume air sampler (Tisch Co.). For monthly representative sampling, five consecutive days during the second week of each month were selected and air samples were simultaneously taken at both the urban-residential and industrial areas. Glass fiber filters (20 cm × 25 cm, Whatman Co.) were used for TSP measurements. The airflow rate for TSP sampling was 1.2–1.5 m^3/min.

2.3. Experimental protocols for TSP and heavy metals

Airborne TSP concentrations were calculated by gravimetry using the weight difference of the filters before and after airborne PM sampling. The filters before and after sampling were kept in electric desiccators at a temperature of $20 \pm 1\,^{\circ}C$ and a relative humidity of $50 \pm 1\%$ for 48 h to minimize moisture effects in the weighing process. Filters conditioned in the desiccators after the collection of air samples were cut into four even strips and then one of the strips was used for heavy metal extraction. Heavy metals in the filters were extracted using an ultrasonic extraction method (1078 W, 220 V, 4.9 A) in a mixture solution of HNO_3:HCl (1:1, v/v) specified in the Korean acts on the standard methods and procedures for extraction of metals for analysis of pseudo-total metal content in air pollutants. The solution was then boiled at 80 °C for 1 h in a water bath to extract the heavy metals. The extracted solution was filtered using a GF/C filter with a 0.45 μm pore size. The filtered solution was used for the analysis of heavy metals.

The qualitative and quantitative analyses of heavy metals were performed using inductively coupled plasma-optical emission spectrometry (ICP-OES). Standard solutions of the trace reference materials (Accu Co. Ltd.), which were accredited by US NIST, were diluted for quantitative analysis of the heavy metals. The relative standard deviation (RSD) in concentrations of all elements measured using the prepared standard solutions of the reference materials was less than 2%. Each analysis solution was measured four times to obtain the concentration values of heavy metals. Differences in the concentrations of the heavy metals in repeated measurements of the analysis solution obtained through duplicate extraction of some sampling filters (about 10%) was less than 5%. Detection limits of the ICP-OES were 0.331 ng mL^{-1} for Cd, 1.520 ng mL^{-1} for Cu, 0.580 ng mL^{-1} for Cr, 4.173 ng mL^{-1} for Pb, 0.263 ng mL^{-1} for Mn, 1.136 ng mL^{-1} for Fe, and 1.668 ng mL^{-1} for Ni.

2.4. Data collection of air pollutants and meteorological conditions

The ambient levels of the air pollutants (PM_{10}, CO, NO_x, SO_2 and O_3) were obtained from the Ulsan air quality monitoring network (UAQMN) operated at the TSP sampling sites selected for this study. This study compared the average levels of the air pollutants, obtained from the hourly based measurement data, between 11 misty days and 31 clear days during the investigated period, from January to December of 2007. Misty days and clear days were identified from the announcement of the Korea Meteorological Administration which evaluated the days based on information on humidity and visibility in the atmosphere. In this study clear days were defined as the days in which rainfall, haze and mist were not observed. Misty days were defined as the days which had a relative humidity above 75% and a visibility range above 1 km but less than 10 km. Simple meteorological conditions, such as temperature, relative humidity, wind speed and direction, were obtained from the UAQMN located in the same place as the TSP sampling sites. Other meteorological data such as visibility and sunlight duration time were obtained from the Ulsan meteorological station (UMS). A ambient ventilation index (AVI) to evaluate air exchange rate in the atmosphere of the study areas was calculated by using the information on maximum mixing depth (MMD) and wind speed (WS), i.e., AVI crate (m^2/s) = MMD (m) × WS (m/s), obtained from the UMS and UAQMN, respectively. This study utilized SPSS v12.0 for statistical analysis. Independent samples *t*-tests were done to compare the means of the sample groups collected on clear and misty days at the study areas.

Table 1
Comparison of fluctuations in TSP concentrations on clear and misty days.

Area	Clear days		Misty days	
	Avg ± SD (μg/m^3)	(SD/Avg) × 100 (%)	Avg ± SD (μg/m^3)	(SD/Avg) × 100 (%)
Urban-residential	62 ± 25	40.3	130 ± 32	24.3
Industrial	73 ± 23	31.5	141 ± 23	16.3
Industrial/urban	1.18	0.78	1.08	0.67

Note: Avg and SD represent average and standard deviation of TSP concentrations, respectively.
Industrial/Urban ratios were calculated based on the average values of TSP concentrations.

3. Results and discussion

3.1. TSP concentrations

Table 1 compares the average (Avg) and standard deviation (SD) of TSP concentrations on clear and misty days at urban-residential and industrial areas during the study period. Fig. 2 shows a time series of the concentrations of TSP measured at the urban-residential area on days with different meteorological conditions, including normal (clear), misty and rainy days. The average concentrations of TSP on misty days at both the urban-residential and industrial areas were approximately two (1.9–2.1) times higher significantly ($p < 0.05$) than those on clear days. The average concentration of airborne TSP on clear days was 62 μg/m^3 with a range of 25–119 μg/m^3 at the urban-residential area and it was 73 μg/m^3 with a range of 41–131 μg/m^3 at the industrial area. The average concentration of TSP at the urban-residential area on misty days was 130 μg/m^3, ranging from 85 to 184 μg/m^3. At the industrial area, the average concentration of TSP was 141 μg/m^3 ranging from 104 to 179 μg/m^3. The degrees of fluctuation in each concentration to the average value of TSP concentrations on misty days (16.3% and 24.3%) were much lower than those on clear days (31.5% and 40.3%) at both study areas. The fluctuation degrees (24.3% and 40.3%) at the urban-residential area were higher than those (16.3% and 31.5%) at the industrial area.

3.2. TSP vs PM_{10} concentrations

Fig. 3 shows the daily average concentrations of TSP and PM_{10} on clear and misty days at the urban-residential area during the study period of one year. Observed values of TSP and PM_{10} (130 ± 32 and 93 ± 14 μg/m^3, respectively) on misty days (shown as rectangular boxes in Fig. 3) were much higher than those values (62 ± 25 and 36 ± 14 μg/m^3, respectively) on clear days (shown as outside of the rectangular boxes in Fig. 3). By comparing the average values, we found that TSP and PM_{10} concentrations on misty days were 2.1 and 2.5 times higher, respectively, than those on clear days. We can infer that an increase in PM_{10} concentrations resulting from meteorological conditions or increased chemical and physical reactions on misty days were higher than those in TSP concentrations [33]. In particular, increased humidity on mist days can lead to increase concentrations in coarse particles via growth mechanisms such as hygroscopic growth and condensation of the particles [34].

The average PM_{10} concentration was from 66% to 71% of the average concentration of TSP, during the study period of one year (including mist and clear days) in Ulsan. The average contribution of PM_{10} to TSP in Ulsan was much higher value as compared 42% in Oxford, Ohio, USA and 47% in Jawaharlal Nehru Port and Surrounding Harbor Region, India [35,36]. The range of average ratio of PM_{10}/TSP in Ulsan was 0.60–0.72 (0.72 ± 0.44) on misty days was higher than on clear days (0.60 ± 0.56). The average ratio of PM_{10}/TSP (0.72 ± 0.44) on misty days was higher than on clear days (0.60 ± 0.56). However, the standard deviation in the ratio of PM_{10}/TSP on misty days was lower than on clear days. This means the correlation between PM_{10} and TSP concentrations on misty days was higher than on clear days. Parameters which affect PM_{10} and TSP concentrations on misty days may be less complicated or more uniform than those on clear days. This explanation is possible because meteorological conditions on misty days fluctuated less than on clear days. For example, ambient temperature, relative humidity, and wind speed on misty days (15.4 ± 7.3 °C, 57.0 ± 12.7%, 1.2 ± 0.2 m/s) showed less variation than on clear days (14.5 ± 8.9 °C, 50.2 ± 15.6%, 1.5 ± 0.4 m/s).

3.3. Pollution roses

Directional profiles of the prevailing and major winds were similar at urban-residential and industrial areas (Fig. 4). However, wind speeds of the prevailing and major winds at the industrial area were much higher (almost two times) than those at the residential area. On clear days at the industrial area, strong winds with speeds of 4.0 m/s or above were coming from all directions, excluding the northern and south-western series of winds. On misty days at the industrial area, however, strong winds were coming from only the north-east and north-west directions.

Figs. 5 and 6 represent SO_2 and NO_2 pollution roses, with comparing on clear days and misty days, at the urban-residential area and the industrial area, respectively. Thus, air samples on clear days at the industrial area were easily affected by SO_2 emissions from the industries mainly located in south and south-south eastern areas of the PC-IC and by NO_2 emissions from the industries mainly located in the north-western and west-west-northern areas of the PC-IC. On misty days the industrial samples were affected by

Table 2
Average and standard deviation (Avg ± SD) data of air pollutants and meteorological conditions from the Ulsan air quality monitoring networks during the study period.

Item		PM_{10}	SO_2	O_3	NO	NO_2	CO	WS	Temp	RH
Unit		μg/m^3	ppb	ppb	ppb	ppb	ppb	m/s	°C	%
Urban residential	Clear	36 ± 14	5 ± 4	22 ± 12	10 ± 12	23 ± 11	380 ± 204	1.5 ± 0.4	14.5 ± 8.9	50.2 ± 15.6
	Misty	93 ± 14	11 ± 8	22 ± 10	18 ± 20	36 ± 12	696 ± 158	1.2 ± 0.2	15.4 ± 7.3	57.0 ± 12.7
Industrial	Clear	52 ± 23	11 ± 8	19 ± 10	23 ± 20	24 ± 10	706 ± 337	2.7 ± 0.8	14.5 ± 8.9	50.2 ± 15.6
	Misty	100 ± 23	13 ± 7	23 ± 8	21 ± 17	34 ± 9	1173 ± 339	2.4 ± 0.4	15.4 ± 7.3	57.0 ± 12.7

Note: WS, Temp, and RH stand for wind speed, temperature, and relative humidity, respectively.

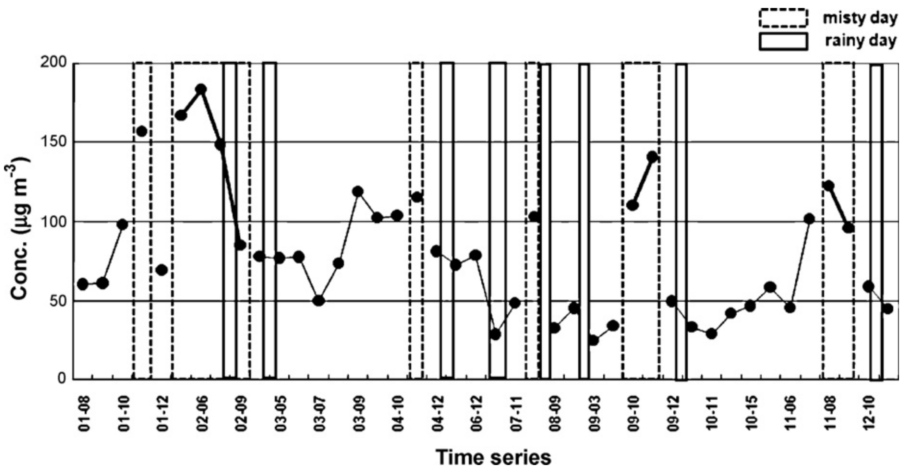

Fig. 2. A time series of the concentrations of TSP at the urban-residential area on days with different meteorological conditions.

NO_2 emissions from similar sources of NO_2 to those on clear days. However, SO_2 at the industrial area on misty days was affected by various SO_2 emission sources including from the industries located in the north-western and north-eastern areas of the PC-IC. Since the urban-residential site was not located near the industrial facilities and the wind speeds at that site were relatively weak, the urban-residential area would not have been substantially affected by industrial air emissions. The urban-residential area would be substantially affected by local traffic emissions. SO_2 and NO_2 at the urban-residential area both on clear and misty days were mainly affected by traffic emissions.

3.4. Air pollution levels

Table 2 and Fig. 7(a) and (b) represent the average concentrations of PM_{10}, O_3, SO_2, NO_x, and CO on clear and misty days at urban-residential and industrial areas, respectively, during the TSP sampling period of one year. The PM_{10} concentrations (based on 24 h average) on 5 days out of 11 misty days during the study period exceeded the ambient daily PM_{10} standard, 100 μg/m^3, in Korea (Table 3). However, PM_{10} concentrations on clear days did not exceed the standard of PM_{10}. In general, average concentrations of air pollutants on misty days were significantly higher than those on clear days at both areas. The average concentrations of PM_{10}, SO_2, NO, NO_2, and CO on misty days were 2.5 ($p < 0.05$), 2.2 ($p < 0.05$), 1.8 ($p < 0.05$), 1.5 ($p < 0.05$) and 1.8 ($p < 0.05$) times higher, respectively, than on clear days at the urban-residential area during one-year study period. Also, the average levels of PM_{10}, O_3, NO_2, and CO on misty days were 1.9 ($p < 0.05$), 1.3 ($p < 0.05$), 1.5 ($p < 0.05$), and 1.9 ($p < 0.05$) times higher, respectively, as compared those on clear days at the industrial area.

The differences in concentrations of PM_{10} and SO_2 at the urban-residential area on misty days compared to clear days were higher than those at the industrial area. Average wind speeds at the urban-residential area were 1.5 and 1.2 m/s on clear days and misty days, respectively. However, average wind speeds observed at the industrial area were 2.7 and 2.4 m/s on clear and misty days, respectively. Average ambient temperature and relative humidity at the urban-residential area were the almost same as those at the industrial area on clear days (14.5 °C and 50.2%) and on misty days (15.4 °C and 57.0%). Thus, the highly increased rates of PM_{10} and SO_2 at the urban-residential area may be associated with its lower wind speeds compared to the industrial area [18]. Lower wind speed at the urban-residential area could reduce the degree of dispersion of relatively heavy air pollutants, such as PM_{10} and SO_2.

The industrial area concentrations of NH_4^+, SO_4^{2-} and NO_3^- (major components of secondary aerosols) in PM_{10} on a misty day were 0.172, 0.080 and 0.167 μmol/m^3, respectively, and on a clear day were 0.052, 0.012 and 0.045 μmol/m^3, respectively. The ratios of NH_4^+, SO_4^{2-} and NO_3^- in PM_{10} on the misty day to the clear day were 3.3, 6.7 and 3.7, respectively. Sun et al. [27] reported that the increased concentration ratios of NH_4^+, SO_4^{2-} and NO_3^- in PM_{10} on haze–fog episodes in the winter season in Beijing were found to be 8.6, 10.8 and 16.8, respectively, as compared to clear days.

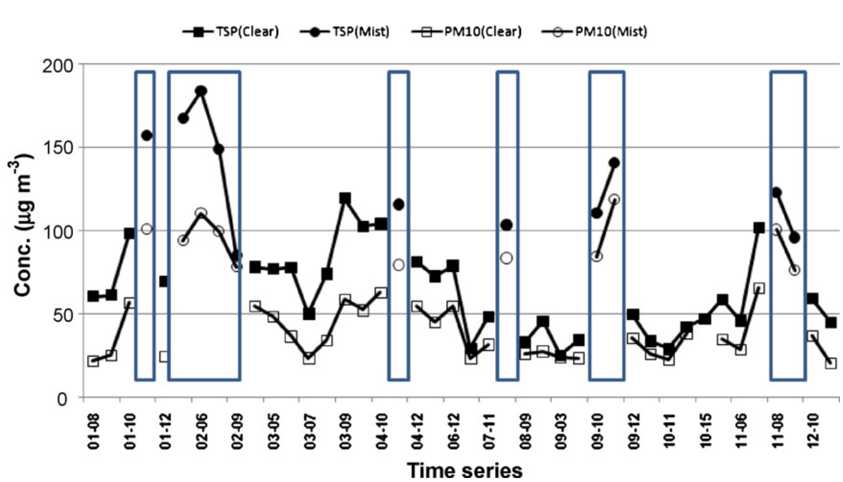

Fig. 3. Daily average concentrations of TSP and PM_{10} on clear days (outside box) and misty days (inside box) at the urban-residential area during the study period.

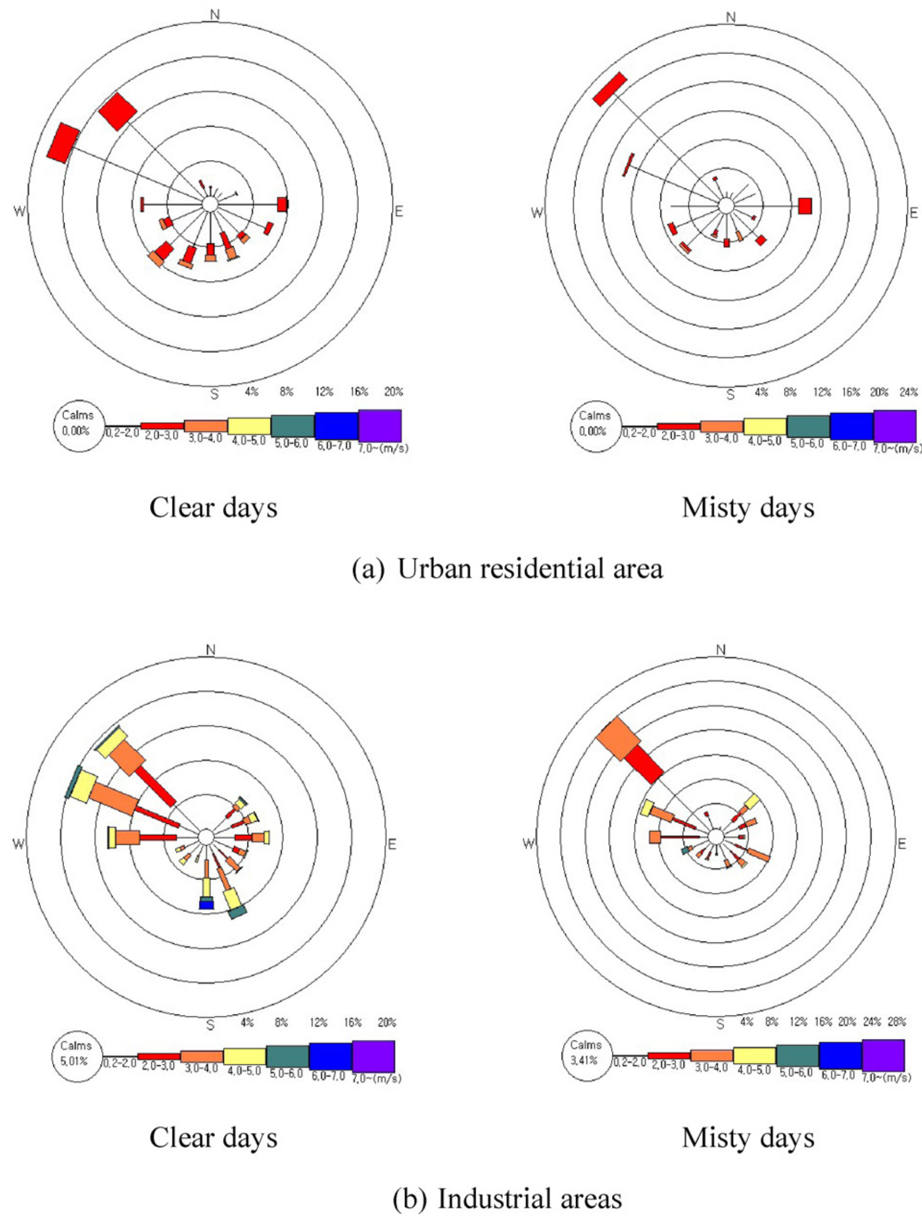

Fig. 4. Wind roses at the urban-residential area (a) and at the industrial area (b) during the study period.

Wang et al. [28] reported that the concentrations of NH_4^+, SO_4^{2-} and NO_3^- in TSP on haze days in spring season in urban Beijing were 3.8, 3.6 and 3.5 times higher than those on clear days, respectively. The increased ratios of NH_4^+ and NO_3^- in PM_{10} on the misty day in Ulsan were similar to those in TSP on spring haze days in Beijing. The ratios of [NH_4^+] to [SO_4^{2-} and NO_3^-] in PM_{10} in Ulsan on the misty and clear days were 0.70 and 0.91, respectively, which are lower than unity. This indicated ammonia, an important alkaline gas in the atmosphere [28], is not completely neutralized by acidic species (H_2SO_4 and HNO_3). The ratios of [NH_4^+] to [NO_3^-] in PM_{10} in Ulsan were 1.02 and 1.16 on the misty and clear days, respectively. This indicated that a major component of the total secondary aerosols (NH_4HSO_4, $(NH_4)_2SO_4$, and NH_4NO_3) in PM_{10} in the industrial area was NH_4NO_3 on both misty and clear days. Wang et al. [28] also reported that the major species of the secondary aerosols in Beijing were $(NH_4)_2SO_4$, NH_4NO_3 and $Ca(NO_3)_2$.

Table 3
Ambient air quality standards in the city of Ulsan, the republic of Korea, and other countries.

Pollutant Unit/time	PM_{10} μg/m^3/24 h	SO_2 ppb/24 h	O_3 ppb/8 h	NO_2 ppb/annual	CO ppb/8 h
Ulsan	100	40	60	30*	7000
Korea	100	50	60	30*	9000
USA	150	140	75	53	9000
EU	50	47.8	61.1	21.3	8732
WHO	50	10.6	50.9	21.3	9000

* 24 h standard: 60 ppb.

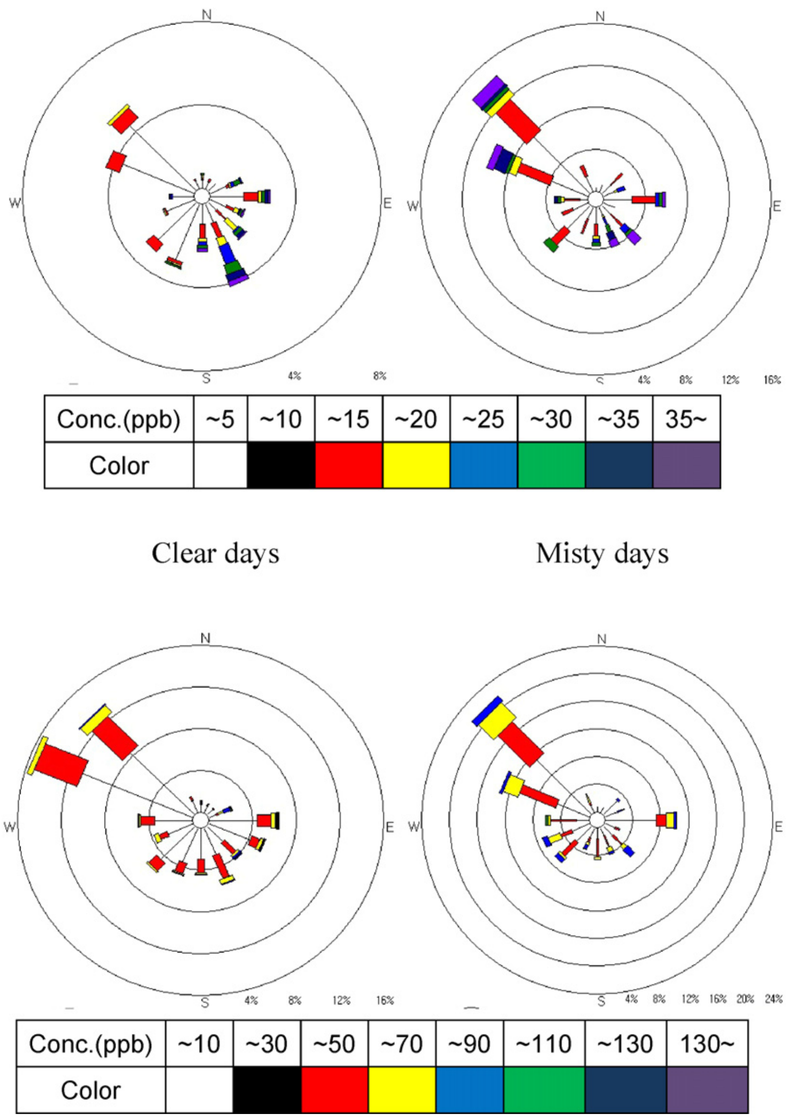

Fig. 5. SO_2 (upper) and NO_2 (bottom) pollution roses at the urban-residential area.

Wang et al. [37] also identified that majority of the total secondary aerosol in Shanghai was identified as $(NH_4)_2SO_4$. The mol ratios of NH_4^+ to SO_4^{2-} in PM_{10} in Ulsan were 1.08 and 2.17 on the misty and clear days, respectively. This showed that in the industrial area of Ulsan, the secondary aerosols in PM_{10} could include NH_4NO_3 as well as $(NH_4)_2SO_4$ on the misty day. However, air emissions of sulfur oxides at the industrial area on misty days would be similar to those on clear days. Thus there might be no large difference in the loading rate of PM_{10} and SO_2 between on misty days and on clear days. Therefore, elevated concentrations in PM_{10} and SO_2 on misty days may be associated with increased humidity and reduced wind speed [27], resulting in decreased atmospheric dispersion and increased ambient accumulation of air pollutants, as compared on clear days.

The substantially higher CO concentrations on misty days may be partially associated with decreased combustion efficiency of fuel or waste in industrial boilers or incinerators, which may be due to increased moisture levels in fuel or waste accompanied

Table 4
Concentrations of TSP and heavy metals in TSP from the urban-residential and industrial areas on clear and misty days [unit: ng/m^3 (all heavy metals), μg/m^3 (TSP)].

Day	Statistics	Urban-residential area								Industrial area							
		TSP	Pb	Cd	Cr	Cu	Mn	Fe	Ni	TSP	Pb	Cd	Cr	Cu	Mn	Fe	Ni
Clear days (n: 31)	Avg	62	46.2	2.0	4.1	139.5	55.3	1307	4.4	73	58.2	2.4	7.8	156.1	101.9	2089	11.5
	Max	119	189.3	10.5	12.3	264.7	118.2	2940	15.9	131	245.1	11.3	19.6	365.9	213.7	4796	27.2
	Min	25	7.4	0.1	1.0	60.7	18.2	358	0.0	41	7.3	0.0	2.6	60.4	45.8	662	1.7
Misty days (n: 11)	Avg	130	110.8	3.5	5.3	142.3	97.5	1979	7.8	141	151.4	4.0	8.3	178.0	173.6	2863	14.7
	Max	184	177.4	7.6	17.1	220.8	217.0	3143	24.4	179	291.6	14.6	14.9	301.8	294.7	5866	30.3
	Min	85	50.4	1.1	1.7	92.2	50.6	1028	3.0	104	56.7	1.2	1.0	111.6	83.9	1214	9.3
M/C	Avg	2.1	2.4	1.8	1.3	1.0	1.8	1.5	1.8	1.9	2.6	1.7	1.1	1.1	1.7	1.4	1.3

Note: M/C: ratio of average concentrations of pollutants on misty days to on clear days.

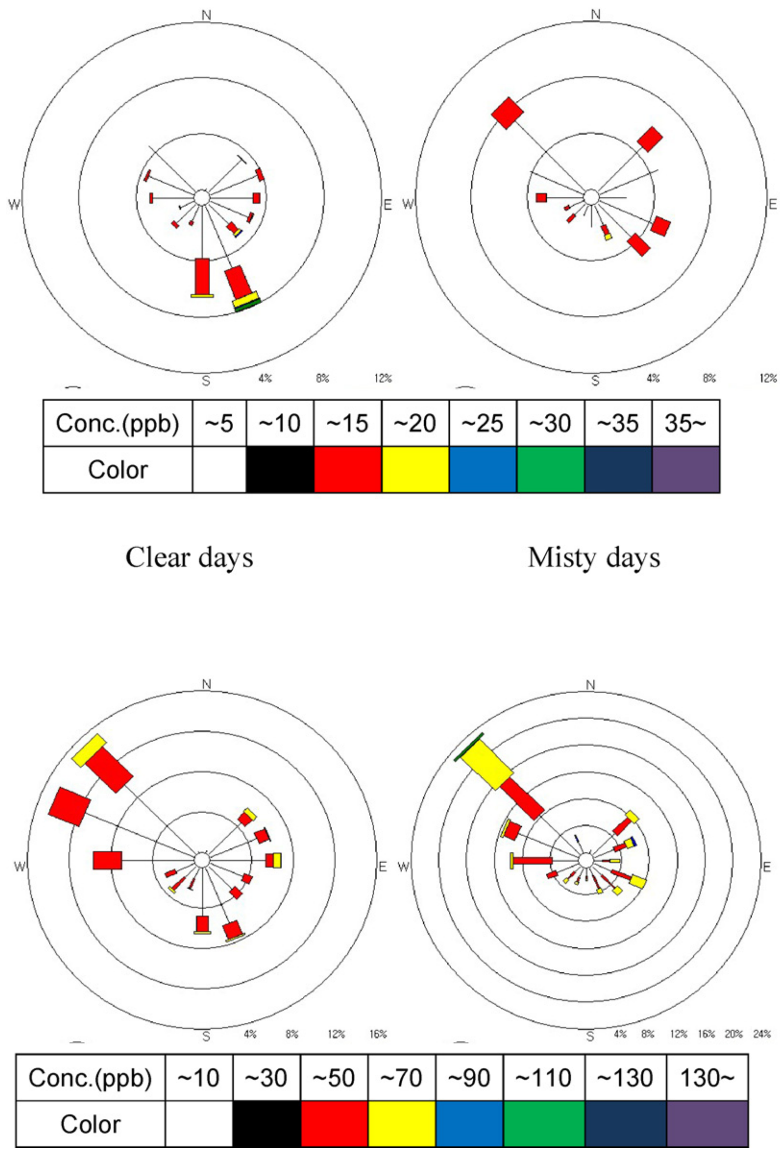

Fig. 6. SO_2 (upper) and NO_2 (bottom) pollution roses at the industrial area.

by increases in relative humidity levels [38]. The decreased efficiency of industrial boilers or incinerators would lead to increases in incomplete combustion of fuel or waste resulting in higher CO concentrations at the industrial area. However, this hypothesis was not confirmed in this study.

3.5. Heavy metal concentrations

Fig. 8(a) and (b) shows the time series concentrations of four heavy metals in TSP collected from the urban-residential and industrial areas for the study period. Concentrations of heavy metals in TSP observed on misty days substantially increased compared to those on clear days, similar to the increasing trend in TSP concentrations on misty days. The increase patterns in concentrations of four heavy metals in the urban-residential and industrial areas were similar to each other. Fig. 9 and Table 4 compare the concentrations of TSP and seven heavy metals extracted from the TSP samples collected from the urban-residential and industrial areas on misty days (11 days) and on clear days (31 days). This study analyzed the results of independent samples *t*-test to compare the means of concentrations obtained on clear and misty days at the study areas. All the components except Ni at the urban-residential area and Mn at the industrial area were satisfied the equal variance assumption between clear and misty days. The concentrations of

Table 5
Average of ventilation index (average ± standard deviation) on clear and misty days.

Item Unit	MMD m	WS m/s	Ventilation index m^2/s
Clear days	1143 ± 464 (446–2784)	1.4 (0.9–2.1)	1613 ± 943 (404–5719)
Misty days	1410 ± 421 (502–2057)	1.1 ± 0.2 (0.9–1.5)	1520 ± 363 (754–1876)

Note: MMD and WS stand for maximum mixing depth and wind speed, respectively.
Ventilation index (m^2/s) = MMD (m) × WS (m/s).

Table 6
Correlation coefficients between concentrations of TSP and the heavy metals in TSP on clear and misty days at the urban-residential area.

(a) Clear days

$n = 31$	TSP	Pb	Cd	Cr	Cu	Mn	Fe	Ni
TSP	1.000							
Pb *p*	**0.595**<0.05	1.000						
Cd *p*	0.483<0.01	**0.961**<0.01	1.000					
Cr *p*	**0.580**<0.01	**0.561**<0.01	**0.543**<0.01	1.000				
Cu *p*	−0.105	0.425<0.05	0.437<0.05	−0.182	1.000			
Mn *p*	**0.872**<0.01	**0.716**<0.01	**0.593**<0.01	0.442<0.05	0.179	1.000		
Fe *p*	**0.733**<0.01	0.363<0.05	0.287	0.091	0.082	**0.829**<0.01	1.000	
Ni *p*	0.344	**0.510**<0.01	**0.519**<0.01	0.011	**0.652**<0.01	**0.543**<0.01	0.439<0.05	1.000

(b) Misty days

$n = 11$	TSP	Pb	Cd	Cr	Cu	Mn	Fe	Ni
TSP	1.000							
Pb *p*	0.581	1.000						
Cd *p*	0.295	**0.808**<0.01	1.000					
Cr *p*	**0.768**<0.01	**0.781**<0.01	0.585	1.000				
Cu *p*	−0.072	0.101	0.562	−0.014	1.000			
Mn *p*	**0.706**<0.05	**0.781**<0.01	**0.704**<0.05	**0.959**<0.01	0.214	1.000		
Fe *p*	0.153	−0.346	−0.157	−0.007	0.377	0.160	1.000	
Ni *p*	0.359	**0.724**<0.05	**0.957**<0.01	**0.661**<0.05	0.602	**0.768**<0.01	−0.049	1.000

Note: Bold values represent significantly correlate with p-values less than 0.01 or 0.05.

TSP, Pb, Cd, Mn, Fe, and Ni at the urban-residential area and TSP, Pb, and Mn on misty days at the industrial area were significantly higher than those on clear days. In particular, the average concentrations of lead (Pb) and cadmium (Cd) as typical anthropogenic heavy metals [39] and manganese (Mn) as a typical soil origin heavy metal in TSP collected on misty days were 2.4–2.6 ($p < 0.05$), 1.7–1.8 ($p < 0.05$), and 1.7–1.8 ($p < 0.05$) times higher from the residential area and industrial area, respectively, than on clear days (Table 2).

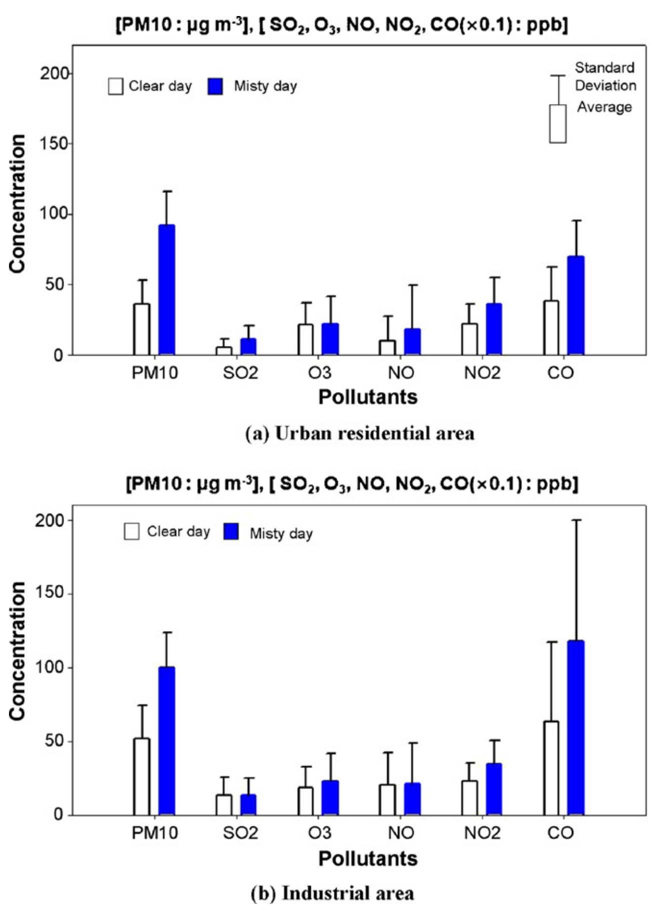

Fig. 7. Concentrations of air pollutants on clear and misty days at the urban-residential area (a) and the industrial area (b) during the study period.

High concentrations of TSP and of heavy metals in TSP on misty days compared to clear days can be explained by the differences between relative humidity and ambient ventilation indices on misty days and clear days [17]. Average ambient temperatures on clear days and on misty days were similar at $15.4 \pm 7.3\,^{\circ}C$ and $14.5 \pm 8.9\,^{\circ}C$, respectively. The average value of relative humidity on clear days was $50.2 \pm 15.6\%$ during the sampling period, while on misty days it was $57.0 \pm 12.7\%$. Particulate matter caught on water droplets or vapors on misty days would experience a sort of increased cage effect compared to clear days. Thus increased humidity on misty days would reduce the volatility of particulate matter collected on the filters and increase solubility and reactivity among materials or air pollutants on the filters and in the ambient air. Table 5 shows the average and standard values of ambient ventilation index, defined by production of the maximum mixing depth and the average wind speed, on clear days and misty days at the study areas. The average ambient ventilation index on misty days was $1520 \pm 363\,m^2/s$, while the index on clear days was $1613 \pm 943\,m^2/s$. The dilution effect of pollutants in the ambient air on misty days would decrease compared to clear days. This relatively limited dilution or dispersion of the ambient air on misty days would increase the possibility of accumulation or incorporation effects of air pollutants, such as acid components, sulfate, nitrate, and ammonium compounds, in the air environment near the ground where mist would easily be observed. Further studies should be performed to determine a better explanation for the increased concentrations in TSP and heavy metals in TSP on misty days.

3.6. Correlation

This study utilized a statistical package (SPSS 12) to identify the correlations among the concentrations of TSP and the heavy metals in TSP collected on clear days and misty days from the urban-residential and industrial areas for the study period. In the analysis of the correlation coefficients of concentrations with significant value (p) as shown in Table 6, there were so many components showing high correlations on clear days and misty days from the urban-residential area than from the industrial area. In the urban-residential area, a lot of the component pairs showed significantly

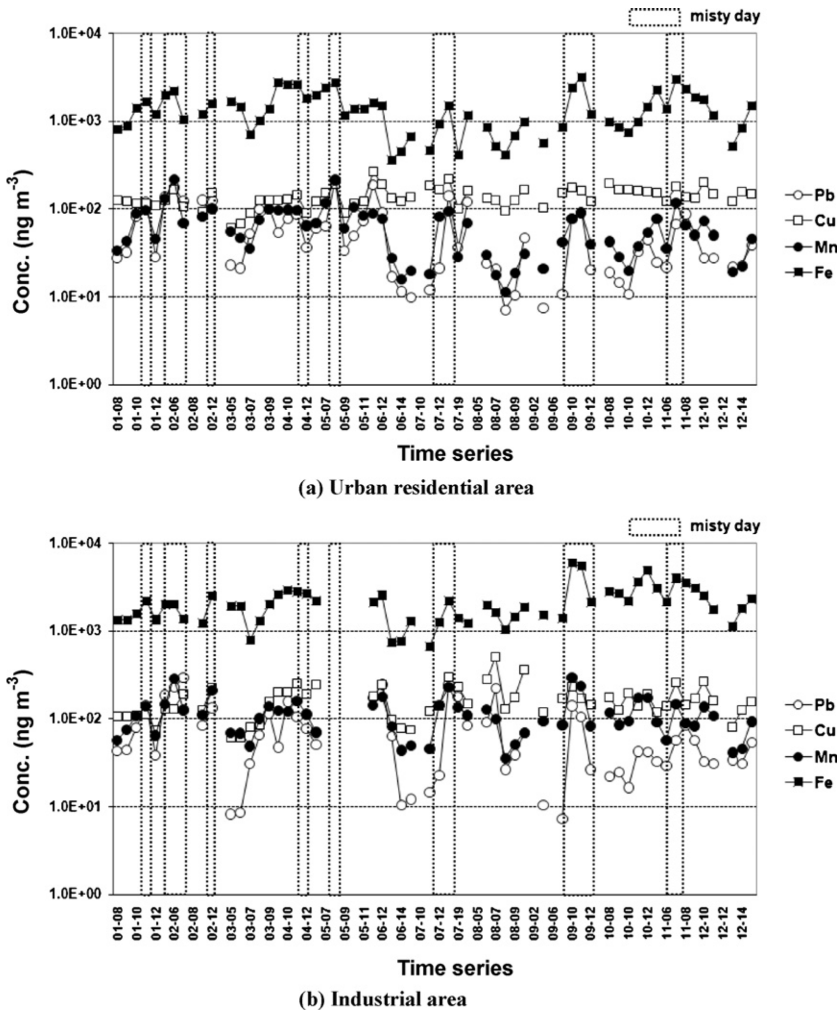

Fig. 8. Concentration variations of four heavy metals in the urban-residential and industrial areas on misty days (inside box) and clear days (outside box).

high correlations at levels of 0.01 and 0.05. In particular, Pb–Cd pairs showed a very high correlation both on clear days (0.961, $p < 0.01$) and on misty days (0.808, $p < 0.01$) representing common sources such as anthropogenic. Mn–TSP, Mn–Pb, and Mn–Cd pairs Mn–Cd pairs also showed high correlations, (0.872, $p < 0.01$), (0.761, $p < 0.01$), and (0.593, $p < 0.01$), respectively, on clear days and (0.706, $p < 0.05$), (0.781, $p < 0.01$), and (0.704, $p < 0.05$), respectively, on misty days representing common sources such as traffic

Table 7
Correlation coefficients between concentrations of TSP and the heavy metals in TSP on clear and misty days at the industrial area.

(a) Clear days

n = 31	TSP	Pb	Cd	Cr	Cu	Mn	Fe	Ni
TSP	1.000							
Pb p	**0.696**<0.01	1.000						
Cd p	**0.616**<0.01	**0.893**<0.01	1.000					
Cr p	−0.051	0.218	0.012	1.000				
Cu p	0.494<0.01	0.401<0.05	**0.622**<0.01	−0.159	1.000			
Mn p	**0.644**<0.01	**0.606**<0.01	0.497<0.01	0.375<0.05	0.475<0.01	1.000		
Fe p	**0.625**<0.01	0.182	0.191	−0.140	0.443<0.05	**0.679**<0.01	1.000	
Ni p	0.446<0.05	0.444<0.05	0.483<0.01	0.160	**0.593**<0.01	**0.589**<0.01	0.438<0.05	1.000

(b) Misty days

n = 11	TSP	Pb	Cd	Cr	Cu	Mn	Fe	Ni
TSP	1.000							
Pb p	−0.118	1.000						
Cd p	−0.005	0.363	1.000					
Cr p	0.026	0.113	−**0.625**<0.05	1.000				
Cu p	0.049	0.250	**0.744**<0.01	−**0.646**<0.05	1.000			
Mn p	0.395	0.370	0.339	0.317	0.365	1.000		
Fe p	**0.698**<0.05	−0.399	−0.102	−0.021	0.261	0.462	1.000	
Ni p	0.302	0.486	**0.763**<0.01	−0.146	**0.570**<0.05	**0.700**<0.05	0.057	1.000

Note: Bold values represent significantly correlate with p-values less than 0.01 or 0.05.

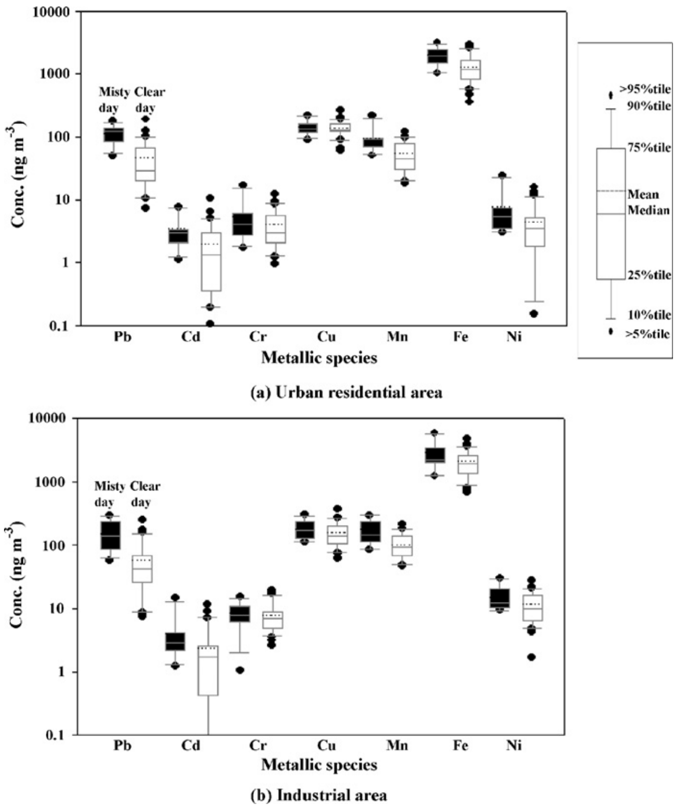

Fig. 9. Concentration distribution of heavy metals in TSP from the urban-residential and industrial areas on misty and clear days.

and soil origins. The pairs of Fe–TSP (0.733, $p < 0.01$) and Fe–Mn (0.829, $p < 0.01$) on clear days and Mn–Cr (0.959, $p < 0.01$), Ni–Cd (0.724, $p < 0.05$), Ni–Cd (0.957, $p < 0.01$), Ni–Cr (0.661, $p < 0.05$) and Ni–Mn (0.768, $p < 0.01$) on misty days represented significant correlations.

In the industrial area, pairs of TSP–Pb (0.696), TSP–Cd (0.616), TSP–Mn (0.644) and TSP–Fe (0.625) on clear days showed high correlations at significant levels of 0.01 (Table 7). There were not many pairs which show commonly high correlations both on clear days and misty days at the industrial area, except TSP–Fe, Cu–Cd, and Cu–Ni pairs. Also, the number of pairs representing high correlations at the industrial area was smaller than that at the urban-residential area. This analysis of correlations among TSP and heavy metals in TSP indicates that TSP from the urban-residential area was mainly affected by local traffic emissions, while TSP from the industrial area was affected by air emissions from both industrial sectors and local traffic sources.

4. Conclusions

By comparing the concentrations of TSP and heavy metals in TSP between misty days and clear days at urban-residential and industrial areas, the following conclusions were obtained:

(1) The average concentrations of TSP on misty days at both the study areas were 1.9–2.1 times significantly ($p < 0.05$) higher than those on clear days. Ratios of PM_{10}/TSP (0.72 ± 0.44) on misty days were higher than those (0.60 ± 0.56) on clear days.
(2) The average concentrations of PM_{10}, NO_2, and CO on misty days were 1.9–2.5, 1.5, and 1.8–1.9 times significantly ($p < 0.05$) higher than those on clear days, respectively.
(3) The average concentrations of Pb and Mn in TSP on misty days were 2.4–2.6 and 1.7–1.8 times significantly ($p < 0.05$) higher than those on clear days.
(4) A lot of pairs among heavy metals in TSP showed significantly high correlations at levels of 0.01 and 0.05. In particular, Pb–Cd (0.961 and 0.808, $p < 0.01$) pair on clear and misty days at both the study areas, and Mn–Cr (0.959, $p < 0.01$) and Ni–Cd (0.957, $p < 0.01$) pairs on misty days at the industrial area showed a very high correlation.

References

[1] P. Møller, J.K. Folkmann, L. Forchhammer, E.V. Bräuner, P.H. Danielsen, L. Risom, S. Loft, Air pollution, oxidative damage to DNA, and carcinogenesis, Cancer Lett. 266 (2008) 84–97.
[2] B.Z. Simkhovich, M.T. Kleinman, R.A. Kloner, Air pollution and cardiovascular injury: epidemiology, toxicology, and mechanisms, J. Am. Coll. Cardiol. 52 (2008) 719–726.
[3] M.S. Goldberg, R.T. Burnett, J.F. Yale, M.F. Valois, J.R. Brook, Association between ambient air pollution and daily mortality among persons with diabetes and cardiovascular disease, Environ. Res. 100 (2006) 255–267.
[4] B. Ostro, R. Broadwin, S. Green, W.Y. Feng, M. Lipsett, Fine particulate air pollution and mortality in nine California counties: results from CALFINE, Environ. Health Perspect. 114 (2006) 29–33.
[5] C.C. Chang, S.S. Tsai, S.C. Ho, C.Y. Yang, Air pollution and hospital admissions for cardiovascular disease in Taipei, Taiwan. Environ. Res. 98 (2005) 114–119.
[6] H. Kan, B. Chen, Air pollution and daily mortality in Shanghai: a time-series study, Arch. Environ. Health 58 (2003) 360–367.
[7] K. Donaldson, W. MacNee, Potential mechanisms of adverse pulmonary and cardiovascular effects of particulate air pollution (PM10), Int. J. Hyg. Environ. Health 203 (2001) 411–415.
[8] J.M. Ondov, A.S. Wexler, Where do particulate toxins reside? An improved paradigm for the structure and dynamics of the urban mid-Atlantic aerosol, Environ. Sci. Technol. 32 (1998) 2547–2555.
[9] T. Dong, B.-K. Lee, Characteristics, toxicity, and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea, Chemosphere 74 (2009) 1245–1253.
[10] Z. Li, A. Sjodin, E.N. Porter, D.G. Patterson Jr., L.L. Needham, S. Lee, A.G. Russell, J.A. Mulholland, Characterization of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Atlanta, Atmos. Environ. 43 (2009) 1043–1050.
[11] B.-K. Lee, C.H. Lee, Analysis of acidic components, heavy metals and PAHs of particulate in the Masan-Changwon Area of Korea, Environ. Monit. Assess. 136 (2008) 21–33.
[12] B.-K. Lee, T. Smith, E. Garshick, J. Natkin, P. Reaser, K. Lane, H.K. Lee, Exposure assessment to particulate matter of trucking company workers during the winter, Chemosphere 61 (2005) 1677–1690.
[13] B.-K. Lee, C.B. Lee, Development of an improved dry and wet deposition collector and the atmospheric deposition of PAHs onto Ulsan Bay, Korea Atmos. Environ. 38 (2004) 863–871.
[14] S. Sarmento, H.T. Wolterbeek, T.G. Verburg, M.C. Freitas, Correlating element atmospheric deposition and cancer mortality in Portugal: Data handling and preliminary results, Environ. Pollut. 151 (2008) 341–351.
[15] R.M. Harrison, D.J.T. Smith, A.J. Kibble, What is responsible for the carcinogenicity of PM2.5? Occup. Environ. Med. 61 (2004) 799–805.
[16] M.P. Tolocka, D.A. Lake, M.V. Johnston, A.S. Wexler, Number concentrations of fine and ultrafine particles containing metals, Atmos. Environ. 38 (2004) 3263–3273.
[17] M.K. Shin, C.D. Lee, H.S. Ha, Y.H. Kim, Meteorological parameter effects on fine particle concentrations, Korean Soc. Atmos. Environ. 23 (3) (2007) 322–331.
[18] H.S. Lee, C.-M. Kang, B.-W. Kang, H.-K. Kim, Seasonal variations of acidic air pollutants in Seoul, South Korea, Atmos. Environ. 33 (1999) 3143–3152.
[19] D.J. Jacob, Heterogeneous chemistry and tropospheric ozone, Atmos. Environ. 34 (2000) 2131–2159.
[20] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd ed., Wiley, New York, 2006, pp. 1–1232.
[21] H. Zhuang, C.K. Chan, M. Fang, A.S. Wexler, Formation of nitrate and non-sea-salt sulfate on coarse particles, Atmos. Environ. 33 (1999) 4223–4233.
[22] M. Ragosta, R. Caggiano, M. D'Emilio, S. Sabia, S. Trippetta, M. Macchiato, PM_{10} and heavy metal measurements in an industrial area of southern Italy, Atmos. Res. 81 (2006) 304–319.
[23] M. Ragosta, R. Caggiano, M. D'Emilio, M. Macchiato, Source origin and parameters influencing levels of heavy metals in TSP in an industrial background area of Southern Italy, Atmos. Environ. 36 (2002) 3071–3087.
[24] JEM News (Legislation), http://www.rsc.org/delivery/_ArticleLinking/DisplayArticleForFree.cfm?doi=b103927j&JournalCode=EM.
[25] B.A. Schichtel, R.B. Husar, S.R. Falke, W.E. Wilson, Haze trends over the United States, 1980–1995, Atmos. Environ. 35 (2001) 5205–5210.

[26] K. Okada, M. Ikegami, Y. Zaizen, Y. Makino, J.B. Jensen, J.L. Gras, The mixture state of individual aerosol particles in the 1997 Indonesian haze episode, J. Aerosol Sci. 32 (2001) 1269–1279.
[27] Y. Sun, G. Zhuang, A. Tang, Y. Wang, Z. An, Chemical characteristics of PM2.5 and PM10 in haze–fog episodes in Beijing, Environ. Sci. Technol. 40 (2006) 3148–3155.
[28] Y. Wang, G. Zhuang, Y. Sun, Z. An, The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing, Atmos. Environ. 40 (2006) 6579–6591.
[29] C.M. Kang, H.S. Lee, B.W. Kang, S.K. Lee, Y. Sunwoo, Chemical characteristics of acidic gas pollutants and PM2.5 species during hazy episodes in Seoul, South Korea, Atmos. Environ. 38 (2004) 4749–4760.
[30] L.W.A. Chen, J.C. Chow, B.G. Doddridge, R.R. Dickerson, W.F. Ryan, P.K. Mueller, Analysis of a summertime PM2.5 and haze episode in the mid-Atlantic region, J. Air Waste Manag. Assoc. 53 (2003) 946–956.
[31] A.K. Yadav, K. Kumar, A. Kasim, M.P. Singh, S.K. Parida, M. Sharan, Visibility and incidence of respiratory diseases during the 1998 haze episode in Brunei Darussalam, Pure Appl. Geophys. 160 (2003) 265–277.
[32] Y.S. Chung, H.S. Kim, M.B. Yoon, Observations of Visibility and Chemical Compositions Related to Fog, Mist and Haze in South Korea, Water Air Soil Pollut. 111 (1999) 139–157.
[33] C.K. Chan, C.S. Kwok, A.H.L. Chow, Water activity of mixed organic and inorganic aerosols, J. Aerosol Sci. (1997) S77–S78.
[34] M. Ragosta, R. Caggiano, M. Macchiato, S. Sabia, S. Trippetta, Trace elements in daily collected aerosol: level characterization and source identification in a four-year study, Atmos. Res. 89 (2008) 206–217.
[35] B. Wojas, C. Almquist, Mass concentrations and metals speciation of $PM_{2.5}$, PM_{10}, and total suspended solids in Oxford, Ohio and comparison with those from metropolitan sites in the Greater Cincinnati region, Atmos. Environ. 41 (2007) 9064–9078.
[36] A.K. Gupta, S.K. Gupta, R.S. Patil, A statistical analysis of particulate datasets for a Jawaharlal Nehru Port and surrounding harbour region in India, J. Environ. Monit. Ass. 95 (2004) 295–309.
[37] Y. Wang, G. Zhuang, X. Zhang, K. Huang, C. Xu, A. Tang, J. Chen, Z. An, The ion chemistry, seasonal cycle, and sources of $PM_{2.5}$ and TSP aerosol in Shanghai, Atmos. Environ. 40 (2006) 2935–2952.
[38] J. Chau, T. Sowlati, S. Sokhansanj, F. Preto, S. Melin, X. Bi, Techno-economic analysis of wood biomass boilers for the greenhouse industry, Appl. Energy 86 (2009) 364–371.
[39] K.F. Ho, S.C. Lee, C.K. Chan, J.C. Yu, J.C. Chow, X.H. Yao, Characterization of chemical species in $PM_{2.5}$ and PM_{10} aerosols in Hong Kong, Atmos. Environ. 37 (2003) 31–39.