

Analysis of Harmful Heavy Metals and Carbonaceous Components in Urban School PM_{2.5}

Seok Won Kang, Sumin Lee, Jiyoun Kwoun, Tae Jung Lee, Young Min Jo*

Department of Applied Environmental Science, Kyung Hee University, Yongin-si, Gyeonggi-do 17104, Korea

ABSTRACT

Harmful heavy metals and carbonaceous substances contained in PM_{2.5} collected from 53 schools located in large Korean cities were closely analyzed based on the hypothesis that emission sources such as automobiles are coincident. The average concentration of PM_{2.5} from the analysis of all classrooms was 20.7 $\mu\text{g m}^{-3}$. Mn was the most prevalent heavy metal with a concentration of 0.018 $\mu\text{g m}^{-3}$, followed by Pb and Cu. The heavy metals were closely related to elemental carbon (EC) introduced mainly from the outside with a correlation coefficient of 0.556, showing consistent significance. Organic carbon (OC) showed a correlation coefficient of 0.357, which statistically supported the presence of obvious OC sources in the classroom. Overall school classroom contamination levels have been shown to be below national guideline.

Keywords: PM_{2.5}, Heavy metals, Indoor air quality, Carbonaceous elements

1 INTRODUCTION

Heavy metals generally referred to air pollutants in atmospheric environment include lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), iron (Fe), nickel (Ni), arsenic (As), and beryllium (Be), only Pb has been limited to an annual average of 0.5 $\mu\text{g m}^{-3}$ or less by National Atmospheric Environment Guidelines in Korea. The World Health Organization (WHO) has also designated heavy metals as hazardous air pollutants (HAPs); the recommended limits of Cd and Mn are 0.005 $\mu\text{g m}^{-3}$ and 0.15 $\mu\text{g m}^{-3}$, respectively. Meanwhile, As, Ni, Cd, Cr, and Be have been designated as Class 1 carcinogens by the International Agency for Research on Cancer (IARC) (Kim *et al.*, 2015).

The Korean Ministry of Environment and local governments operate atmospheric heavy metal monitoring systems that regularly collect and measure the heavy metals at various regions (Lee *et al.*, 2000). The monitoring system analyzes the air quality mainly of large cities and industrial complexes, and the overall domestic concentration of heavy metals in the atmosphere is steadily decreasing (MOE, 2021). The concentration level varies depending on the region, and the Busan Health and Environment Research Institute has released the results for their 2021 air quality survey, indicating that the average concentration of major heavy metals was 3.7% to 23.3% of the national guideline (IHE, 2020).

In addition to the geological constituent Cu, particulate heavy metals in the air of large cities are often associated with automobiles; for example, Cr and Ni result from engine wear and brake pad friction (Karar *et al.*, 2006; Das *et al.*, 2015). Pb, which is emitted into the atmosphere due to various fuel combustion activities, is a relatively common and uniformly present substance in urban atmosphere, a large amount of which can be found in re-suspended road dust (Lough *et al.*, 2005). Mn, of which atmospheric levels are quite low, is generally emitted from industrial facilities handling Fe or non-ferrous metals. Although it is less toxic than Ni or Cu, continuous exposure to Mn dust or vapors is known to cause critical damage to the nervous system (Zhang *et al.*, 2016).

Most of the particulate carbon pollutants in the atmosphere are primary pollutants generated

OPEN ACCESS

Received: September 28, 2022

Revised: November 25, 2022

Accepted: January 3, 2023

* **Corresponding Author:**

ymjo@khu.ac.kr

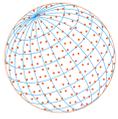
Publisher:

Taiwan Association for Aerosol
Research

ISSN: 1680-8584 print

ISSN: 2071-1409 online

 **Copyright:** The Author(s).
This is an open access article
distributed under the terms of the
[Creative Commons Attribution
License \(CC BY 4.0\)](https://creativecommons.org/licenses/by/4.0/), which permits
unrestricted use, distribution, and
reproduction in any medium,
provided the original author and
source are cited.



by incomplete combustion in the elemental carbon (EC) forms of soot, smoke, and haze. In particular, the carbon particles generated by automobile internal combustion engines are very small in size (ca. 50 nm) and may act as genotoxic materials (Jansen *et al.*, 2005). In addition, their structure with a high specific surface area provides high adsorption capacity that can absorb various pollutants including heavy metal ions.

Organic carbon (OC) exists as compounds such as VOCs and PAHs generated from natural sources including plants, soil and oceans as well as anthropogenic combustion processes. OC is also formed as a secondary material through photochemical reactions (Xu *et al.*, 2015). The total carbon component (OC + EC) contained in PM_{2.5} in Seoul's atmosphere accounts for about 14.4–21.2 w.w%. It was also reported that the OC/EC proportion in the air of large cities ranged from 1.1 to 4.1 (Park *et al.*, 2015; Lim *et al.*, 2010). A practical experiment reported that the exhaust gas of diesel vehicles operating in large cities contained 3,461 µg m⁻³ of OC, 1,140 µg m⁻³ of EC, and 2,051 µg m⁻³ of PM_{2.5} (Lin *et al.*, 2020). Depending on the fuel type and driving condition, various heavy metals were emitted concurrently.

Harmful heavy metals and carbon contained in PM_{2.5} than PM₁₀ have been occasionally studied for school environments (Moghtaderi *et al.*, 2020; Alghamdi *et al.*, 2019; Cho, 2000). In particular, urban schools adjacent to high-traffic roads are prone to exposure to a variety of vehicle-emission pollutants (Zhang *et al.*, 2021). However, since access to schools is limited, a more comprehensive study on classroom air quality could not be conducted. Recently, the quantitative concentration distribution of indoor fine dust was investigated for 34 elementary schools in Korea; however, due to limited research conditions, it was not possible to proceed the profound composition analysis that required long-term sampling (Park *et al.*, 2020).

In this study, highly toxic heavy metal substances such as Cu, As, Ni, Cr, Pb, and Mn and carbonaceous components contained in PM_{2.5} in school classrooms was closely analyzed, and their correlation with outdoor air quality was evaluated to understand the characteristics of urban school fine particulate matters. The obtained data would be effectively utilized for school indoor air quality (IAQ) management.

2 METHODS

This study was conducted at 53 schools located in large cities during six semesters from the 2nd semester (September–December) in 2019 to the 1st semester (March–July) of 2022. Analysis was performed for OC, EC and six harmful heavy metals contained in PM_{2.5} collected from classrooms and playgrounds. Sampling and measurements were carried out while maintaining normal class work without any intentional control over class content and student activities.

2.1 Site Description and Sampling

The schools for the study were elementary (44 schools), middle school (7 schools), and high schools (2 schools) in urban areas across the country as shown in Fig. 1; most schools were adjacent to roads with more than two lanes. Dust samples were collected from three to four classrooms in each school and an open podium of a playground located within 10 m from the building.

According to the standard test method of the Ministry of Environment for indoor air quality, two low-volume air samplers (Model BMW 2500, Total Eng., Seoul, Korea) were placed on personal lockers at a height of 1.2 to 1.5 m at the rear of the classroom. Sample collection was performed at a suction flow rate of 5 L min⁻¹ from just before class to about 30 minutes after dismissal (elementary school; 08:00–15:30, middle and high school; 07:30–17:00). The sample collection was carried out simultaneously in each of the three classrooms per school for 4 days from Monday to Thursday. A Teflon filter (Anow, Beijing, China) was used for PM_{2.5} weight concentration evaluation and heavy metal component analysis. The filter was preserved in a desiccator at 20 ± 1°C, 45 ± 5% before and after sampling for more than 24 hours. The filter was then weighed with an analytical balance (AT261, Mettler Toledo, Switzerland) having a sensitivity of 0.001 mg. For carbon analysis, a quartz filter (QM-A1851, Whatman, England) pre-heated at 700°C was applied. The numbers of PM_{2.5} samples were 179 indoors and 61 outdoors, including some repeat measures of some schools.

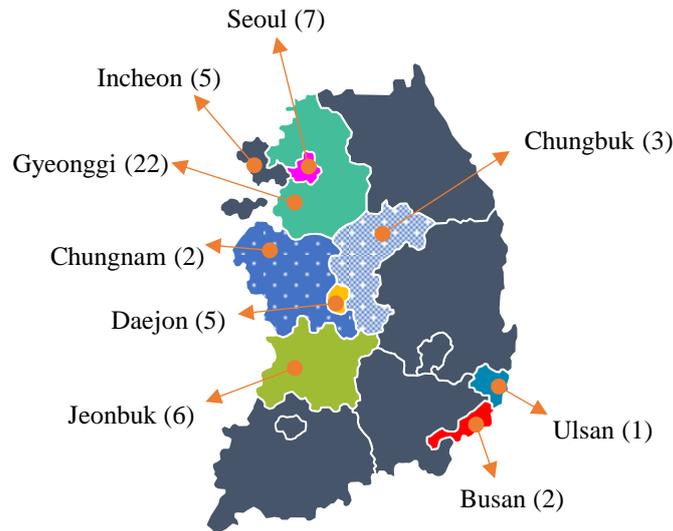
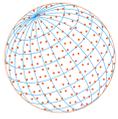


Fig. 1. Locations and number of study schools across the country.

2.2 Sample Analysis

In this study, six harmful heavy metals (Mn, Pb, Cu, As, Cr, Ni) were quantitatively analyzed via energy-dispersive X-ray fluorescence spectrometry (ARL QUANT'X High Performance ED-XRF, Thermo Inc., USA) (Heo *et al.*, 2021). To determine the method detection limit (MDL) recommended by the U.S. EPA, the standard deviation was obtained from seven repeated analyses and multiplied by π . As a result of analysis of the unit area of each filter (cm^2), detection limit for each element was as follows: Mn: 1.03 ng cm^{-2} , Pb: 0.44 ng cm^{-2} , Cu: 0.30 ng cm^{-2} , As: 0.14 ng cm^{-2} , Cr: 0.56 ng cm^{-2} , Ni: 0.12 ng cm^{-2} .

The mass concentrations of OC and EC contained in $\text{PM}_{2.5}$ particles were analyzed using a TOT analyzer (Thermal/Optical Transmittance, Sunset Lab., USA) based on a protocol by NIOSH5040 (National Institute of Occupational Safety & Health) (Park *et al.*, 2014). The precision of the OC and EC measurements was 0.95 or higher for each sample as a result of twice repeated analysis of the field samples. Accuracy was estimated as the amount of carbon in $50 \mu\text{g}$ of artificially prepared sucrose, and the difference was less than 5% when repeated seven times. The MDL values of OC and EC concentrations were 3.939 and $0.000 \mu\text{g cm}^{-2}$, respectively, calculated as three times the standard deviation of the blank sample value.

2.3 Data Analysis

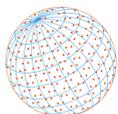
All data ($\text{PM}_{2.5}$, carbon, heavy metals) obtained from 53 schools were analyzed using the SPSS program (Ver. 25, SPSS Inc., USA). The statistical significance of school classroom and outdoor air concentrations was compared using T-test. The concentration distribution of collected data was presented using a boxplot. The symbol '0' in the boxplot indicates the percentile values for the first and 99th data points as outliers. The lines below and above the box represented the 5th and 95th percentiles, the bottom and top edges were the 25th and 75th percentiles. Respectively; the solid line inside the box indicates the median, and \bar{x} is the mean value.

The correlation between $\text{PM}_{2.5}$, the carbon component, and heavy metals was examined by calculating the correlation coefficient (r) through Pearson correlation analysis. In addition, the coefficient of determination (R^2) was derived through regression analysis implying the relationship between variables. In general, the closer is the R^2 value to 1, the higher is the correlation between the independent variable and the dependent variable.

3 RESULTS AND DISCUSSION

3.1 Distribution of $\text{PM}_{2.5}$ Inside and Outside the Classroom

Table 1 shows the average concentration, standard deviation, and concentration range for



PM_{2.5} measured in the classrooms and playgrounds of test schools. The average PM_{2.5} concentration was $20.7 \pm 7.7 \mu\text{g m}^{-3}$ and $28.5 \pm 14.8 \mu\text{g m}^{-3}$ in classrooms and playgrounds, with a significantly higher values outdoors than indoors ($p < 0.001$). The indoor and outdoor PM_{2.5} concentration ranges were 3.3–46.0 $\mu\text{g m}^{-3}$ and 3.8–70.5 $\mu\text{g m}^{-3}$, respectively, indicating that the outdoor regime was wider than the indoor space. This was because when the outdoor air quality deteriorated teachers frequently operated the air purifier according to the advice of the school administrator. The average indoor/outdoor ratio (I/O) was 0.73, confirming that the outdoor concentration was higher overall. Since there were few internal sources, classroom PM_{2.5} was mostly caused by infiltration from the outside, unlike the 1.0 I/O ratio of PM₁₀, significant amounts of which were resuspended by student activities in the classroom (Pallarés *et al.*, 2019; Yang *et al.*, 2009; Stranger *et al.*, 2008).

Fig. 2 shows the summary of the PM_{2.5} concentration range for total samples from classrooms and outdoors. Classrooms with a concentration distribution in the range of 21–35 $\mu\text{g m}^{-3}$ accounted for 49.4%, and 11–20 $\mu\text{g m}^{-3}$ was observed to account for 34.5%. It was finally found that 96% of classrooms maintained a standard PM_{2.5} concentration under the School Health Act of 35 $\mu\text{g m}^{-3}$ (average for 24 hours). Since the measurement data were obtained for 7 to 9 hours of class time, it could be concluded that most classrooms would satisfy the guidelines because the test condition of this study were relatively harsh compared to the national standard that included the time without class.

Table 1. Mass concentrations of PM_{2.5}, carbon, and heavy metals inside and outside the classroom during the sampling period.

Site (Unit: $\mu\text{g m}^{-3}$)	Indoor (n = 179)				Outdoor (n = 61)				I/O ^a
	Average	Std.	Min.	Max.	Average	Std.	Min.	Max.	
PM _{2.5}	20.666	7.741	3.300	45.972	28.447	14.763	3.800	70.500	0.73
OC	8.454	2.573	1.691	16.616	5.558	2.146	0.295	9.550	1.52
EC	0.767	0.308	0.141	1.832	0.828	0.340	0.270	1.960	0.93
TC	9.213	1.445	1.691	18.449	6.373	1.249	0.295	11.510	1.45
OC/EC	11.14				6.82				
Pb	0.019	0.026	0.001	0.187	0.019	0.015	0.001	0.117	0.99
As	0.004	0.003	0.000	0.015	0.004	0.003	0.000	0.016	0.72
Cu	0.009	0.023	0.001	0.149	0.009	0.016	0.000	0.117	1.03
Ni	0.003	0.009	0.000	0.062	0.002	0.007	0.000	0.051	1.38
Mn	0.018	0.035	0.001	0.404	0.022	0.015	0.002	0.073	0.81
Cr	0.002	0.002	0.001	0.016	0.003	0.003	0.001	0.020	0.80
Sum of heavy metals	0.053	0.070	0.001	0.505	0.057	0.045	0.002	0.318	0.93

^a Indoor to outdoor ratio.

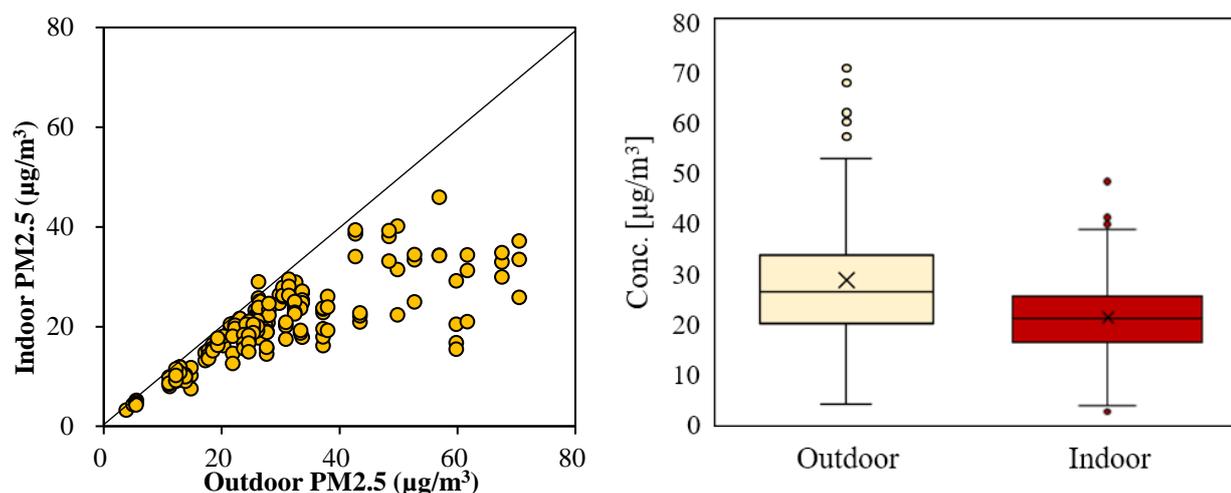


Fig. 2. PM_{2.5} concentration distribution inside and outside the classroom.

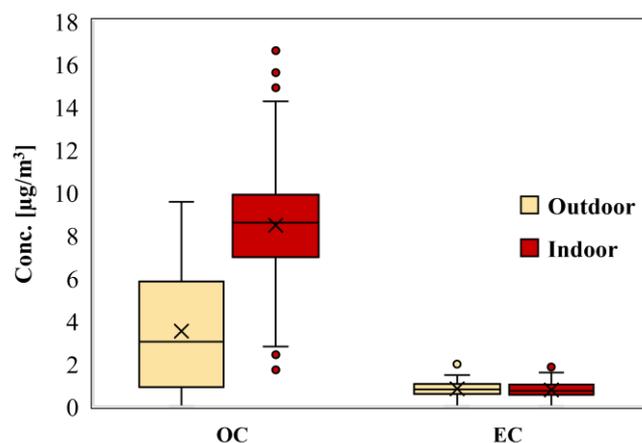
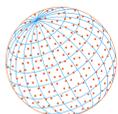


Fig. 3. Carbon content found inside and outside the classroom.

During the measurement period, 22.8% of the local air quality exceeded the national standard for the 24-hour $PM_{2.5}$ level. However, the number of days exceeding $35 \mu g m^{-3}$ in the classrooms was only 4%. In accordance, it was presumed that a significant amount of fine particulate matter was blocked from penetrating through windows or building structure; air purifiers or mechanical ventilation were also operated when high concentrations of fine dust were forecast.

In addition, 12.1% of classrooms had a very low concentration of $10 \mu g m^{-3}$ or less. This low level was due to rain outside, resulting in extremely low $PM_{2.5}$ concentrations. For example, the air quality monitoring system (AQMS) near the test schools reported $3.8\text{--}5.5 \mu g m^{-3}$ in Gyeonggi and $4.4\text{--}11.1 \mu g m^{-3}$ in Daejeon during the sampling period. Besides, as the COVID-19 pandemic occurred during this time, some schools allowed only 50% attendance of the class capacity, and attendance every other day or online classes were conducted concurrently. Refraining from active student movement in the classroom was also considered as a factors that reduced the spatial level of particulate matter below the average.

3.2 Carbon Components

Fig. 3 is a box-plot representing the minimum, maximum, percentile, medium and average values for the concentration distribution of OC and EC detected inside and outside classrooms. The average indoor and outdoor OC concentrations in all schools were $8.5 \pm 2.6 \mu g m^{-3}$ and $5.6 \pm 2.2 \mu g m^{-3}$, respectively. Indoor values were significantly higher than outdoors ($p < 0.001$). However, the average EC concentrations were distributed between indoors and outdoors by $0.77 \pm 0.32 \mu g m^{-3}$ and $0.83 \pm 0.34 \mu g m^{-3}$, respectively, with no statistically significant difference. Thus, the I/O ratios of OC and EC were summarized as 1.52 and 0.93.

As could be seen from a summary of the analysis for all site samples, OC and EC yielded quite different distribution patterns. In the case of OC emitted from a wide variety of sources, the amount contained in $PM_{2.5}$ suspended in school classrooms was noticeably higher than that in outdoors. This was different from a study conducted in a middle school in Xi'an, China, which reported that $PM_{2.5}$ in the outside air contained more OC and EC (5–10%) than inside the classroom (Xu *et al.*, 2015). The use of various education or learning tools and personal beauty products, abrasion of building materials made from synthetic chemical materials, and spraying of disinfection and cleaning agents for COVID-19 prevention may have caused volatilization of organic carbon components in the classroom. In practice, the relative ratio of indoor OC to $PM_{2.5}$ before and after the Corona pandemic period (2019 and 2022) distributed from 0.37 to 0.38, but it was 0.42 during the COVID-19 period. The concentration of indoor EC, which is introduced almost entirely from the outside, was almost the same as that outdoors.

3.3 Heavy Metals

3.3.1 Heavy metal concentrations in indoor and outdoor $PM_{2.5}$

As summarized in Fig. 4, a reduced amount of heavy metals (6-species) contained in indoor $PM_{2.5}$ was found compared to outside, but the difference was not significant. The amount of

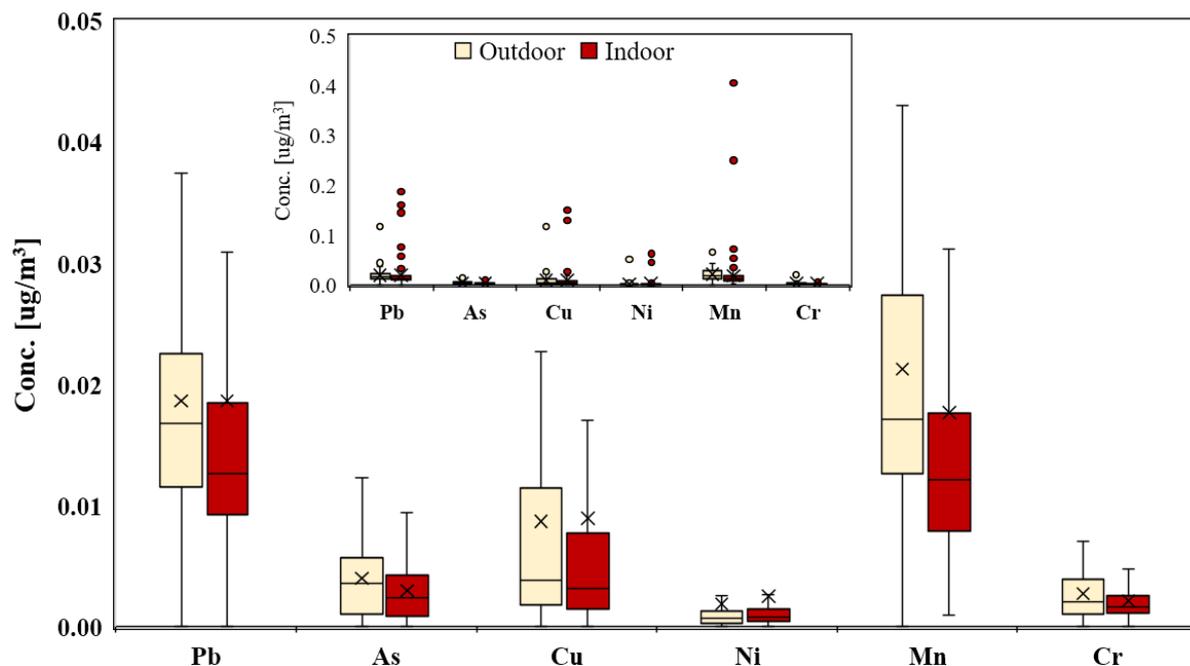
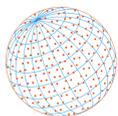


Fig. 4. Heavy metal concentration distributions in PM_{2.5} inside and outside the classroom.

outdoor heavy metals distributed more widely. Among indoor metals, Pb and Mn were significantly more frequent, followed by Cu, As, Ni and Cr. Although the carcinogens designated by the IARC were distributed at low concentrations, the average concentration of Pb, a potentially carcinogenic substance, was relatively high at 0.0187 and 0.0189 $\mu\text{g m}^{-3}$ in the classroom and outside air, respectively. In this study, indoor Pb accounted for approximately 98.9% of the outdoor value, however, according to a study from domestic middle and high schools conducted 20 years ago, Pb contamination of classroom PM_{2.5} exceeded the outdoor value up to 20% (Cho, 2000). Reductions in heavy metals in school particulate matters reflect consistent improvements in air quality across the country as national guidelines become more stringent.

On the other hand, Ni and Cr were present in school classrooms in small amounts with average concentrations of 0.0029 and 0.0025 $\mu\text{g m}^{-3}$ or less, respectively, but showed a high correlation (0.827) as could be seen in Table 2. This was presumed to be because both components originated from external sources related to road vehicles. However, PM_{2.5} in the classroom had more than twice as much Cr as Ni, as seen in other studies (Cho, 2000; Moghtaderi *et al.*, 2020).

The inner graph of Fig. 4 including outliers found in some classes showed extremely high content of Mn of 0.4 $\mu\text{g m}^{-3}$, which was more than 20 times the average concentration; Pb also has risen to 0.2 $\mu\text{g m}^{-3}$ in a classroom. These maximum concentration levels of Mn and Pb were 10 to 20 times higher than the amount of heavy metals found in air conditioner filters of school classrooms discovered from a recent Saudi Arabian study (Alghamdi *et al.*, 2019). The U.S. EPA previously reported that Mn in the atmosphere is approximately 6.25 times higher in cities than in rural area (Corbin *et al.*, 2015).

If elementary school students are continuously exposed to such high levels, the heavy metal intake could be 0.11 to 0.13 $\mu\text{g-Pb}$ based on calculations by assuming 190 school days per year, an average of 6 hours a day and 5 days a week based on the 'Korean Children's Exposure Factor Handbook (2–19)' published by the National Academy of Environmental Sciences. This appeared to be a very small amount, but according to a recent research result, continuous inhalation of various heavy metals over several years can affect the cranial nervous system (Miah *et al.*, 2020). Thus, it is estimated that schools located in large cities were always exposed to harmful air pollutants emitted from vehicles.

3.3.2 Correlation of heavy metals and carbon in PM_{2.5}

Table 2 summarizes the correlation coefficients between PM_{2.5}, carbon and major heavy metals

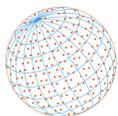


Table 2. Correlation coefficients between measured OC, EC and heavy metal concentrations in PM_{2.5} inside and outside the classroom.

	Indoor									
	PM _{2.5}	OC	EC	Pb	As	Cu	Ni	Mn	Cr	heavy metals
PM _{2.5}	1.000									
OC	0.518**	1.000								
EC	0.290**	0.236**	1.000							
Pb	0.116	0.143	0.116	1.000						
As	0.224*	0.174	0.452**	0.392**	1.000					
Cu	0.151	0.185*	-0.028	0.936**	0.055	1.000				
Ni	0.088	-0.039	0.315**	0.288**	0.069	0.053	1.000			
Mn	0.450**	0.263**	0.448**	0.149	0.265**	0.072	0.580**	1.000		
Cr	0.193*	0.058	0.326**	0.076	0.141	-0.012	0.827**	0.711**	1.000	
heavy metals	0.465**	0.357**	0.556**	0.832**	0.402**	0.592**	0.554**	0.878**	0.697**	1.000

	Outdoor									
	PM _{2.5}	OC	EC	Pb	As	Cu	Ni	Mn	Cr	heavy metals
PM _{2.5}	1.000									
OC	0.621**	1.000								
EC	0.443**	0.559**	1.000							
Pb	0.582**	0.581**	0.636**	1.000						
As	0.141	0.263	0.429**	0.406**	1.000					
Cu	0.412**	0.512**	0.090	0.551**	0.113	1.000				
Ni	0.477**	0.523**	0.353*	0.469**	0.081	0.510**	1.000			
Mn	0.724**	0.597**	0.294*	0.572**	0.386**	0.563**	0.533**	1.000		
Cr	0.569**	0.533**	0.262	0.565**	0.232	0.734**	0.713**	0.745**	1.000	
heavy metals	0.701**	0.685**	0.574**	0.837**	0.462**	0.778**	0.609**	0.891**	0.831**	1.000

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level.

found inside and outside classrooms. The correlation between PM_{2.5} and heavy metals was higher outdoors (r : 0.701, p -value: 0.000) than indoors (r : 0.465, p -value: 0.000). The indoor correlation was high in the order of Mn (0.450) > As (0.224) > Cr (0.193), and outdoor was Mn (0.724) > Pb (0.582) > Cr (0.569) > Ni (0.477) > Cu (0.412). The correlation coefficient between heavy metals amongst indoor PM_{2.5} was highest for Cu and Pb at 0.936, followed by Cr and Ni (0.827) and Cr and Mn (0.711). Outside, this coefficient was high for Cr and Mn at 0.745; Cr and Cu at 0.734; and Cr and Ni at 0.713. On the other hand, despite a lower coefficient for indoor PM_{2.5} and total heavy metals, the correlation between metal elements was similar to that outside. This indicates that most internal heavy metals originated from external sources such as industrial exhaust, automobiles and waste incineration, particularly for Mn, Cr and Ni.

The correlation coefficient values between heavy metals and EC did not show a significant difference as, 0.574 and 0.556, respectively. This may have been due to similar emission sources for the two substances. However, a higher coefficient, 0.685, was found in the classroom than outside 0.358. This implies that there are various additional sources of OC in the classroom (Pegas *et al.*, 2012).

Fig. 5 depicts the quantitative amount of total heavy metals present in PM_{2.5} excluding outliers. The gradients for the linear regression were 0.0011 and 0.0014, respectively. As also observed visually, the concentration distribution of the classroom was more widely scattered (R^2 : 0.21) than the outside (R^2 : 0.49) which was already evaluated in the standard deviation of Table 1. The distribution was estimated to be wide because the number of data was much greater indoors (179 data) than outdoors (61 data points). Despite less dependency on PM_{2.5}, the average concentration was 52.9 ng m⁻³, which was lower than the outside, 57.2 ng m⁻³. There was no statistically significant difference ($p < 0.001$). After all, most of the ultrafine dust came from the outside and the amount of heavy metals suspended in the classroom was inevitably dependent on the environmental conditions around the school. Thus, despite various environmental variables of classrooms, it could be concluded that an increase in indoor PM_{2.5} inevitably would increase the possibility of suspending heavy metals.

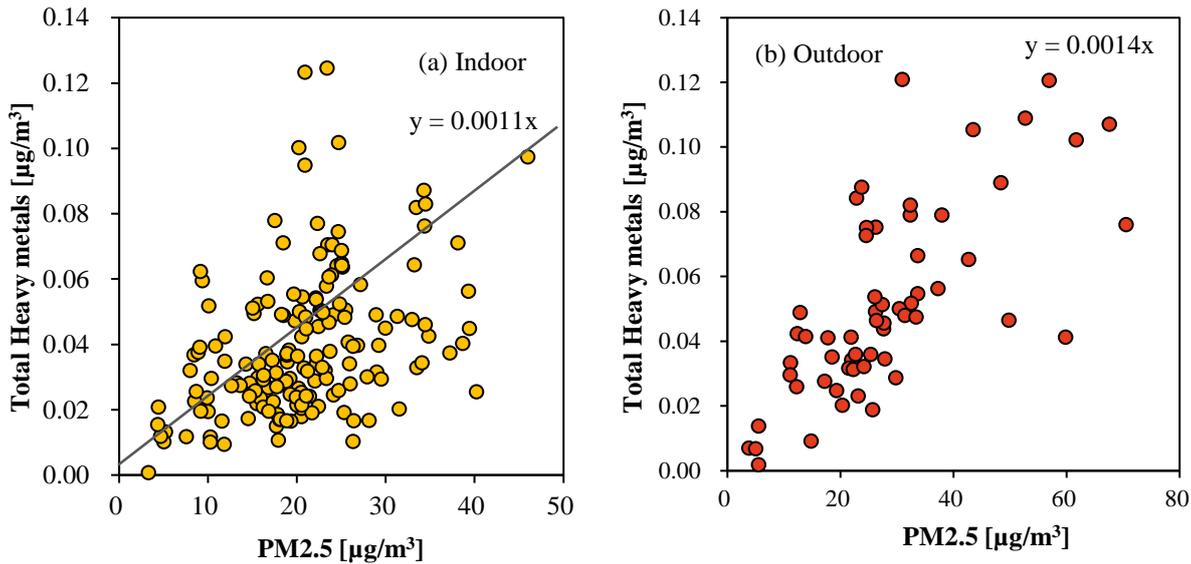
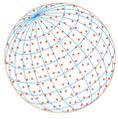


Fig. 5. Correlation of six heavy metals with PM_{2.5} (a) indoors and (b) outdoors.

Meanwhile, the amount of heavy metals versus the concentration of carbonaceous substances is summarized in Fig. 6. Regardless of location, the larger was the carbon amount, the greater was the heavy metal content. The correlation between EC and heavy metal content was 1.03 times larger for PM_{2.5} outdoors than indoors. Since EC is discharged into the atmosphere in the form of primary pollutants produced by fuel combustion or biomass burning, there may be a proportional relationship with regard to heavy metals frequently resulting from combustion processes. In particular, since automobiles are a major emission source for air pollutants in large cities, both heavy metals and carbon components are concurrently generated with PM_{2.5}, a certain relationship between those substances can be assumed (Lin *et al.*, 2020). Ultrafine particles contain a large amount of EC due to their large specific surface area, and long residence time indoors can result in a high accumulation within the classroom (Corbin *et al.*, 2015; Cho, 2000).

The relationship of heavy metal content over OC absorbed in PM_{2.5} was larger outdoors (0.09) than in the classroom (0.003). This indicated that, as mentioned above, a large amount of OC could be generated indoors, resulting in a relatively lower increase rate of heavy metals compared

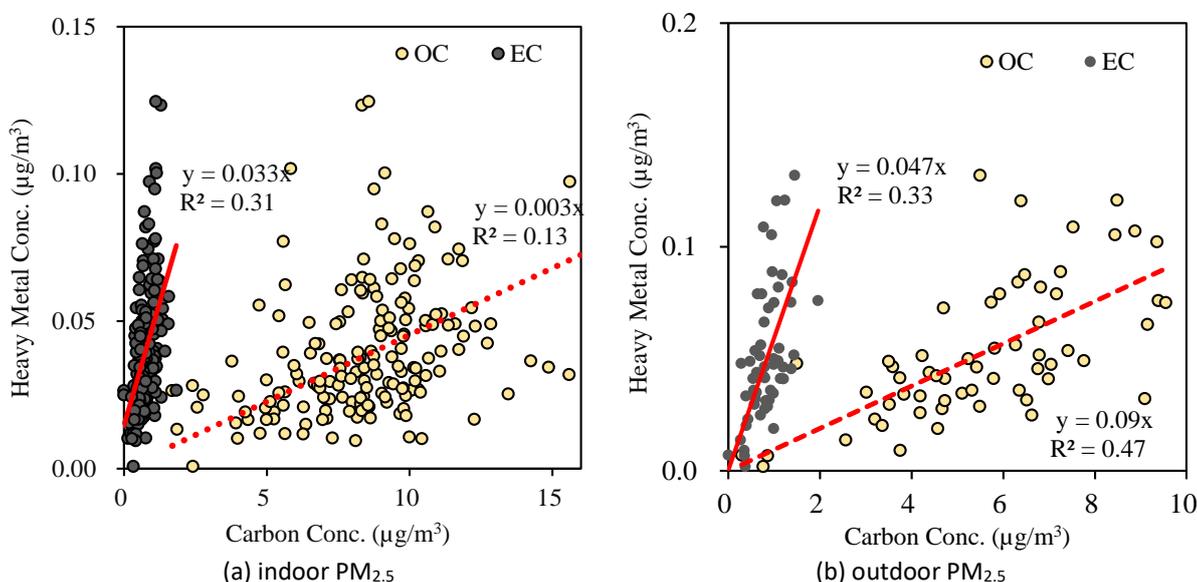
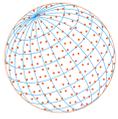


Fig. 6. Correlation of the total heavy metals and carbon content of PM_{2.5}.



to outdoor air. In other words, while the amount of heavy metal components contained in particles flowing into the classroom from the outside was constant, OC may be generated from various indoor sources and adhere to the particles, resulting in a low relative ratio against other contaminants such as heavy metals.

4 CONCLUSIONS

Since automobiles are a major source for air pollution, it was hypothesized that there is a consistent correlation between harmful heavy metals and carbon components contained in fine dust (PM_{2.5}) in school classrooms located in large modern cities. In this study, the distribution of indoor and outdoor PM_{2.5} concentrations were collected from 179 classrooms of 53 schools in large cities across the country; and OC, EC and 6 major heavy metals contained in PM_{2.5} were comparatively analyzed. As a result of the quantitative analysis, the average concentration of PM_{2.5} was 20.7 µg m⁻³, which was lower than the School Health Act guidelines (35 µg m⁻³-24 hr avg.), and 96% of the entire classroom satisfied this standard. However, compared with the WHO 24-hour recommendation standard (15 µg m⁻³), only 20.1% of the test classrooms were satisfied, indicating that more efforts are needed with regard to school air quality management.

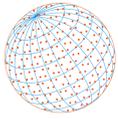
This study found that carbonaceous components, especially EC of which main source is incomplete combustion, had consistent quantitative correlations with heavy metals (0.556 and 0.574). In contrast, because OC was generated in large quantities in the classroom, its correlation with the heavy metal content decreased from 0.685 to 0.357 for outdoors to indoors, respectively. In a situation where access to schools for research purposes is very limited due to an increase in teacher authority and human rights, the experimental results obtained in this study will provide valuable data to protect the health of young children.

ACKNOWLEDGMENTS

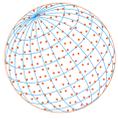
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT, MOE) and (No. 2019M3E7A1113077).

REFERENCES

- Alghamdi, M., Salwa K.H., Alzahrani, N.A., Almeahmadi, F.M., Khoder, M.I. (2019). Risk assessment and implications of schoolchildren exposure to classroom heavy metals particles in Jeddah, Saudi Arabia. *Int. J. Environ. Res. Public Health* 16, 1–24. <https://doi.org/10.3390/ijerph16245017>
- Cho, K.S. (2000). Heavy metal contamination of indoor, outdoor and playground in middle and high school in the Jeonju-city, Korea. *J. Korean Environ. Sci.* 9, 495–503. (in Korean with English Abstract)
- Corbin, J.C., Lohmann, U., Sierau, B., Keller, A., Burtscher, H., Mensah, A.A. (2015). Black carbon surface oxidation and organic composition of beech-wood soot aerosols. *Atmos. Chem. Phys.* 15, 11885–11907. <https://doi.org/10.5194/acp-15-11885-2015>
- Das, R., Khezri, B., Srivastava, B., Datta, S., Sikdar, P.K., Webster, R.D., Wang, X. (2015). Trace element composition of PM_{2.5} and PM₁₀ from Kolkata – A heavily polluted Indian metropolis. *Atmos. Pollut. Res.* 6, 742–750. <https://doi.org/10.5094/APR.2015.083>
- Heo, S., Kim, D.Y., Kwoun, Y., Lee, T.J., Jo, Y.M. (2021). Characterization and source identification of fine dust in Seoul elementary school classrooms. *J. Hazard. Mater.* 414, 125531. <https://doi.org/10.1016/j.jhazmat.2021.125531>
- Institute of Health & Environment, Busan (IHE) (2020). Annual Report: 2020. Institute of Health & Environment, Busan, Korea.
- Jansen, K.L., Larson, T.V., Koenig, J.Q., Mar, T.F., Fields C., Stewart, J., Lippmann, M. (2005). Associations between health effects and particulate matter and black carbon in subjects with respiratory disease. *Environ. Health Perspect.* 113, 1741–1746. <https://doi.org/10.1289/ehp.8153>



- Karar, K., Gupta, A.K., Kumar, A., Biswas, A.K. (2006). Characterization and Identification of the Sources of Chromium, Zinc, Lead, Cadmium, Nickel, Manganese and Iron in PM₁₀ Particulates at the Two Sites of Kolkata. India. *Environ. Monit. Assess.* 120, 347–360. <https://doi.org/10.1007/s10661-005-9067-7>
- Kim, H.S., Kim, Y.J., Seo, Y.R. (2015). An overview of carcinogenic heavy metal: Molecular toxicity mechanism and prevention. *J. Cancer Prev.* 20, 232–240. <https://doi.org/10.15430/JCP.2015.20.4.232>
- Lee, J.H., Jang, M.S., Lim, J. M., Ku, B.M. (2000). Health risk assessment of airborne toxic metals in Taejon third and fourth industrial complexes. *J. Environ. Impact Assess.* 9, 271–276. (in Korean with English Abstract)
- Lim, S.H., Lee, M.H., Kang, K.S. (2010). Seasonal Variations of OC and EC in PM₁₀, PM_{2.5}, PM_{1.0} at Gosan Superstation on Jeju Island. *J. Korean Soc. Atmos. Environ.* 26, 567–580. <https://doi.org/10.5572/KOSAE.2010.26.5.567> (in Korean with English Abstract)
- Lin, Y.C., Li, Y.C., Amesho, K.T., Chou, F.C., Cheng, P.C. (2020). Filterable PM_{2.5}, metallic elements, and organic carbon emissions from the exhausts of diesel vehicles. *Aerosol Air Qual. Res.* 20, 1319–1328. <https://doi.org/10.4209/aaqr.2020.02.0081>
- Lough, G.C., Schauer, J.J., Park, J.S., Shafer, M.M., DeMinter, J.T., Weinstein, J.P. (2005). Emissions of metals associated with motor vehicle roadways. *Environ. Sci. Technol.* 39, 826–836. <https://doi.org/10.1021/es048715f>
- Miah, M., Ijomone, O.M., Okoh, C.O.A., Ijomone, O.K., Akingbade, G.T., Ke, T., Krum, B., Martins, A.C., Akinyemi, A., Aranoff, N., Soares, F.A.A., Bowman, A.B., Aschner, M. (2020). The effects of manganese overexposure on brain health. *Neurochemistry Int.* 135, 104688. <https://doi.org/10.1016/j.neuint.2020.104688>
- Ministry of Environment (MOE) (2021) Annual Report of Air Quality in Korea. Korean Ministry of Environment, Korea. https://www.airkorea.or.kr/web/detailViewDown?pMENU_NO=125
- Moghtaderi, M., Ashraf, M.A., Moghtaderi, T., Teshnizi, S.H., Nabavizadeh, S.H. (2020). Heavy metal concentration in classroom dust samples and its relationship with childhood asthma: A study from Islamic Republic of Iran. *EMHJ* 26, 594–598. <https://doi.org/10.26719/emhj.19.072>
- Pallarés, S., Gómez, E.T., Martínez, A., Jordán, M.M. (2019). The relationship between indoor and outdoor levels of PM₁₀ and its chemical composition at schools in a coastal region in Spain. *Heliyon* 5, 1–8. <https://doi.org/10.1016/j.heliyon.2019.e02270>
- Park, D.J., Ahn, J.Y., Shin, H.J., Bae, M.S. (2014). Characteristics of PM_{2.5} Carbonaceous Aerosol using PILS-TOC and GC/MS-TD in Seoul. *J. Korean Soc. Atmos. Environ.* 30, 461–476. <https://doi.org/10.5572/KOSAE.2014.30.5.461> (in Korean with English Abstract)
- Park, J.H., Lee, T.J., Park M.J., Oh, H., Jo, Y.M. (2020). Effects of air cleaners and school characteristics on classroom concentrations of particulate matter in 34 elementary schools in Korea. *Build. Environ.* 167, 106437. <https://doi.org/10.1016/j.buildenv.2019.106437>
- Park, J.S., Song, I.H., Park, S.M., Shin, H., Hong, Y. (2015) The characteristics and seasonal variations of OC and EC for PM_{2.5} in Seoul metropolitan area in 2014. *J. Environ. Impact. Assess.* 24, 578–592. <https://doi.org/10.14249/eia.2015.24.6.578>
- Pegas, P.N., Nunes, T., Alves, C.A., Silva, J.R., Vieira, S.L.A., Caseiro, A., Pio, C.A. (2012). Indoor and outdoor characterization of organic and inorganic compounds in city center and suburban elementary schools of Aveiro, Portugal. *Atmos. Environ.* 55, 80–89. <https://doi.org/10.1016/j.atmosenv.2012.03.059>
- Stranger, M., Potgieter-Vermark, S.S., Van Grieten, R. (2008). Characterization of indoor air quality in primary schools in Antwerp Belgium. *Indoor Air* 18, 454–463. <https://doi.org/10.1111/j.1600-0668.2008.00545.x>
- Xu, H., Guinot, B., Shen Z., Ho, K.F., Niu, X., Xiao, S., Huang, R.J., Cao, J. (2015). Characteristics of organic and elemental carbon in PM_{2.5} and PM_{0.25} in indoor and outdoor environments of a middle school: Secondary formation of organic carbon and sources identification. *Atmosphere* 6, 361–379. <https://doi.org/10.3390/atmos6030361>
- Yang, W., Sohn, J., Kim, J., Son, B., Park, J. (2009). Indoor air quality investigation according to age of the school buildings in Korea. *J. Environ. Manage.* 90, 348–354. <https://doi.org/10.1016/j.jenvman.2007.10.003>
- Zhang, A.L., Balmes, J.R., Lutzker, L., Mann, J.K., Margolis, H.G., Tyner, T., Holland, N., Noth, E.M., Lurmann, F., Hammond, S.K., Holm, S.M. (2022). Traffic-related air pollution, biomarkers of



metabolic dysfunction, oxidative stress, and CC16 in children. *J. Exposure Sci. Environ. Epidemiol.* 32, 530–537. <https://doi.org/10.1038/s41370-021-00378-6>

Zhang, Z., Juying, L., Mamat, Z., QingFu, Y. (2016). Sources identification and pollution evaluation of heavy metals in the surface sediments of Bortala River, Northwest China. *Ecotoxicol. Environ. Saf.* 126, 94–101. <https://doi.org/10.1016/j.ecoenv.2015.12.025>