보건학박사 학위논문

Study on the health effects of $PM_{2.5}$ constituents and source contributions in major metropolitan cities (Seoul, Daejeon, Gwangju, and Ulsan), South Korea

우리나라 주요 대도시(서울, 대전, 광주, 울산)의
$PM_{2.5}$ 구성성분 및 오염원 기여도에 의한
건강영향 분석

2023년 2월

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2022년 12월

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Study on the health effects of $PM_{2.5}$ constituents and source contributions in major metropolitan cities (Seoul, Daejeon, Gwangju, and Ulsan), South Korea

A dissertation submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy in Public Health

To the faculty of the Graduate School of Public Health
at **Seoul National University**
by
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December, 2022

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Abstract

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Exposure to fine particulate matter ($PM_{2.5}$) has been revealed as a severe threat to human health and one of the major risk factors driving both death and disability. South Korea is one of the countries that have been suffering from serious air pollution, especially problems related to $PM_{2.5}$.

$PM_{2.5}$ is a heterogeneous mixture of numerous components such as sulfate, nitrate, organic carbon, elemental carbon, and trace elements. The chemical compositional characteristics are highly region-specific because most of the $PM_{2.5}$ mass concentration is attributable to secondary particles, formed by the reactions among gaseous precursors in the atmosphere. In general,

the factors affecting secondary formation are meteorological conditions, source locations, geographical features of the region as well as the ambient concentration of gaseous pollutants including sulfur oxides and nitrogen oxides. Therefore, understanding the chemical composition and source profiles of $PM_{2.5}$ in the region of interest is crucial for controlling $PM_{2.5}$. Moreover, the assessment of health risk caused by $PM_{2.5}$ exposure needs to conducted to mitigate the adverse health effects from a public health perspective.

In this study, the associations of cause-specific mortality and morbidity with both $PM_{2.5}$ constituents and source contributions were investigated in four metropolitan cities, namely Seoul, Daejeon, Gwangju, and Ulsan. Each city represents the *air control zone* in the country designated by a special act as of April 2020 to mitigate and control the air pollution on a regional basis. For the analyses, generalized linear model (GLM) was applied to the data including daily health outcomes, the average concentrations of $PM_{2.5}$ constituents, and the results of PMF modelling.

The findings show that short-term exposure to $PM_{2.5}$ constituents largely increased the relative risk (RR) of mortality and morbidity. However, the significance and strength of associations were different among the cities. In addition, source contributions also increased the RR of mortality and morbidity with different strength. In summary, the results of the study imply the importance of approaches based on compositional characteristics and health risk in making proper policies in the region of interest to mitigate the negative health effects of $PM_{2.5}$ exposure more efficiently.

Keywords : $PM_{2.5}$, PMF modelling, source apportionment, mortality, morbidity, relative risk, generalized linear model

Student Number : 2017-32636

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Abbreviations

CMB	Chemical Mass Balance
CPF	Conditional Probability Function
EC	Elemental Carbon
EDVs	Emergency Department Visits
GAM	Generalized Additive Model
GLM	Generalized Linear Model
NOx	Nitrogen Oxides
OC	Organic Carbon
PMF	Positive Matrix Factorization
PSCF	Potential Source Contribution Function
ROS	Reactive Oxygen Species
RR	Relative Risk
SIA	Secondary Inorganic Aerosols
SOx	Sulfur Oxides
VOCs	Volatile Organic Compounds

Chapter 1.

Background

1. Introduction

Ambient particulate matter (PM) has become one of the most concerning factors affecting human health in many large cities around the globe. Especially, fine particulate matter ($PM_{2.5}$), defined as particles with aerodynamic diameter less than or equal to 2.5 ㎛, has been reported to have more serious impacts on human organ systems than bigger particles due to its physicochemical properties (Schins et al., 2004).

First, extremely small sizes lead $PM_{2.5}$ to both high mobility and difficulty of removal once inhaled into human body through breath. Contrast to bigger airborne particles, easily removed by mucociliary clearance, considerable amount of $PM_{2.5}$ we breath in can reach the deeper region of respiratory tract and retain in the human lung for a long period of time. Thus, $PM_{2.5}$ accounts for most of particles observed in human pulmonary parenchyma and it is very difficult to be removed (Churg and Brauer, 1997).

Huge specific surface area is another physical property of $PM_{2.5}$ explaining the relationship between the exposure to $PM_{2.5}$ and adverse health outcomes. The great specific surface area enables $PM_{2.5}$ to act as a carrier of highly toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) and transition metals (Pandey et al., 2013).

Third, the chemical heterogeniety of $PM_{2.5}$ composition also plays an important role in affecting human health because each constituent of $PM_{2.5}$ has its own target organ and toxicity mechanism. These properties mainly originate from the formational mechanisms of $PM_{2.5}$ represented by secondary formation among various gaseous precursors in the atmosphere.

Due to the complexity of formation processes among gaseous precursors, $PM_{2.5}$ is composed of a number of constituents including ionic compounds (e.g. sulfate, nitrate, and ammonium), carbonaceous species (organic carbon and element carbon), trace elements (e.g. nickel, cadmium, lead, and vanadium) (Ye et al., 2003; Dai et al., 2013; Amil et al., 2016). In addition, the proportion of each constituent varies considerably according to spatial and temporal conditions of the samples because $PM_{2.5}$ is highly region-specific secondary aerosol (Cheng et al., 2012; He et al., 2012; Li et al., 2017).

In the same context, the toxicity of $PM_{2.5}$ differs significantly depending on time and space and it should be evaluated exactly considering chemical composition in the region requiring proper plans and policies to reduce the health effects of $PM_{2.5}$. Nevertheless, many administrative policies and plans with regard to $PM_{2.5}$ have been focused on the mass concentration of particles.

Accordingly, the chemical composition and source profiles of $PM_{2.5}$ in the region of interest should be considered to design appropriate policies for managing $PM_{2.5}$. Moreover, the associations of health outcomes with $PM_{2.5}$ exposure need to be evaluated to mitigate the negative health effects more efficiently.

2. Potential mechanisms of health effects of $PM_{2.5}$ exposure

2.1 Respiratory system

PM deposits on different parts of human respiratory system based on its physicochemical properties while the diameter of particles is particularly important. In general, coarse PM with the diameter between 2.5 ㎛ and 10 ㎛ mostly settles down on nasal cavity, pharynx and Larynx in upper airway, whereas particles less than 5 ㎛ deposit on trachea. However, $PM_{2.5}$ can reach and easily deposit on pulmonary alveoli where gas exchange occurs (Peng et al., 2019).

Many studies have revealed possible mechanisms for the effects of $PM_{2.5}$ exposure on respiratory system including injury from free radical peroxidation, imbalance of intracellular calcium homeostasis, and inflammation (Wang et al., 2020; Xing et al., 2016). Owing to the huge specific surface area, a variety of

hazardous pollutants can be absorbed or adsorbed in $PM_{2.5}$, which can cause toxicological effects (Sharma et al., 2020). $PM_{2.5}$ -bound substances in lung epithelial cells such as transition metals (e.g. arsenic, cadmium, and chromium) and hydrocarbons including PAH are reported to generate reactive oxygen species (ROS), consequently inducing oxidative stress and genotoxicity (Choi et al., 2004; Mohseni Bandpi et al., 2017).

Secondly, calcium ion (Ca^{2+}) plays an important role as an intracellular carrier that controls various biological functions such as proliferation, differentiation, apoptosis, etc (Bagur and Hajnoczky, 2017; Brini et al., 2013; Orrenius and Nicotera, 2003). $PM_{2.5}$-induced ROS can cause damage on the cell membrane, which can result in the elevation in the concentration of intracellular Ca^{2+}. Increased Ca^{2+} is consequently connected to apoptosis of cells through influencing calcium-sensing receptors (Xing et al., 2011).

Inflammation, the third mechanism, is widely known as the cause of cell damages on respiratory system. A series of inflammatory reactions are triggered by macrophages, a kind of phagocytic cells (Fu et al., 2020). Increased pro-inflammatory responses were observed in macrophages after the exposure of phagocytes to $PM_{2.5}$.

2.2 Cardiovascular system

Cardiovascular diseases (CVDs) are the top leading causes of death around the world. CVDs include cerebrovascular diseases, ischemic heart diseases, and heart failure (Abbas et al., 2009) and accounted for approximately 32% of total death around the world in 2017 (GBD 2017 Causes of Death Collaborators, 2018; Zou et al., 2020). Air pollution has been recognized as a risk factor for CVDs as well as traditional factors such as tobacco and alcohol. Specifically, previous studies revealed the association of $PM_{2.5}$ exposure with CVDs (Hayes et al., 2020; Qiu et al., 2020).

A few pathophysiological mechanisms of the effects on cardiovascular system have been suggested although the exact principles are not clear. First, oxidative stress and inflammation induced by $PM_{2.5}$ in lung epithelial cells affect cardiovascular system. The inflammation in lung cells facilitates the release of pro-inflammatory cytokine such as interleukin 6 (IL-6), tumor necrosis factor-α (TNF-α) which may spread to circulatory system (Wang et al., 2015). Increased cytokines subsequently can cause CVDs such as myocardial infarction, angina pectoris (Kosmala et al., 2005).

Second, the dysfunction of autonomic nervous system (ANS) by $PM_{2.5}$ can have negative impacts on cardiovascular

diseases. The ANS, composed of the sympathetic nervous system and the parasympathetic nervous system, regulates the function of multiple internal organs for homeostasis (McCorry, 2007). One of the most important roles of ANS is controlling the cardiac functions and the dysfunction of ANS is closely related to a variety of CVDs. Once the irritation of pulmonary alveoli by PM is recognized by the C-fibers in the lung, the signals are transmitted to respiratory center (Paton, 1998), which subsequently stimulates the sympathetic nervous system. Finally, the activation of sympathetic nervous system brings about the increase of heat rate and decrease of heart rate variability, which are related to CVDs

The third mechanism, the translocation of $PM_{2.5}$, is a direct pathway different from the two mechanisms discussed earlier. Due to the extremely small sizes, $PM_{2.5}$ can penetrate into the systemic circulation, which may cause direct effects in the deposition site (Rajagopalan et al., 2018).

3. Objectives of the study

The aim of the present study was to investigate the compositional characteristics of $PM_{2.5}$ and to estimate source contributions in major metropolitan cities in South Korea: Seoul,

Daejeon, Gwangju, and Ulsan. Also, evaluating adverse health effects associated with $PM_{2.5}$ chemical constituents and source contributions was another goal to be achieved for providing fundamental information on understanding and controlling ambient $PM_{2.5}$ from a public health perspective. The followings were detailed objectives addressed in each chapter.

Chapter 2

$PM_{2.5}$ is a heterogeneous mixture of numerous toxic substances such as sulfate, nitrate, organic carbon and the chemical composition of $PM_{2.5}$ differs depending on spatiotemporal conditions. The objective of this chapter was to identify the compositional characteristics of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan using daily $PM_{2.5}$ speciation data during 2014-2018.

Chapter 3

The objective of this chapter was the source apportionment of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan, South Korea. PMF modelling was conducted for the period 2014–2018 for identifying the sources and estimating their contributions in the four cities. In addition, conditional probability function (CPF)

and potential source contribution function (PSCF) were also conducted to locate possible source areas of each factor resolved in the study cities.

Chapter 4

Among various health outcomes, one of the most representative parameters is mortality data widely used for assessing the adverse health effects of external factors including exposure to environmental pollutants. The objective of this chapter was to examine the associations of cause-specific mortality with both $PM_{2.5}$ chemical constituents and source contributions in Seoul, Daejeon, Gwangju, and Ulsan, South Korea.

Chapter 5

The objective of this chapter was to investigate the negative health effects of $PM_{2.5}$ exposure on morbidity. Disease is a rather acute and primary health outcome of exposure to external factors in human bodies. The adverse health effects on morbidity were analyzed by applying generalized linear model (GLM) to cause-specific emergency department visit data from 2014 to 2018 acquired from national emergency department information system (NEDIS), South Korea.

References

Abbas, S., Kitchlew, A. R. and Abbas, S., 2009. Disease burden of ischemic heart disease in Pakistan and its risk factors. *Annals of Pakistan Institute of Medical Sciences*, 5(3), pp.145-150.

Amil, N., Latif, M. T., Khan, M. F. and Mohamad, M., 2016. Seasonal variability of $PM_{2.5}$ composition and sources in the Klang Valley urban-industrial environment. *Atmospheric Chemistry and Physics*, 16(8), pp.5357-5381.

Bagur, R. and Hajnoczky, G., 2017. Intracellular Ca_2^+ sensing: its role in calcium homeostasis and signaling. *Molecular cell*, 66(6), pp.780-788.

Brini, M., Cali, T., Ottolini, D. and Carafoli, E., 2013. Intracellular calcium homeostasis and signaling. *Metallomics and the Cell*, 12, pp.119-168.

Cheng, M. C., You, C. F., Cao, J. and Jin, Z., 2012. Spatial and seasonal variability of water-soluble ions in $PM_{2.5}$ aerosols in 14 major cities in China. *Atmospheric Environment*, 60, pp.182-192.

Choi, J. H., Kim, J. S., Kim, Y. C., Kim, Y. S., Chung, N. H. and Cho, M. H., 2004. Comparative study of $PM_{2.5}$- and PM_{10}- induced oxidative stress in rat lung epithelial cells. *Journal of veterinary science*, 5(1), pp.11-18.

Churg, A. and Brauer, M., 1997. Human lung parenchyma retains $PM_{2.5}$. *American journal of respiratory and critical care medicine*, 155(6), pp.2109-2111.

Dai, W., Gao, J., Cao, G. and Ouyang, F., 2013. Chemical composition and source identification of $PM_{2.5}$ in the suburb of Shenzhen, China. *Atmospheric Research*, 122, pp.391-400.

Fu, H., Liu, X., Li, W., Zu, Y., Zhou, F., Shou, Q. and Ding, Z., 2020. $PM_{2.5}$ exposure induces inflammatory response in macrophages via the TLR4/COX-2/NF-κB pathway. *Inflammation*, 43, pp.1948-1958.

GBD 2017 Causes of Death Collaborators, 2018. Global, regional, and national age-sex-specific mortality for 282 causes of death in 195 countries and territories, 1980-2017: a systematic analysis for the Global Burden of Disease Study 2017. *The Lancet*, 392(10159), pp.1736-1788.

Hayes, R. B., Lim, C., Zhang, Y., Cromar, K., Shao, Y., Reynolds, H. R., Silverman, D. T., Jones, R. R., Park, Y., Jerrett M., Ahn, J. and Thurston, G. D., 2020. $PM_{2.5}$ air pollution and cause-specific cardiovascular disease mortality. *International journal of epidemiology*, 49(1), pp.25-35.

He, K., Zhao, Q., Ma, Y., Duan, F., Yang, F., Shi, Z. and Chen, G., 2012. Spatial and seasonal variability of $PM_{2.5}$ acidity at two Chinese megacities: insights into the formation of secondary inorganic aerosols. *Atmospheric Chemistry and Physics*, 12(3), pp.1377-1395.

Kosmala, W., Przewlocka-Kosmala, M. and Mazurek, W., 2005. Proinflammatory cytokines and myocardial viability in patients after acute myocardial infarction. *International*

journal of cardiology, 101(3), pp.449-456.

Li, X., Chen, X., Yuan, X., Zeng, G., León, T., Liang, J., Chen, G. and Yuan, X., 2017. Characteristics of particulate pollution ($PM_{2.5}$ and PM_{10}) and their spacescale-dependent relationships with meteorological elements in China. *Sustainability*, 9(12), p.2330.

McCorry, L. K., 2007. Physiology of the autonomic nervous system. *American journal of pharmaceutical education*, 71(4).

Mohseni Bandpi, A., Eslami, A., Shahsavani, A., Khodagholi, F., Aliaghaei, A. and Alinejad, A., 2017. Water-soluble and organic extracts of ambient $PM_{2.5}$ in Tehran air: assessment of genotoxic effects on human lung epithelial cells (A549) by the Comet assay. *Toxin reviews*, 36(2), pp.116-124.

Orrenius, S., Zhivotovsky, B. and Nicotera, P., 2003. Regulation of cell death: the calcium–apoptosis link. *Nature reviews Molecular cell biology*, 4(7), pp.552-565.

Pandey, P., Patel, D. K., Khan, A. H., Barman, S. C., Murthy, R. C. and Kisku, G. C., 2013. Temporal distribution of fine particulates ($PM_{2.5}$, PM_{10}), potentially toxic metals, PAHs and Metal-bound carcinogenic risk in the population of Lucknow City, India. *Journal of Environmental Science and Health*, Part A, 48(7), pp.730-745.

Paton, J. F., 1998. Pattern of cardiorespiratory afferent convergence to solitary tract neurons driven by pulmonary vagal C-fiber stimulation in the mouse. *Journal of neurophysiology*, 79(5), pp.2365-2373.

Peng, J., Zhang, L., Meng, Q., Zhang, F., Mao, X., Liu, J., Chen, Y., Zou, H., Shi, B., Wu, R., Huang, B., Huang, Y., Tan, J., Feng, C. and Zhang, X., 2019. Adverse impact of ambient $PM_{2.5}$ on expression and trafficking of surfactant protein A through reactive oxygen species damage to lamellar bodies. *Toxicology letters*, 315, pp.47-54.

Qiu, X., Wei, Y., Wang, Y., Di, Q., Sofer, T., Awad, Y. A. and Schwartz, J., 2020. Inverse probability weighted distributed lag effects of short-term exposure to $PM_{2.5}$ and ozone on CVD hospitalizations in New England Medicare participants-exploring the causal effects. *Environmental research*, 182, 109095.

Rajagopalan, S., Al-Kindi, S. G. and Brook, R. D., 2018. Air pollution and cardiovascular disease: JACC state-of-the-art review. *Journal of the American College of Cardiology*, 72(17), pp.2054-2070.

Schins, R. P., Lightbody, J. H., Borm, P. J., Shi, T., Donaldson, K. and Stone, V., 2004. Inflammatory effects of coarse and fine particulate matter in relation to chemical and biological constituents. *Toxicology and applied pharmacology*, 195(1), pp.1-11.

Sharma, D. and Jain, S., 2020. Carcinogenic risk from exposure to $PM_{2.5}$ bound polycyclic aromatic hydrocarbons in rural settings. *Ecotoxicology and environmental safety*, 190, 110135.

Wang, C., Tu, Y., Yu, Z. and Lu, R., 2015. $PM_{2.5}$ and cardiovascular diseases in the elderly: an overview. *International journal of*

environmental research and public health, 12(7), pp.8187-8197.

Wang, C., Meng, X., Meng, M., Shi, M., Sun, W., Li, X., Zhang, X., Liu, R., Fu, Y. and Song, L., 2020. Oxidative stress activates the TRPM2-Ca2+-NLRP3 axis to promote $PM_{2.5}$-induced lung injury of mice. *Biomedicine & Pharmacotherapy*, 130, 110481.

Xing, W. J., Kong, F. J., Li, G. W., Qiao, K., Zhang, W. H., Zhang, L., Bai, S. Z., Xi, Y. H., Li, H. X., Tian, Y., Ren, H., Wu, L. Y., Wang, R. and Xu, C. Q., 2011. Calcium-sensing receptors induce apoptosis during simulated ischaemia–reperfusion in Buffalo rat liver cells. *Clinical and Experimental Pharmacology and Physiology*, 38(9), pp.605-612.

Xing, Y. F., Xu, Y. H., Shi, M. H. and Lian, Y. X., 2016. The impact of $PM_{2.5}$ on the human respiratory system. *Journal of thoracic disease*, 8(1), E69.

Ye, B., Ji, X., Yang, H., Yao, X., Chan, C. K., Cadle, S. H., Chan, T. and Mulawa, P. A., 2003. Concentration and chemical composition of $PM_{2.5}$ in Shanghai for a 1-year period. *Atmospheric Environment*, 37(4), pp.499-510.

Zou, Z., Cini, K., Dong, B., Ma, Y., Ma, J., Burgner, D. P. and Patton, G. C., 2020. Time trends in cardiovascular disease mortality across the BRICS: an age-period-cohort analysis of key nations with emerging economies using the global burden of disease study 2017. *Circulation*, 141(10), pp.790-799.

Chapter 2.

Compositional characteristics of ambient $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018

Abstract

Ambient $PM_{2.5}$ is a heterogeneous mixture of various chemical component such as sulfate, nitrate, organic carbon. The compositional characteristics of $PM_{2.5}$ have been reported to vary depending on the spatiotemporal conditions because $PM_{2.5}$ is mostly generated from secondary formation among gaseous precursors in the atmosphere such as sulfur oxides and nitrogen oxides rather than directly emitted into the air from sources. Thus, $PM_{2.5}$ chemical composition is highly region-specific and understanding it is fundamental to figure out the characteristics of $PM_{2.5}$ such as the relative proportion of each constituent and the dominant chemical groups as well as $PM_{2.5}$ mass concentration.

The compositional characteristics of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018 were investigated and the temporal variations in the concentration of $PM_{2.5}$ mass and major chemical groups were also examined. From the analyses, gradual decreases in the concentration of $PM_{2.5}$ mass and gaseous precursors were observed while $PM_{2.5}$ compositional characteristics were highly region-specific. The findings of the study are considered to be the results of the government-led policies and plans intensively implemented since the mid 2000's and the reflection of regional characteristics.

1. Introduction

$PM_{2.5}$ is a mixture of various chemical species such as sulfate (SO_4^{2-}), nitrate (NO_3^-), organic carbon (OC), elemental carbon (EC), calcium (Ca), titanium (Ti), arsenic (As), lead (Pb), etc. These chemical species can be largely classified into three major groups, namely ionic compounds, carbonaceous compounds and trace elements.

Ionic compounds (e.g. NO_3^-, SO_4^{2-}, NH_4^+) mostly originate from the secondary formation by the physicochemical processes among gaseous pollutants in the atmosphere such as nitrogen oxides, sulfur oxides, and ammonia (Bae et al., 2020). Ionic constituents normally make up the largest fraction of $PM_{2.5}$ mass.

Carbonaceous species, composed of OC and EC, also explain a large proportion of $PM_{2.5}$ mass concentration and originate from a broad range of sources related to combustion of hydrocarbons including vehicles, fossil fuel combustion. OC constitutes of hydrocarbons with low molecular weight and derivatives (Zenker et al., 2017). EC, the product of incomplete combustion or pyrolysis of carbon-containing materials (Long et al, 2013), is referred to as black carbon (BC) when analyzed by the optical method (Hitzenberger et al., 2006).

Trace elements are largely divided into two sub categories according to their origins; crustal and anthropogenic components (Lonati et al., 2005). Crustal elements include Ca, Ti, Si, Al, and Mg which are abundant in the earth crust. In contrast, anthropogenic components generally originate from their related sources (e.g. As and Se from coal combustion and Fe, Mn, and Cr from steel processing) (Lee and Hopke, 2006).

The chemical composition of $PM_{2.5}$ highly depends on the time and location of samples, implying understanding the $PM_{2.5}$ composition in the region of interest is important. In a similar context, analyses on $PM_{2.5}$ speciation data need to be conducted as the first step to control and manage the ambient $PM_{2.5}$ because it can provide fundamental information including dominant constituents of $PM_{2.5}$.

In this study, the concentrations of $PM_{2.5}$ mass and chemical constituents in Seoul, Daejeon, Gwangju, and Ulsan were investigated from January 2014 to December 2018 to better understand the compositional characteristics of $PM_{2.5}$ in each city.

2. Materials and methods

2.1 Study area and period

As of April 2020, the "Special act on the improvement of

air quality in air control zone" came into effect to manage the air quality efficiently and systemically on a regional basis in South Korea. According to the special act, four *air control zones* where air pollution was much severer than other regions were designated: Seoul metropolitan area, Middle area, Southern area, and Southeastern area. The study areas were major metropolitan cites standing for *air control zones* as shown in Figure 2-1.

Seoul, the capital of South Korea, represents the Seoul metropolitan area. It is located in the northwestern region of and is adjacent to the Yellow Sea lying between mainland China on the west and north and the Korean peninsula on the east. Its area and population were 605 ㎢ and approximately 9.6 million, respectively. Daejeon, the largest city in the Middle area, is located in the central region of the country and had a population of 1.5 million in 2019. Gwangju in the Southern area is a city in the southwest region of the country. Its population and area were approximately 1.5 million and 501 ㎢, which were similar to those of Daejeon. Ulsan is located in the southeast region of the country and borders the sea. It had a population of 1.1 million in 2019 with total area of 1062 ㎢. Ulsan has two huge industrial complexes and is widely known as a city of heavy industry (Kim et al., 2018).

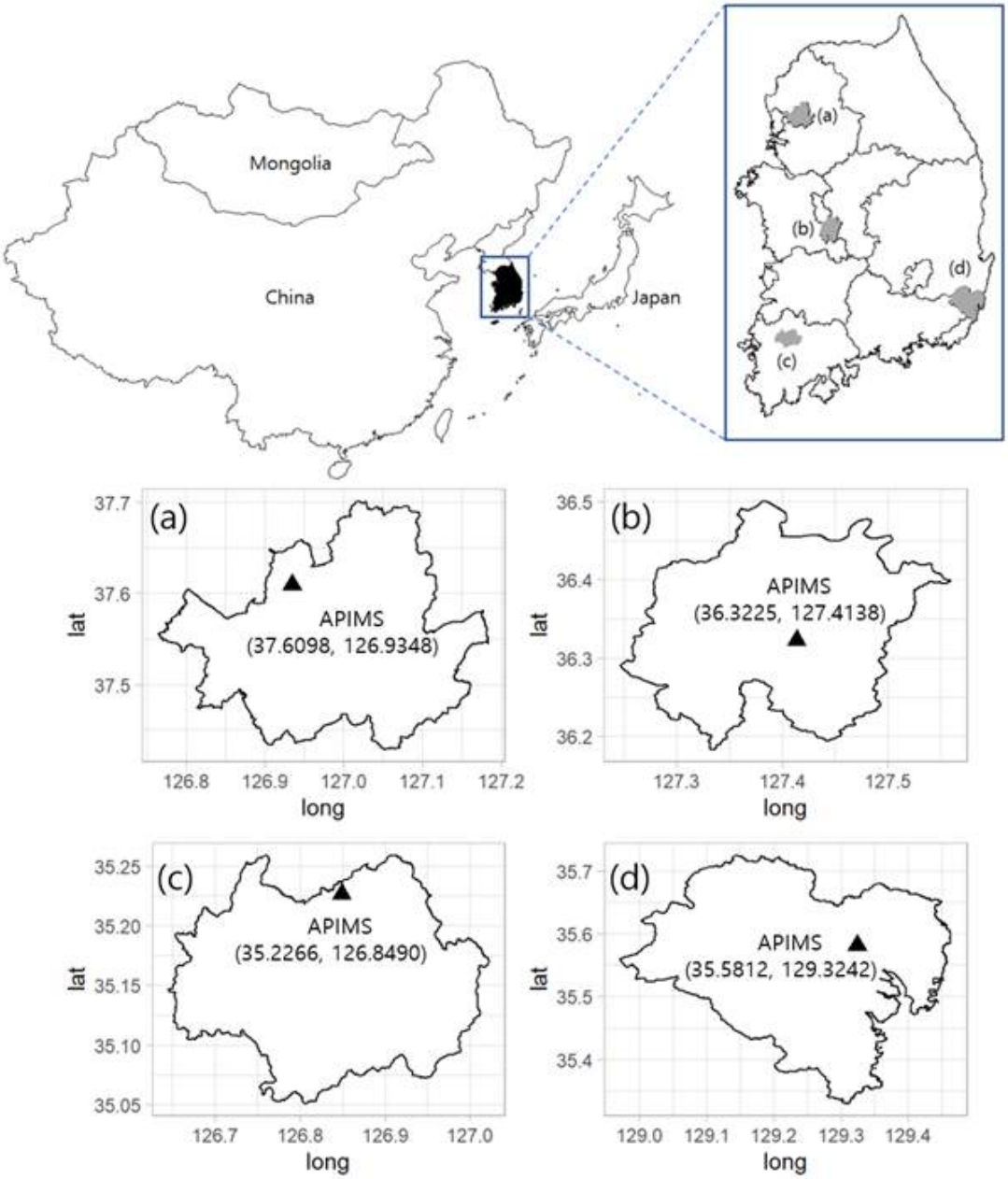


Figure 2-1 Geographical locations of the study area; (a) Seoul, (b) Daejeon, (c) Gwangju, and (d) Ulsan

2.2 Data

National institute of environmental research (NIER), under the Ministry of Environment (MoE) of South Korea, has been operating several air pollution intensive monitoring stations (APIMS) across the country for investigating $PM_{2.5}$ speciation as well as monitoring gaseous pollutants such as nitrogen dioxide, carbon monoxide. Nearly real-time $PM_{2.5}$ speciation data is produced on a hourly basis. The 24-h integrated values of $PM_{2.5}$ mass concentration and chemical speciation in Seoul, Daejeon, Gwangju, and Ulsan during January 2014 to December 2018 on a daily basis were obtained from NIER.

The chemical constituents of $PM_{2.5}$ investigated in the present study were eight ionic species [i.e. sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), sodium ion (Na^+), ammonium (NH_4^+), potassium ion (K^+), magnesium ion (Mg^{2+}), and calcium ion (Ca^{2+})], two carbonaceous compounds [i.e. organic carbon (OC) and elemental carbon (EC)] and 15 trace elements [i.e. sulfur (S), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), bromine (Br), and lead (Pb)].

3. Results and discussion

3.1 $PM_{2.5}$ mass and gaseous precursors

During the five years of study period, the average $PM_{2.5}$ mass concentrations in all cities exceeded 15 $\mu g/m^3$, annual $PM_{2.5}$ standard set by the government of South Korea. $PM_{2.5}$ mass concentrations in Seoul, Daejeon, and Gwangju showed similar values which were much higher than that in Ulsan.

Long-term trends of $PM_{2.5}$ mass concentration during 2014-2018 were similar in all cities, showing gradual decrease as suggested in Figures 2-2, 2-3, 2-4, and 2-5, which led to considerably reduced $PM_{2.5}$ concentration in 2018. These changes in the average concentration are considered to be the results of government-led plans and policies intensively implemented from the middle 2010s for mitigating air pollution, particularly $PM_{2.5}$. These administrative efforts include "The 2nd master plan for metropolitan air quality control", "Special countermeasures on fine dust", and "Comprehensive plan on fine dust management" (Leem et al., 2015; Ning and Lee, 2019).

As $PM_{2.5}$ is mostly composed of secondary particles generated by the reactions among gaseous pollutants in the atmosphere, administrative plans and policies were focused on the reduction of gaseous precursors as well as $PM_{2.5}$.

Representative constituents of $PM_{2.5}$ are sulfate and nitrate originating from sulfur oxides and nitrogen oxides in ambient air, respectively. Thus, the decreases in gaseous precursors might have resulted in the overall reduction of ambient $PM_{2.5}$.

The variations of ambient sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) concentrations also showed patterns similar to $PM_{2.5}$ (Figures 2-2, 2-3, 2-4, and 2-5). SO_2 concentrations in all cities have obviously decreased, resulting in approximately 22.6–33.0% lower concentration in 2018 compared to baseline in 2014. Moreover, SO_2 concentrations have been continuously below the annual *National Environmental Standards* of 20 ppb set by the government of South Korea. With regard to the differences among cities, SO_2 concentrations in Ulsan showed higher values than those in Seoul, Daejeon, and Gwangju. The average of annual SOx emission in Ulsan during 2014-2018 has been much larger than other cities due to the city, reflecting the effects of heavy and petrochemical industry as well as marine vessel activities.

However, NO_2 concentrations in Seoul were higher than those in Daejeon, Gwangju, and Ulsan and the concentration has decreased less than SO_2. NOx is largely emitted from the sources with thermal processes such as gasoline/diesel vehicles, industry, power stations because NOx is mostly generated from

thermal NOx mechanism. Contrast to SOx emission, the complex mechanism of NOx formation makes it difficult to reduce the emission of NOx because the temperature range of thermal processes need to be maintained stable. Consequently, it seems that the reduction of NO_2 emission was relatively limited when compared to SO_2 reduction in all cities during 2014-2018, which resulted in frequent cases of high NO_2 concentrations exceeding the *National Environmental Standards*.

Table 2-1 Concentrations of $PM_{2.5}$, SO_2, and NO_2 in Seoul, Daejeon, Gwangju, and Ulsan during 2014-2018

Pollu-tants	City	Unit	Total		2014		2015		2016		2017		2018	
			Avg.	S.D.	Avg.	S.D.	Avg.	S.D.	Avg.	S.D.	Avg.	S.D.	Avg.	S.D.
$PM_{2.5}$	Seoul	㎍/㎥	27.7	17.2	36.5	24.2	25.7	14.3	27.6	13.0	26.2	16.0	23.8	15.0
	Daejeon		29.2	16.0	30.7	14.8	35.6	18.5	30.9	15.7	26.0	13.3	24.2	14.5
	Gwangju		26.9	15.8	34.6	21.6	28.4	15.4	25.2	12.9	25.0	13.5	23.8	14.5
	Ulsan		20.4	11.8	21.8	12.8	20.7	11.9	23.1	11.8	18.8	10.0	18.8	12.0
SO_2	Seoul	ppb	5	5	6	2	5	1	5	1	5	1	4	1
	Daejeon		3	3	4	2	4	2	3	1	3	1	2	1
	Gwangju		3	1	4	1	3	1	3	1	3	1	3	1
	Ulsan		7	3	8	3	7	3	6	3	6	3	6	3
NO_2	Seoul	ppb	29	31	33	13	32	12	31	10	30	11	28	12
	Daejeon		17	19	20	9	19	8	19	7	18	8	19	9
	Gwangju		19	8	19	8	19	7	18	7	19	8	17	9
	Ulsan		22	3	23	9	23	8	23	7	22	8	20	8

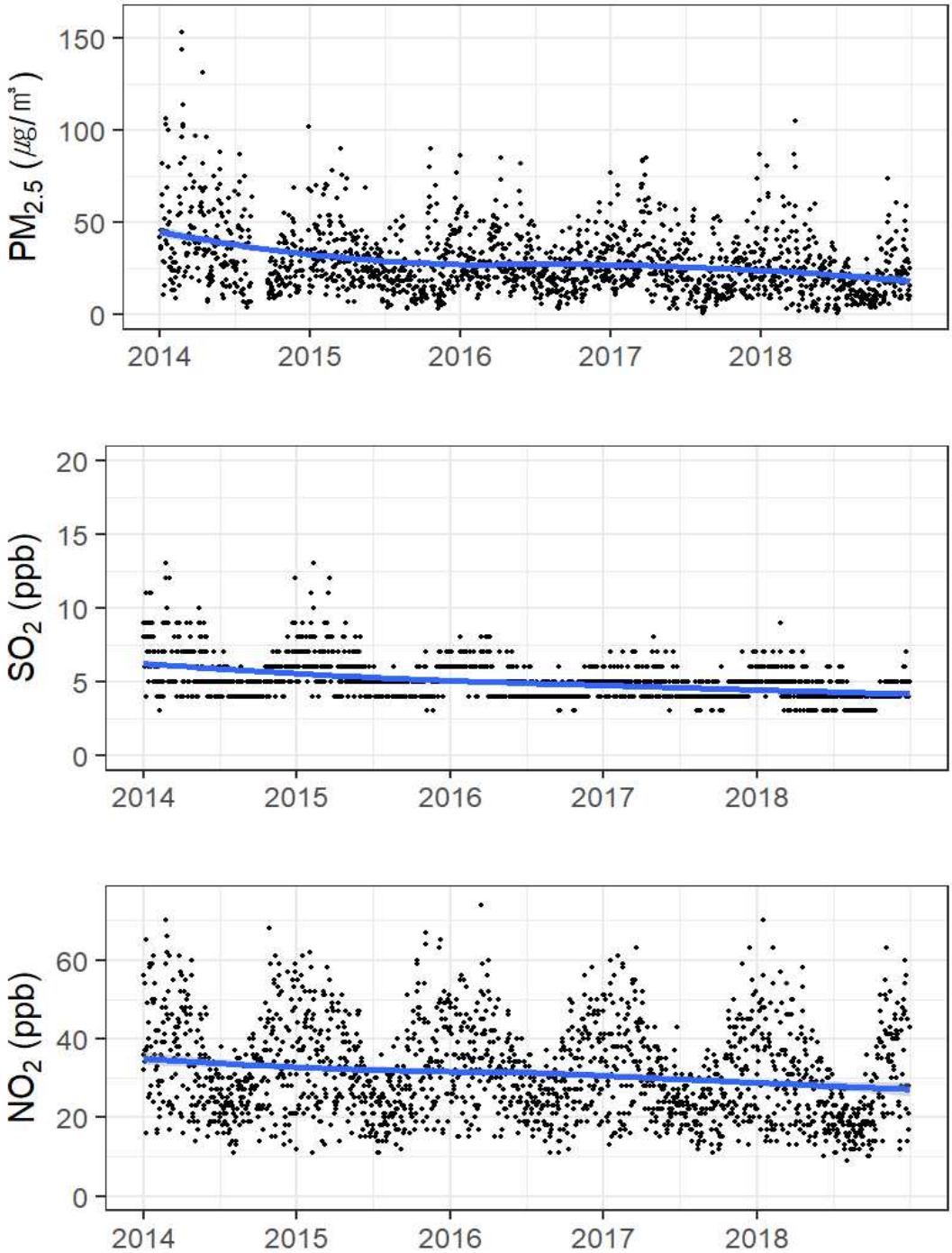


Figure 2-2 Time series of the concentration of $PM_{2.5}$ and gaseous precursors in Seoul during 2014-2018

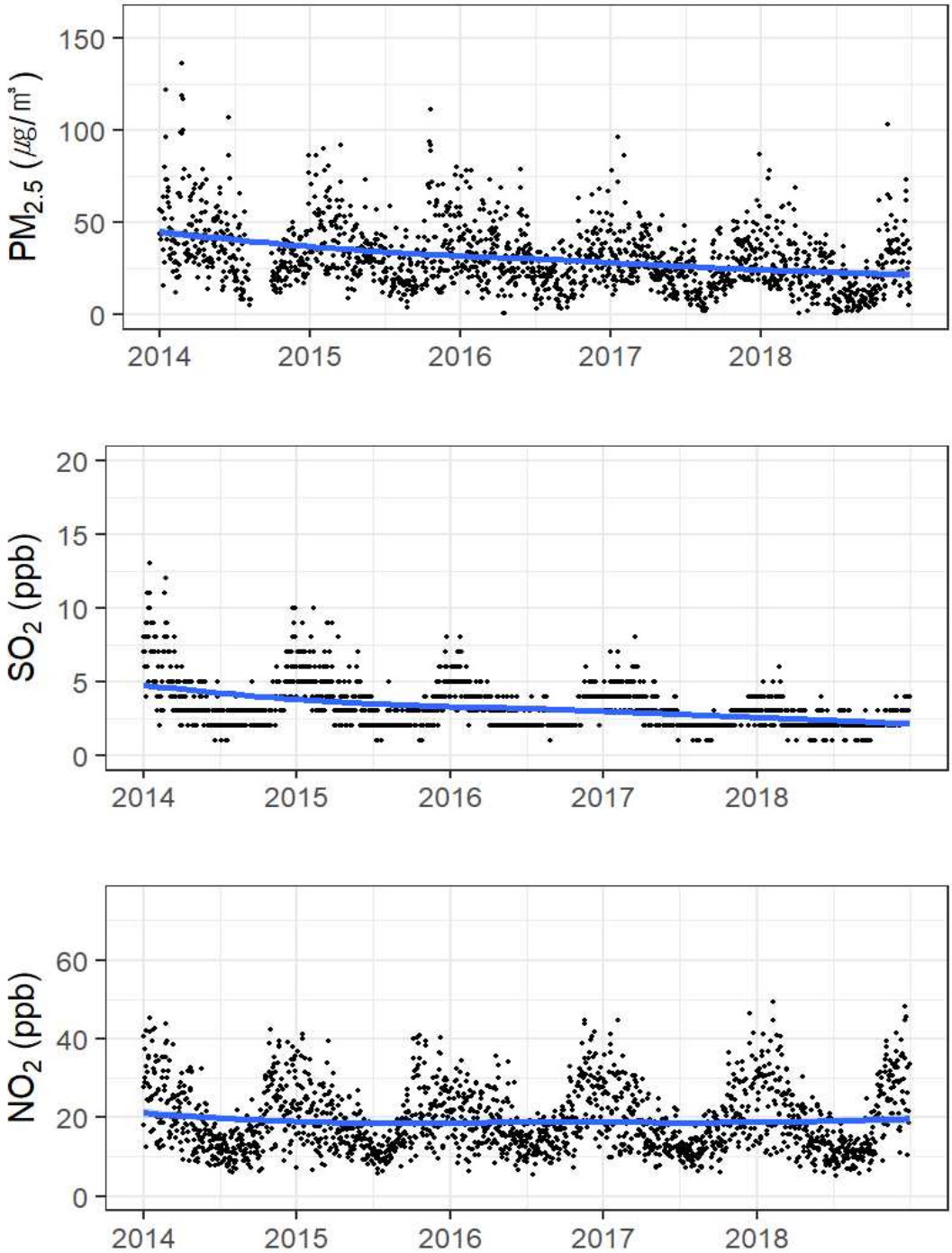


Figure 2-3 Time series of the concentration of $PM_{2.5}$ and gaseous precursors in Daejeon during 2014-2018

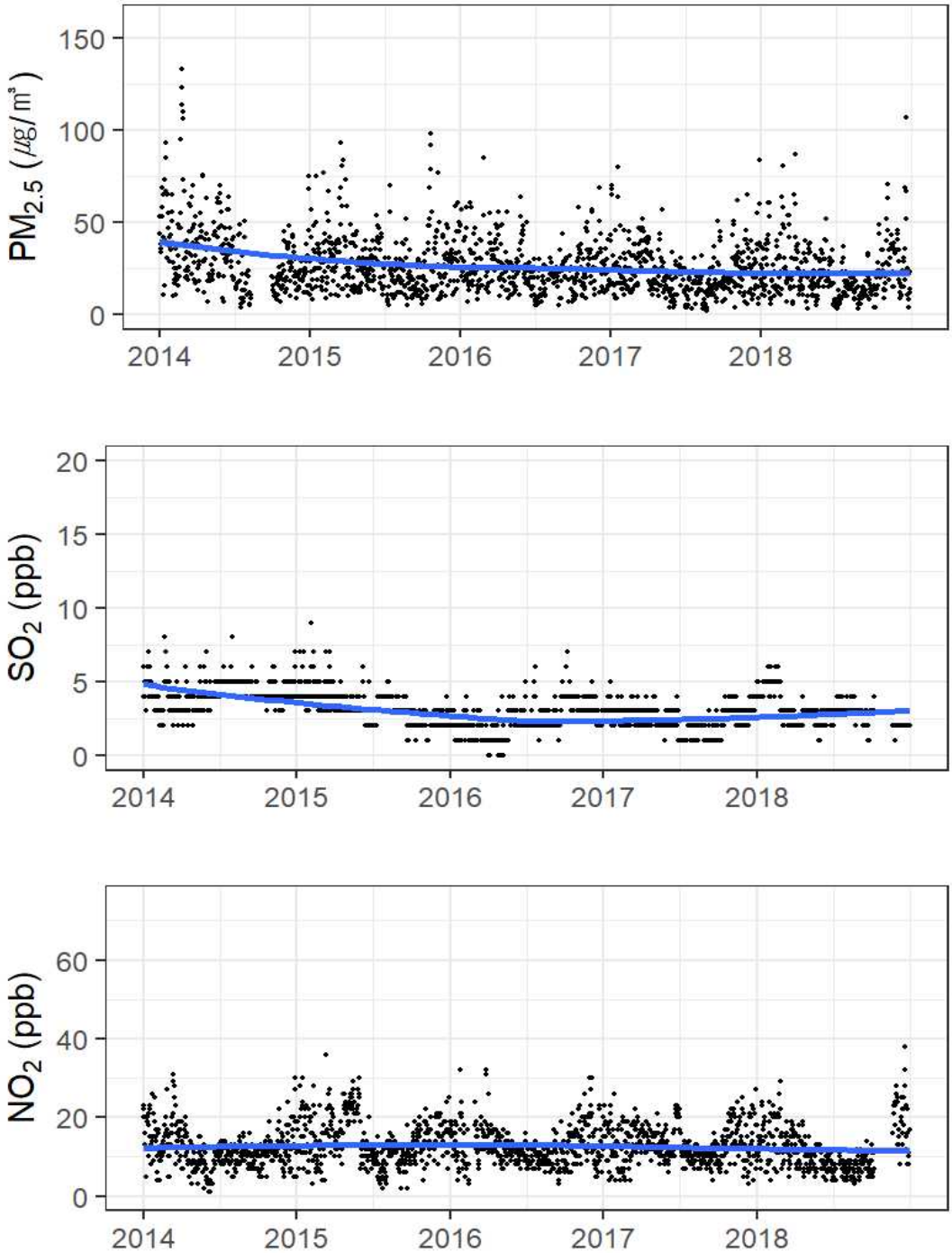


Figure 2-4 Time series of the concentration of $PM_{2.5}$ and gaseous precursors in Gwangju during 2014-2018

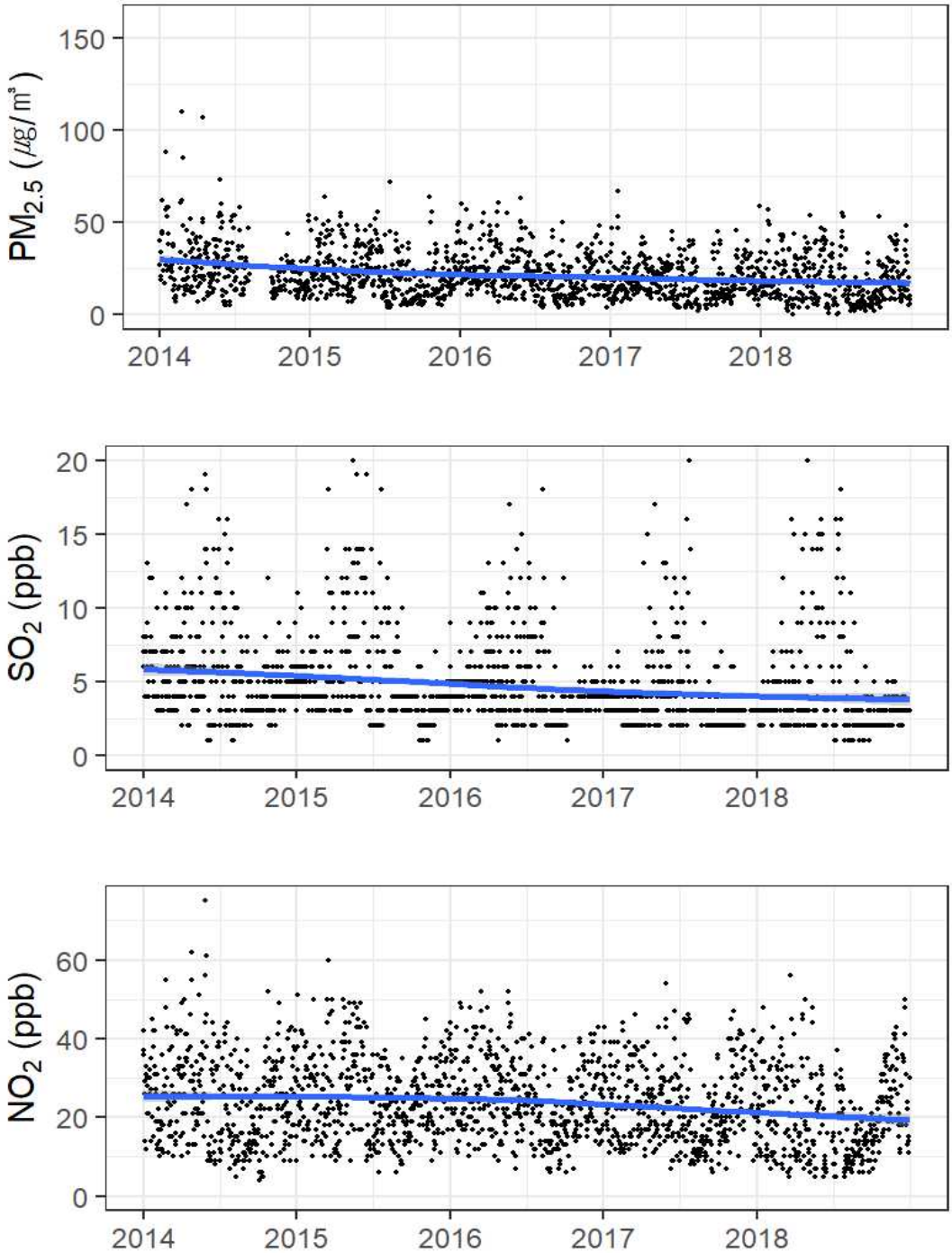


Figure 2-5 Time series of the concentration of $PM_{2.5}$ and gaseous precursors in Ulsan during 2014-2018

3.2 $PM_{2.5}$ chemical constituents

A summary of the concentrations of $PM_{2.5}$ chemical constituents in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018 is presented in Tables 2-2, 2-3, 2-4, and 2-5, respectively. Also, the relative proportion of major components during heating seasons (Nov-Mar) and non-heating seasons (Apr-Oct) is suggested in Figure 2-6.

In Seoul, ionic species constituted the largest fraction (60.3%) followed by carbonaceous species (18.2%), trace elements (13.5%). Among ionic species, secondary inorganic aerosols (SIA) accounted for about 90% of total ion mass. SO_4^{2-}/NO_3^- ratio was 0.88, the lowest value among the four cities, which implies that nitrate was dominant over sulfate in secondary formation during the study period.

In Daejeon, ionic, carbonaceous and trace elemental species accounted for 51.5%, 20.1%, and 14.3%, respectively. The sum of mass concentration of SO_4^{2-}, NO_3^-, and NH_4^+ together was 94.8% of total ionic species. This value was very similar to that in other cities (Gwangju: 93.2%, Ulsan: 93.4%), indicating that ionic components of $PM_{2.5}$ were significantly affected by secondary inorganic aerosols (Huang et al., 2014; Voutsa et al., 2014).

The chemical composition of $PM_{2.5}$ in Gwangju was quite similar to that in Daejeon. Ionic species accounted for the majority of $PM_{2.5}$ mass followed by carbon species (19.6%) and trace elements (11.4%). In Ulsan, the proportion of ionic species (50.2%) and carbonaceous species (18.9%) was similar to that in Daejeon and Gwangju while that of trace elements was the largest among the study cities. Especially, trace elements obviously contributed more to $PM_{2.5}$ mass concentration than other cities, reflecting the industrial characteristics of Ulsan. Located in the southeast coastal area of the country, Ulsan has two huge national industrial complexes (Ulsan petrochemical industrial complex and Onsan national industrial complex) and a number of large ports. The combustion of heavy oil containing much sulfur might have influenced the large share of sulfur in $PM_{2.5}$ composition. Large fractions of Ni and V in $PM_{2.5}$ in Ulsan than other cities support the assumption because those components are marker species for oil combustion (Dos Anjos, 2018; Jang et al., 2007).

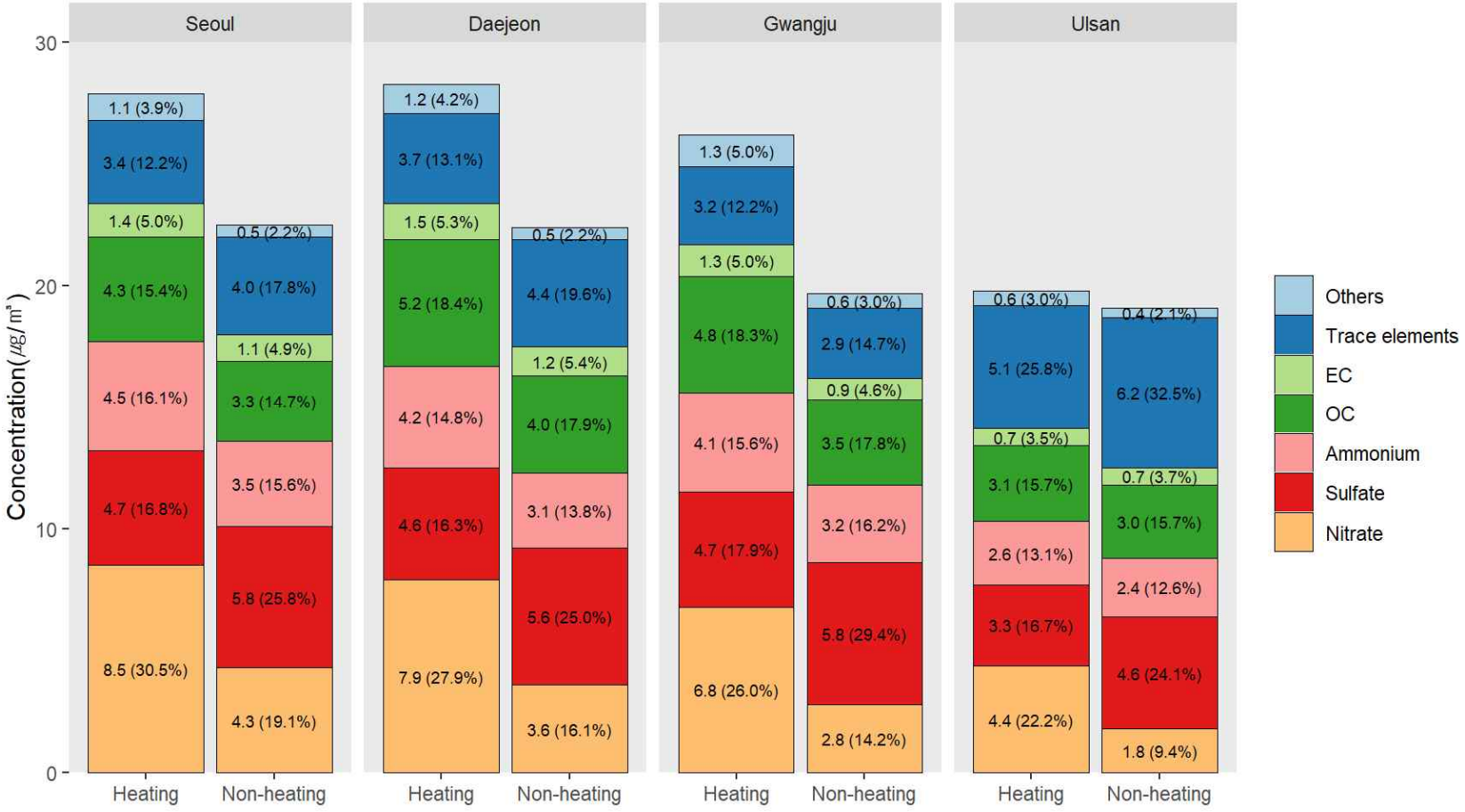


Figure 2-6 Chemical composition of $PM_{2.5}$ during heating and non-heating seasons in Seoul, Daejeon, Gwangju, and Ulsan

Table 2-2 Summary of $PM_{2.5}$ chemical composition in Seoul

Constituents	unit	Avg.	S.D.	Min.	Median	Max.
Mass conc.	μg/㎥	27.7	17.2	1.0	23.6	153.4
Ion species	μg/㎥	16.69	13.43	0.07	12.66	101.89
SO_4^{2-}	μg/㎥	5.38	4.74	0.01	4.05	39.15
NO_3^-	μg/㎥	6.09	5.90	0.02	4.28	35.57
Cl^-	μg/㎥	0.34	0.38	0.00	0.21	2.57
Na^+	μg/㎥	0.12	0.11	0.00	0.10	0.97
NH_4^+	μg/㎥	3.92	3.19	0.01	3.02	24.05
K^+	μg/㎥	0.16	0.15	0.00	0.12	1.05
Mg^{2+}	μg/㎥	0.05	0.13	0.00	0.01	1.45
Ca^{2+}	μg/㎥	0.12	0.29	0.00	0.04	3.16
Carbon species	μg/㎥	5.05	2.44	0.47	4.63	18.83
OC	μg/㎥	3.78	1.90	0.29	3.39	16.79
EC	μg/㎥	1.27	0.64	0.07	1.12	4.50
Trace elements	μg/㎥	3.75	2.52	0.22	3.10	25.64
S	μg/㎥	3.05	2.31	0.10	2.42	23.28
K	ng/㎥	306.70	215.03	12.25	263.60	2287.96
Ca	ng/㎥	65.76	69.55	1.47	48.52	1104.97
Ti	ng/㎥	9.79	7.76	0.53	8.26	106.54
V	ng/㎥	3.66	4.64	0.27	1.81	31.60
Cr	ng/㎥	1.30	1.00	0.35	1.09	7.46
Mn	ng/㎥	12.27	8.50	0.25	10.07	56.10
Fe	ng/㎥	195.00	112.23	20.93	172.76	1074.53
Ni	ng/㎥	1.57	1.63	0.20	1.03	10.14
Cu	ng/㎥	7.52	5.16	0.99	6.58	34.97
Zn	ng/㎥	65.55	43.58	2.50	54.03	302.25
As	ng/㎥	4.02	3.27	0.27	3.39	25.66
Se	ng/㎥	1.24	1.20	0.27	0.86	8.62
Br	ng/㎥	8.85	6.96	0.10	6.87	63.13
Pb	ng/㎥	21.77	15.73	0.66	18.23	132.91

Table 2-3 Summary of $PM_{2.5}$ chemical composition in Daejeon

Constituents	unit	Avg.	S.D.	Min.	Median	Max.
Mass conc.	μg/㎥	29.2	16.0	1.7	26.5	117.2
Ion species	μg/㎥	15.03	10.74	0.48	12.31	70.12
SO_4^{2-}	μg/㎥	5.23	3.71	0.16	4.24	28.25
NO_3^-	μg/㎥	5.38	5.23	0.07	3.64	31.20
Cl^-	μg/㎥	0.36	0.40	0.00	0.21	2.77
Na^+	μg/㎥	0.24	0.27	0.00	0.16	2.48
NH_4^+	μg/㎥	3.64	2.57	0.07	3.11	17.99
K^+	μg/㎥	0.15	0.16	0.00	0.10	1.54
Mg^{2+}	μg/㎥	0.01	0.01	0.00	0.01	0.17
Ca^{2+}	μg/㎥	0.05	0.05	0.00	0.03	0.50
Carbon species	μg/㎥	5.87	2.65	1.00	5.48	21.41
OC	μg/㎥	4.53	2.08	0.61	4.23	16.48
EC	μg/㎥	1.34	0.67	0.29	1.21	4.93
Trace elements	μg/㎥	4.18	3.93	0.18	2.94	41.85
S	μg/㎥	3.89	3.95	0.10	2.57	40.10
K	ng/㎥	223.39	174.82	4.55	180.07	1651.46
Ca	ng/㎥	58.05	73.80	1.47	36.36	1112.98
Ti	ng/㎥	7.74	7.98	0.53	5.76	78.65
V	ng/㎥	3.05	2.59	0.27	2.35	16.94
Cr	ng/㎥	1.20	1.15	0.35	0.91	10.11
Mn	ng/㎥	9.96	6.61	0.25	8.64	39.92
Fe	ng/㎥	183.00	113.89	16.64	160.01	1002.67
Ni	ng/㎥	1.57	1.43	0.20	1.30	16.82
Cu	ng/㎥	6.95	4.40	0.99	6.14	33.57
Zn	ng/㎥	50.68	32.05	2.18	43.94	254.05
As	ng/㎥	2.67	2.62	0.27	1.85	20.04
Se	ng/㎥	1.80	1.36	0.27	1.51	8.49
Br	ng/㎥	7.28	5.79	0.10	5.91	48.59
Pb	ng/㎥	18.80	13.93	0.66	15.30	115.32

Table 2-4 Summary of $PM_{2.5}$ chemical composition in Gwangju

Constituents	unit	Avg.	S.D.	Min.	Median	Max.
Mass conc.	μg/㎥	26.9	15.8	3.3	23.6	132.9
Ion species	μg/㎥	14.64	10.47	0.96	12.27	78.47
SO_4^{2-}	μg/㎥	5.36	3.92	0.30	4.25	32.16
NO_3^-	μg/㎥	4.64	4.79	0.06	2.97	41.15
Cl^-	μg/㎥	0.58	0.48	0.01	0.46	3.04
Na^+	μg/㎥	0.17	0.14	0.01	0.13	1.26
NH_4^+	μg/㎥	3.65	2.54	0.24	3.10	19.33
K^+	μg/㎥	0.20	0.21	0.00	0.14	3.10
Mg^{2+}	μg/㎥	0.01	0.02	0.00	0.01	0.26
Ca^{2+}	μg/㎥	0.03	0.04	0.00	0.02	0.67
Carbon species	μg/㎥	5.26	2.70	0.43	4.80	20.09
OC	μg/㎥	4.11	2.21	0.20	3.75	17.48
EC	μg/㎥	1.15	0.58	0.07	1.04	3.69
Trace elements	μg/㎥	3.07	1.99	0.19	2.56	15.11
S	μg/㎥	2.33	1.68	0.10	1.88	13.04
K	ng/㎥	247.45	232.54	6.17	180.11	2785.23
Ca	ng/㎥	58.07	81.83	1.47	32.96	912.61
Ti	ng/㎥	8.46	9.72	0.53	5.63	103.88
V	ng/㎥	3.54	3.06	0.27	2.75	23.52
Cr	ng/㎥	0.84	0.75	0.35	0.35	7.08
Mn	ng/㎥	11.93	7.87	0.25	10.28	52.59
Fe	ng/㎥	177.01	118.34	12.11	149.11	1129.77
Ni	ng/㎥	1.28	1.13	0.20	1.03	9.85
Cu	ng/㎥	4.03	3.59	0.99	3.33	46.31
Zn	ng/㎥	57.14	35.27	2.43	48.66	230.40
As	ng/㎥	3.66	2.20	0.27	3.26	16.05
Se	ng/㎥	1.29	1.09	0.27	1.00	6.59
Br	ng/㎥	8.80	6.10	0.27	7.27	43.49
Pb	ng/㎥	19.66	17.25	0.66	15.02	115.36

Table 2-5 Summary of $PM_{2.5}$ chemical composition in Ulsan

Constituents	unit	Avg.	S.D.	Min.	Median	Max.
Mass conc.	μg/㎥	20.4	11.8	2.0	17.8	88.3
Ion species	μg/㎥	10.25	7.18	1.19	8.38	56.52
SO_4^{2-}	μg/㎥	4.10	3.15	0.36	3.11	24.81
NO_3^-	μg/㎥	2.96	3.05	0.09	1.98	21.82
Cl^-	μg/㎥	0.23	0.18	0.01	0.19	1.43
Na^+	μg/㎥	0.14	0.11	0.01	0.12	0.84
NH_4^+	μg/㎥	2.51	1.79	0.17	2.09	14.48
K^+	μg/㎥	0.11	0.16	0.00	0.08	2.05
Mg^{2+}	μg/㎥	0.02	0.02	0.00	0.02	0.15
Ca^{2+}	μg/㎥	0.05	0.04	0.00	0.03	0.44
Carbon species	μg/㎥	3.85	1.91	0.24	3.52	10.99
OC	μg/㎥	3.10	1.59	0.07	2.84	9.46
EC	μg/㎥	0.75	0.42	0.07	0.66	3.43
Trace elements	μg/㎥	5.79	4.05	0.68	4.52	28.47
S	μg/㎥	5.20	3.87	0.52	4.01	27.62
K	ng/㎥	183.20	174.66	9.29	133.37	1897.84
Ca	ng/㎥	51.88	50.99	1.47	36.29	581.44
Ti	ng/㎥	9.13	8.80	0.53	6.79	89.81
V	ng/㎥	7.75	10.98	0.27	3.08	86.60
Cr	ng/㎥	2.01	1.31	0.35	1.74	8.99
Mn	ng/㎥	18.62	14.65	0.25	15.34	130.97
Fe	ng/㎥	197.02	128.39	10.34	169.78	1177.56
Ni	ng/㎥	2.99	3.55	0.20	1.62	25.85
Cu	ng/㎥	6.72	4.60	0.99	5.70	56.05
Zn	ng/㎥	64.33	53.11	0.63	52.00	487.46
As	ng/㎥	5.89	7.51	0.27	3.21	64.90
Se	ng/㎥	1.54	1.61	0.27	1.04	10.81
Br	ng/㎥	7.99	5.67	0.40	6.51	55.37
Pb	ng/㎥	17.69	15.42	0.66	13.39	121.66

Table 2-6 Descriptive statistics of $PM_{2.5}$ mass and major components in Seoul

Components	Year	Avg.	S.D.	Min.	Median	Max.
$PM_{2.5}$ ($\mu g/m^3$)	2014	36.5	24.2	8.1	29.3	153.4
	2015	25.7	14.3	3.6	22.4	90.4
	2016	27.6	13.0	3.3	24.4	86.3
	2017	26.2	16.0	3.8	22.6	87.4
	2018	23.8	15.0	1.0	20.4	104.8
Ionic species ($\mu g/m^3$)	2014	24.87	18.88	2.74	19.38	101.89
	2015	14.65	10.46	1.39	12.02	55.57
	2016	14.97	9.38	0.74	12.71	55.45
	2017	15.46	11.35	1.20	12.37	67.01
	2018	13.99	11.75	0.07	10.63	80.11
Carbon species ($\mu g/m^3$)	2014	5.68	2.87	0.93	4.92	18.83
	2015	4.74	2.08	1.36	4.31	11.43
	2016	4.97	2.19	0.64	4.54	14.29
	2017	5.46	2.37	1.60	5.00	13.22
	2018	4.50	2.34	0.47	4.23	12.47
Trace elements ($\mu g/m^3$)	2014	3.89	2.54	0.92	3.04	15.61
	2015	5.76	4.14	1.54	4.79	25.64
	2016	4.34	2.40	0.84	3.67	15.62
	2017	3.26	1.91	0.22	2.88	10.43
	2018	2.78	1.70	0.45	2.37	13.77

Table 2-7 Descriptive statistics of SO_4^{2-} and NO_3^- in Seoul

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in ion(%)
SO_4^{2-} (㎍/㎥)	Total	5.38	4.74	0.01	4.05	39.15	32.2
	2014	8.31	7.72	0.51	5.72	39.15	33.4
	2015	5.18	3.86	0.20	4.31	24.38	35.4
	2016	5.74	3.45	0.36	5.12	20.89	38.3
	2017	4.38	3.14	0.47	3.30	19.36	28.3
	2018	4.06	3.32	0.01	3.07	27.48	29.0
NO_3^- (㎍/㎥)	Total	6.09	5.90	0.02	4.28	35.57	36.5
	2014	9.35	6.94	0.71	7.61	34.64	37.6
	2015	4.22	3.98	0.02	2.92	21.06	28.8
	2016	5.00	4.39	0.13	3.57	21.85	33.4
	2017	5.95	5.94	0.05	4.18	35.57	38.5
	2018	5.87	6.17	0.04	3.72	32.80	42.0

Table 2-8 Descriptive statistics of OC and EC in Seoul

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in carbon(%)
OC (㎍/㎥)	Total	3.78	1.90	0.29	3.39	16.79	74.9
	2014	4.06	2.22	0.37	3.44	16.79	71.5
	2015	3.57	1.55	0.84	3.25	8.36	75.3
	2016	3.71	1.79	0.44	3.34	12.55	74.6
	2017	4.18	1.88	1.36	3.69	11.21	76.6
	2018	3.49	1.84	0.29	3.32	9.26	77.6
EC (㎍/㎥)	Total	1.26	0.64	0.07	1.12	4.50	25.1
	2014	1.62	0.78	0.33	1.43	4.50	28.5
	2015	1.17	0.58	0.28	1.11	3.32	24.7
	2016	1.26	0.54	0.20	1.14	2.99	25.4
	2017	1.28	0.60	0.23	1.15	3.26	23.4
	2018	1.01	0.54	0.07	0.91	3.21	22.4

Table 2-9 Descriptive statistics of $PM_{2.5}$ mass and major components in Daejeon

Components	Year	Avg.	S.D.	Min.	Median	Max.
$PM_{2.5}$ ($\mu g/m^3$)	2014	30.7	14.8	8.5	28.1	117.2
	2015	35.6	18.5	7.7	31.1	111.2
	2016	30.9	15.7	3.3	28.4	79.1
	2017	26.0	13.3	1.8	23.8	96.3
	2018	24.2	14.5	1.7	21.2	86.7
Ionic species ($\mu g/m^3$)	2014	13.10	6.63	2.07	12.37	32.86
	2015	18.69	13.13	1.51	14.72	70.12
	2016	15.43	9.62	0.86	13.43	52.64
	2017	10.77	7.36	0.48	9.42	31.25
	2018	14.18	10.61	0.84	11.18	56.16
Carbon species ($\mu g/m^3$)	2014	6.72	2.82	2.35	6.07	21.41
	2015	7.03	2.67	2.20	6.47	20.11
	2016	5.54	2.67	1.00	4.97	14.24
	2017	5.56	2.32	1.68	5.13	15.52
	2018	4.86	2.29	1.07	4.42	12.12
Trace elements ($\mu g/m^3$)	2014	2.30	1.53	0.59	1.77	7.41
	2015	3.37	2.27	0.36	2.74	15.89
	2016	8.97	5.62	0.59	7.75	41.85
	2017	2.69	1.62	0.43	2.25	8.67
	2018	2.72	1.52	0.18	2.36	8.23

Table 2-10 Descriptive statistics of SO_4^{2-} and NO_3^- in Daejeon

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in ion(%)
SO_4^{2-} (㎍/㎥)	Total	5.23	3.71	0.16	4.24	28.25	34.8
	2014	5.37	3.30	0.48	4.75	16.72	41.0
	2015	6.87	4.49	0.27	5.80	28.25	36.8
	2016	5.41	3.67	0.38	4.43	26.21	35.1
	2017	4.11	2.85	0.23	3.38	15.32	38.2
	2018	4.27	2.97	0.16	3.42	15.97	30.1
NO_3^- (㎍/㎥)	Total	5.38	5.23	0.07	3.64	31.20	35.8
	2014	4.69	3.47	0.21	3.86	15.08	35.8
	2015	6.53	6.31	0.11	4.09	31.03	34.9
	2016	4.86	4.21	0.09	3.95	20.56	31.5
	2017	4.61	4.76	0.07	2.90	27.71	42.8
	2018	5.77	5.77	0.19	3.88	31.20	40.7

Table 2-11 Descriptive statistics of OC and EC in Daejeon

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in carbon(%)
OC (㎍/㎥)	Total	4.53	2.08	0.61	4.23	16.48	77.2
	2014	5.17	2.18	1.70	4.72	16.48	76.9
	2015	5.24	2.14	1.71	4.83	15.81	74.9
	2016	4.19	2.12	0.61	3.67	11.27	75.6
	2017	4.54	1.88	1.31	4.23	12.02	81.6
	2018	3.71	1.74	0.72	3.50	8.98	76.4
EC (㎍/㎥)	Total	1.35	0.67	0.29	1.21	4.93	22.8
	2014	1.55	0.67	0.55	1.37	4.93	23.1
	2015	1.79	0.70	0.32	1.73	4.30	25.6
	2016	1.35	0.60	0.38	1.24	3.37	24.3
	2017	1.02	0.48	0.29	0.92	3.50	18.4
	2018	1.15	0.61	0.32	1.01	3.17	23.6

Table 2-12 Descriptive statistics of $PM_{2.5}$ mass and major components in Gwangju

Components	Year	Avg.	S.D.	Min.	Median	Max.
$PM_{2.5}$ ($\mu g/m^3$)	2014	34.6	21.6	6.8	29.0	132.9
	2015	28.4	15.4	6.3	25.6	98.3
	2016	25.2	12.9	4.9	22.9	84.8
	2017	25.0	13.5	3.9	22.9	83.9
	2018	23.8	14.5	3.3	19.6	107.4
Ionic species ($\mu g/m^3$)	2014	16.74	12.44	1.75	13.53	78.47
	2015	15.17	11.16	0.96	13.18	78.12
	2016	13.74	9.13	1.17	12.01	76.09
	2017	13.09	8.86	1.1	10.95	52.91
	2018	15.05	10.76	2.15	12.14	72.07
Carbon species ($\mu g/m^3$)	2014	5.44	2.98	1.11	4.66	17.68
	2015	5.62	2.92	1.27	5.05	20.09
	2016	5.27	2.54	1.15	4.88	15.49
	2017	5.39	2.39	1.16	4.98	13.59
	2018	4.72	2.61	0.43	4.24	17.73
Trace elements ($\mu g/m^3$)	2014	5.05	2.88	1.08	4.54	15.11
	2015	3.33	1.92	0.56	2.87	12.24
	2016	2.26	1.36	0.19	1.93	8.99
	2017	2.85	1.41	0.34	2.62	7.84
	2018	1.01	0.98	0.05	0.64	5.95

Table 2-13 Descriptive statistics of SO_4^{2-} and NO_3^- in Gwangju

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in ion(%)
SO_4^{2-} (㎍/㎥)	Total	5.36	3.92	0.30	4.25	32.16	36.6
	2014	6.58	5.14	0.35	4.71	32.16	39.3
	2015	5.55	4.22	0.47	4.57	31.76	36.6
	2016	5.62	3.77	0.50	4.77	21.48	40.9
	2017	4.33	2.85	0.30	3.47	14.52	33.1
	2018	4.91	3.28	0.61	4.02	19.09	32.6
NO_3^- (㎍/㎥)	Total	4.64	4.79	0.06	2.97	41.15	31.7
	2014	4.82	4.63	0.17	3.38	25.24	28.8
	2015	4.88	4.7	0.09	3.59	31.15	32.2
	2016	3.80	3.97	0.06	2.50	32.17	27.6
	2017	4.63	4.54	0.29	2.92	24.48	35.4
	2018	5.29	5.87	0.15	3.09	41.15	35.1

Table 2-14 Descriptive statistics of OC and EC in Gwangju

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in carbon(%)
OC (㎍/㎥)	Total	4.11	2.21	0.20	3.75	17.48	78.1
	2014	4.30	2.38	0.79	3.74	13.99	79.1
	2015	4.59	2.47	0.94	4.17	17.48	81.7
	2016	4.09	2.07	0.77	3.79	11.92	77.6
	2017	3.97	1.92	0.56	3.70	10.53	73.7
	2018	3.72	2.11	0.20	3.35	14.18	78.7
EC (㎍/㎥)	Total	1.15	0.58	0.07	1.04	3.69	21.9
	2014	1.14	0.65	0.23	0.95	3.69	20.9
	2015	1.03	0.50	0.27	0.93	3.01	18.3
	2016	1.18	0.52	0.26	1.07	3.57	22.4
	2017	1.42	0.52	0.49	1.34	3.16	26.3
	2018	1.00	0.59	0.07	1.00	3.55	21.3

Table 2-15 Descriptive statistics of $PM_{2.5}$ mass and major components in Ulsan

Components	Year	Avg.	S.D.	Min.	Median	Max.
$PM_{2.5}$ ($\mu g/m^3$)	2014	21.8	12.8	5.3	18.3	88.3
	2015	20.7	11.9	3.8	18.2	64.2
	2016	23.1	11.8	6.7	19.8	62.5
	2017	18.8	10.1	4.1	16.9	66.7
	2018	18.8	12.0	2.0	16.1	57.2
Ionic species ($\mu g/m^3$)	2014	12.86	8.90	2.07	10.60	56.52
	2015	8.98	6.04	1.19	7.53	30.31
	2016	9.66	5.56	1.96	8.39	32.02
	2017	7.95	4.36	1.92	6.95	24.35
	2018	12.22	8.97	1.78	9.56	46.07
Carbon species ($\mu g/m^3$)	2014	4.06	1.91	0.95	3.65	10.99
	2015	4.14	1.83	1.30	3.77	9.30
	2016	3.96	1.75	0.97	3.65	9.17
	2017	3.70	1.68	0.74	3.45	9.44
	2018	3.57	2.17	0.24	3.17	10.96
Trace elements ($\mu g/m^3$)	2014	3.02	1.73	1.09	2.47	9.37
	2015	3.64	2.38	0.68	3.18	13.71
	2016	5.54	2.79	1.03	5.06	14.05
	2017	6.20	3.92	0.85	4.93	19.9
	2018	6.60	4.70	0.85	5.15	28.47

Table 2-16 Descriptive statistics of SO_4^{2-} and NO_3^- in Ulsan

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in ion(%)
SO_4^{2-} (㎍/㎥)	Total	4.10	3.15	0.36	3.11	24.81	40.0
	2014	4.63	3.16	0.79	3.69	19.00	36.0
	2015	3.78	2.66	0.53	2.87	12.99	42.1
	2016	4.19	2.75	0.41	3.44	15.01	43.4
	2017	3.11	2.19	0.36	2.5	12.01	39.1
	2018	4.73	3.99	0.48	3.35	24.81	38.7
NO_3^- (㎍/㎥)	Total	2.96	3.05	0.09	1.98	21.82	28.9
	2014	3.47	3.31	0.22	2.55	21.82	27.0
	2015	2.43	2.45	0.09	1.48	14.38	27.1
	2016	2.47	2.23	0.22	1.77	10.09	25.6
	2017	2.41	2.14	0.15	1.95	14.77	30.3
	2018	3.87	3.99	0.21	2.46	20.11	31.7

Table 2-17 Descriptive statistics of OC and EC in Ulsan

Species	Year	Avg.	S.D.	Min.	Median	Max.	Proportion in carbon(%)
OC (㎍/㎥)	Total	3.10	1.59	0.07	2.84	9.46	80.5
	2014	2.96	1.43	0.64	2.66	7.56	72.9
	2015	3.41	1.51	0.99	3.11	7.64	82.4
	2016	3.29	1.53	0.72	2.90	8.36	83.1
	2017	3.04	1.38	0.53	2.85	7.90	82.2
	2018	2.90	1.85	0.07	2.52	9.46	81.2
EC (㎍/㎥)	Total	0.75	0.42	0.07	0.66	3.43	19.5
	2014	1.10	0.56	0.21	0.97	3.43	27.1
	2015	0.73	0.39	0.19	0.65	2.21	17.6
	2016	0.67	0.28	0.24	0.61	1.86	16.9
	2017	0.66	0.35	0.17	0.57	2.00	17.8
	2018	0.67	0.37	0.07	0.58	1.79	18.8

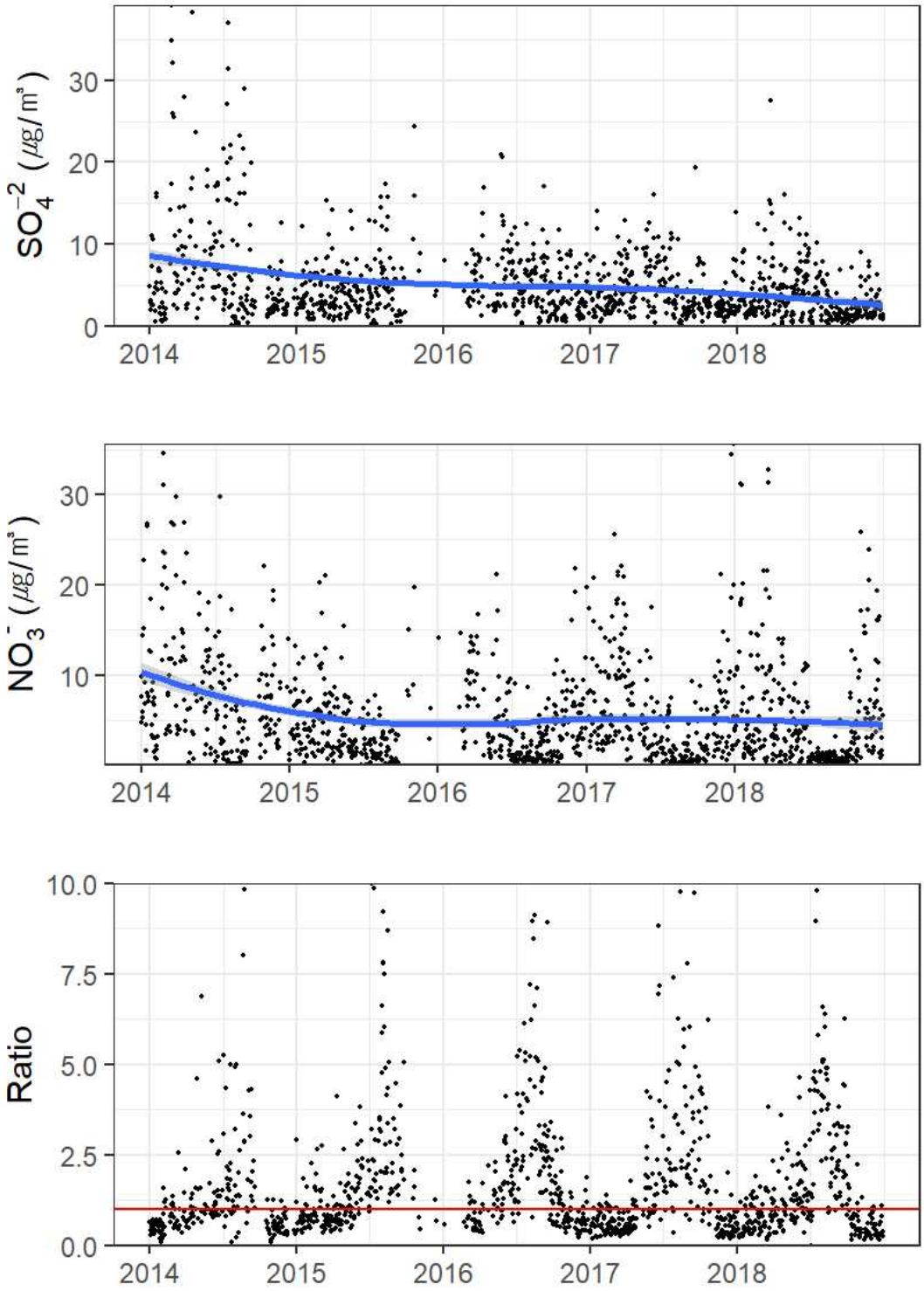


Figure 2-7 Time series of sulfate, nitrate concentration and sulfate/nitrate ratio in Seoul during 2014-2018

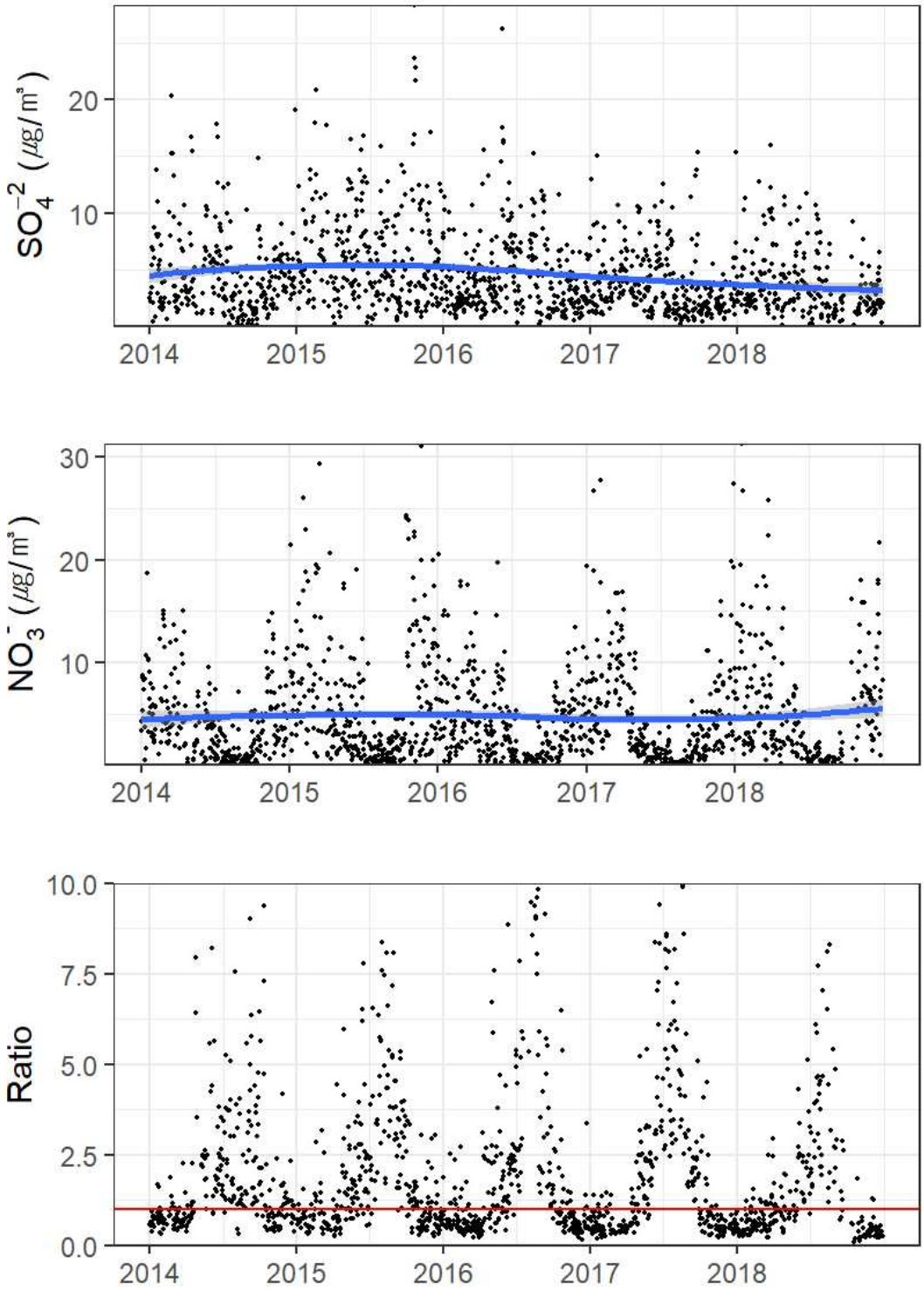


Figure 2-8 Time series of sulfate, nitrate concentration and sulfate/nitrate ratio in Daejeon during 2014-2018

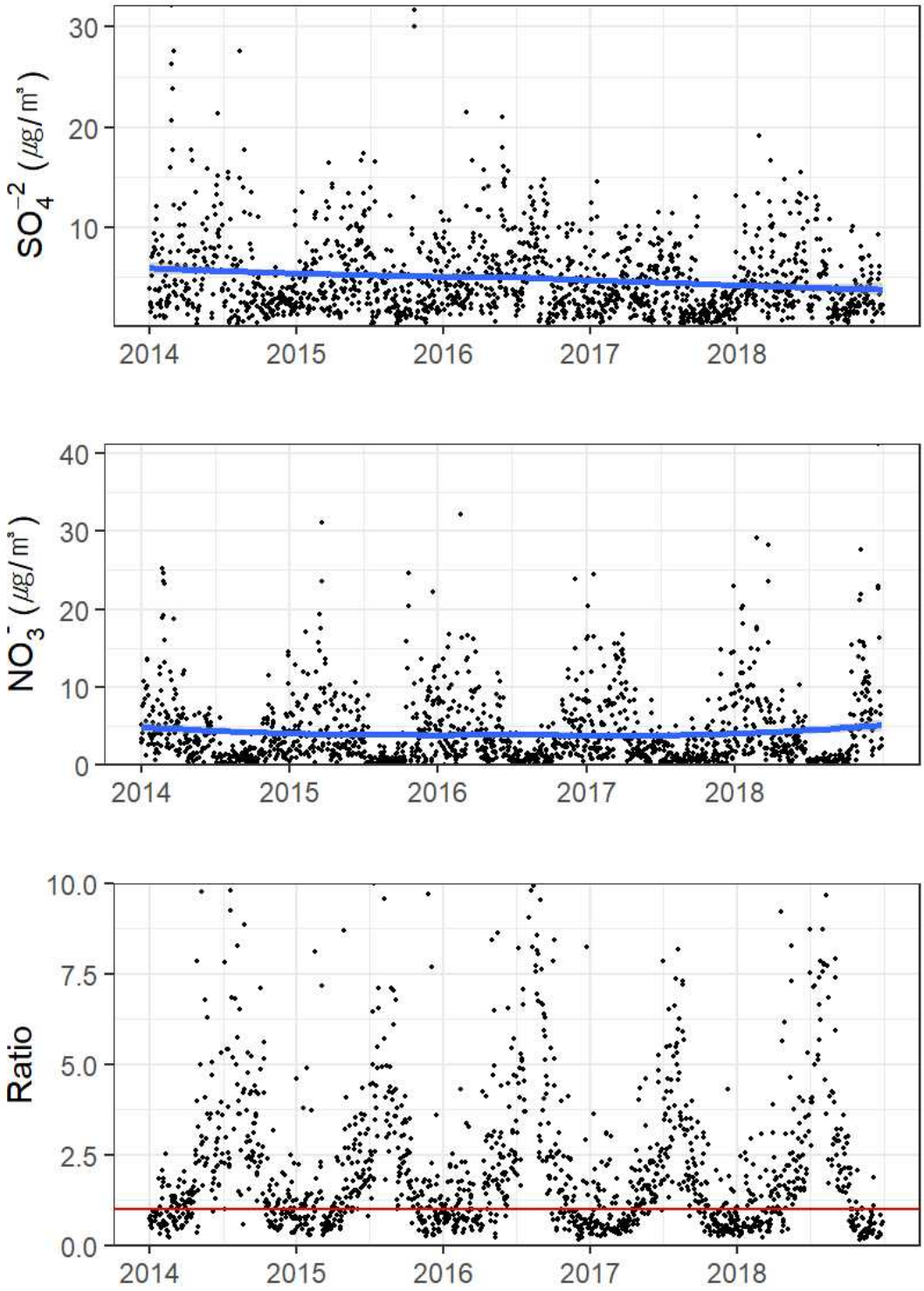


Figure 2-9 Time series of sulfate, nitrate concentration and sulfate/nitrate ratio in Gwangju during 2014-2018

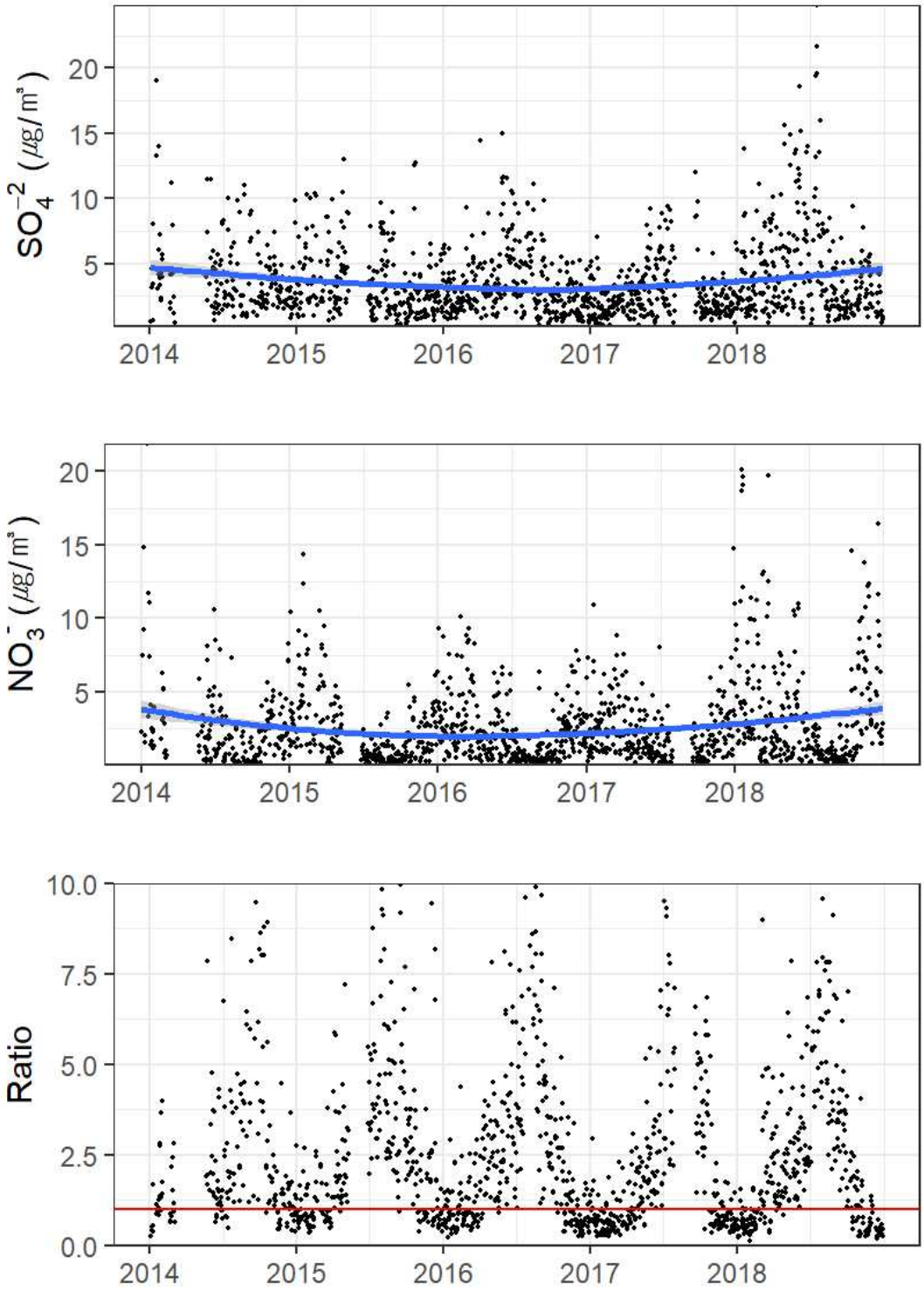


Figure 2-10 Time series of sulfate, nitrate concentration and sulfate/nitrate ratio in Ulsan during 2014–2018

4. Conclusions

$PM_{2.5}$ is a complex substance composed of various chemical components and the compositional characteristics are highly region-specific depending on the spatiotemporal conditions including the emission of gaseous precursors, meteorological conditions, and source locations.

The concentrations of $PM_{2.5}$ chemical constituents and gaseous precursors in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018 were investigated for better understanding the characteristics of $PM_{2.5}$ in each city. Overall, the concentrations of $PM_{2.5}$ mass and gaseous precursors have decrease gradually over the five years in common, considered to be the results of the government-led plans and policies for the mitigation of air pollution. In addition, the chemical composition of $PM_{2.5}$ in the cities showed similarity, where the largest fraction of $PM_{2.5}$ was attributable to ionic species, especially nitrate, sulfate and ammonium. These characteristics suggest that secondary particles are dominant over primary particles in the formation of ambient $PM_{2.5}$.

However, the relative proportion of each component was different among cities, which showed the heterogeneous composition of $PM_{2.5}$. In Seoul, nitrate was dominant over

sulfate, whereas the sulfate/nitrate ratios in the other cities were equal to or more than 1.0. The chemical composition of $PM_{2.5}$ in Daejeon and Gwangju was quite comparable to each other while that in Ulsan was different from other cities, thought to be affected by the geographical location and industrial characteristics.

References

Bae, C., Kim, B. U., Kim, H. C., Yoo, C. and Kim, S., 2020. Long-range transport influence on key chemical components of $PM_{2.5}$ in the Seoul Metropolitan Area, South Korea, during the years 2012-2016. *Atmosphere*, 11(1), 48.

Dos Anjos, S. L., Alves, J. C., Soares, S. A. R., Araujo, R. G., de Oliveira, O. M., Queiroz, A. F. and Ferreira, S. L., 2018. Multivariate optimization of a procedure employing microwave-assisted digestion for the determination of nickel and vanadium in crude oil by ICP OES. *Talanta*, 178, pp. 842-846.

Hitzenberger, R., Petzold, A., Bauer, H., Ctyroky, P., Pouresmaeil, P., Laskus, L. and Puxbaum, H., 2006. Intercomparison of thermal and optical measurement methods for elemental carbon and black carbon at an urban location. *Environmental science & technology*, 40(20), pp.6377-6383.

Huang, X. H., Bian, Q., Ng, W. M., Louie, P. K. and Yu, J. Z., 2014. Characterization of $PM_{2.5}$ major components and source investigation in suburban Hong Kong: a one year monitoring study. *Aerosol and Air Quality Research*, 14(1), pp.237-250.

Jang, H. N., Seo, Y. C., Lee, J. H., Hwang, K. W., Yoo, J. I., Sok, C. H. and Kim, S. H., 2007. Formation of fine particles enriched by V and Ni from heavy oil combustion: Anthropogenic sources and drop-tube furnace experiments. *Atmospheric Environment*, 41(5), pp.1053-1063.

Kim, H. W., Dong, L., Choi, A. E. S., Fujii, M., Fujita, T. and Park, H. S., 2018. Co-benefit potential of industrial and urban symbiosis using waste heat from industrial park in Ulsan, Korea. *Resources, Conservation and Recycling*, 135, pp.225-234.

Lee, J. H. and Hopke, P. K., 2006. Apportioning sources of $PM_{2.5}$ in St. Louis, MO using speciation trends network data. *Atmospheric Environment*, 40, pp.360-377.

Leem, J. H., Kim, S. T. and Kim, H. C., 2015. Public-health impact of outdoor air pollution for 2nd air pollution management policy in Seoul metropolitan area, Korea. *Annals of occupational and environmental medicine*, 27(1), pp.1-9.

Lonati, G., Giugliano, M., Butelli, P., Romele, L. and Tardivo, R., 2005. Major chemical components of $PM_{2.5}$ in Milan (Italy). *Atmospheric Environment*, 39(10), pp.1925-1934.

Long, C. M., Nascarella, M. A. and Valberg, P. A., 2013. Carbon black vs. black carbon and other airborne materials containing elemental carbon: Physical and chemical distinctions. *Environmental pollution*, 181, pp.271-286.

Ning, P. and Lee, S. H., 2019. Estimating the Young Generation's Willingness to Pay (WTP) for $PM_{2.5}$ Control in Daegu, Korea, and Beijing, China. *Sustainability*, 11(20), 5704.

Voutsa, D., Samara, C., Manoli, E., Lazarou, D. and Tzoumaka, P., 2014. Ionic composition of $PM_{2.5}$ at urban sites of northern Greece: secondary inorganic aerosol formation. *Environmental Science and Pollution Research*, 21(7), pp.4995-5006.

Zenker, K., Vonwiller, M., Szidat, S., Calzolai, G., Giannoni, M., Bernardoni, V., Jedynska, A. D., Henzing, B., Meijer, H. A. J. and Dusek, U., 2017. Evaluation and inter-comparison of oxygen-based OC-EC separation methods for radiocarbon analysis of ambient aerosol particle samples. *Atmosphere*, 8(11), 226.

Chapter 3.

Source apportionment of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during 2014-2018

Abstract

Receptor models are useful tools to identify the sources of environmental pollutants including $PM_{2.5}$ and PM_{10} based on the chemical analyses of samples taken at a receptor. Positive matrix factorization (PMF), a representative receptor model, has been widely performed for identifying $PM_{2.5}$ sources and estimating their contributions to $PM_{2.5}$.

In this study, PMF model was applied to daily $PM_{2.5}$ speciation data in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018 to investigate source profiles for the cities. A total of 1,438, 1,278, 1,419, 1,211 datasets filtered based on mass balance and ion balance were used as input data for modelling. Ten identical factors were resolved for Seoul, Gwangju, and Ulsan in common while nine-factor solution was drawn for Daejeon where aged sea salt source was not found due to the geographical location. In all study cities, large fractions of $PM_{2.5}$ mass were found to be attributable to three major sources: secondary sulfate, secondary nitrate, and mobile. The results of source apportionment for the study cities imply secondary formation mainly affected $PM_{2.5}$ formation in South Korea, whereas the contributions of the other sources varied considerably depending on the region-specific factors.

1. Introduction

Various types of air quality models widely used for air pollutants can be largely classified into dispersion models and receptor models according to the purposes and principles. Dispersion models are mainly used for predicting air quality by simulating the movement of gaseous and/or particulate pollutants and the reactions among pollutants in the atmosphere along with climate prediction (Langner and Klemm 2011; Krishna et al., 2005).

Contrast to dispersion models, receptor models are generally used to identify sources and estimate their contributions to the total pollutant based on the chemical analyses data of samples taken in the location of receptors (Hopke, 2003). Widely used receptor-oriented models are positive matrix factorization (PMF), chemical mass balance (CMB), graphical ratio analysis for composition estimates (GRACE), etc (Guo et al., 2004).

In the present study, source apportionment of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018 was performed by employing PMF model. In addition, error estimation was conducted through displacement method (DISP) for acquiring uncertainty estimates for each factor of the PMF solutions.

2. Materials and methods

2.1 Input data

For executing PMF model, a total of 1,438, 1,278, 1,419, and 1,211 datasets were used as input data for Seoul, Daejeon, Gwangju, and Ulsan, respectively. The datasets were composed of the daily measured value of each chemical constituent as well as $PM_{2.5}$ mass concentration during 2014–2018. To prepare the input datasets, data filtering was conducted based on the mass balance and ion balance of chemical species of $PM_{2.5}$. First, datasets on the day when the sum of the all chemical species mass was out of the range of 50%-150% of $PM_{2.5}$ mass concentration were excluded. Then, datasets of which ion balance among NO_3^-, SO_4^{2-}, and NH_4^+ was not satisfactory were additionally removed from the input datasets.

2.2 PMF modelling

Among various receptor models based on chemical analyses, PMF and CMB have been generally performed for revealing the sources of fine particulate matter and estimating their contributions. Previous studies showed the results from PMF and CMB were quite comparable (Begum et al., 2007; Ke

et al., 2008; Teixeira et al., 2015). However, PMF is more flexible than CMB in terms of applicability because PMF modelling doesn't need source profiles for model execution. Source profile is a list of pollutants and their relative proportion in the exhaust of the source which is very dependent on the country, region, and sources of receptors. It is difficult to obtain suitable source profile constructed for a region although it strongly affects the results of source apportionment. Therefore, PMF was selected to investigate the sources and their contributions to $PM_{2.5}$ in four cities. In PMF, modeled data can be expressed as Eq. (1)

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (i = 1,...,m \quad j = 1,...,n \quad k = 1,...,p) \qquad (1)$$

where x_{ij} is the concentration of species j in sample i, g_{ik} is the source contribution of source k in sample i, f_{kj} is the species j mass fraction in source k, and e_{ij} is error. The values of g_{ik} and f_{kj} are repeatedly adjusted until Q value reaches a minimum value for a given p in the following equation.

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{\sigma_{ij}} \right)^2 \qquad (2)$$

As for PMF input data, both concentration and corresponding uncertainty for the chemical species of $PM_{2.5}$ were constructed according to the method from the guidebook of US EPA PMF 5.0 (Norris et al., 2014). Data values below the MDL were replaced with half of the MDL and 5/6 × MDL were used as their corresponding uncertainties. For the measured values greater than the MDL, the uncertainties were calculated by Eq. (3) and 10% was used as error fraction.

$$\text{Uncertainty}=[(\text{Error Fraction}\times\text{Concentration})^2 + (0.5\times\text{MDL})^2]^{1/2} \quad (3)$$

Further information on PMF modelling can be easily found elsewhere (Scerri et al., 2018; Watson et al., 2008; Manousakas et al., 2017).

2.3 Conditional probability function

The conditional probability function (CPF) is a method to estimate the possible source locations from various wind directions by combining source contributions with meteorological data such as wind speed and wind direction. This method can suggest the likely source areas exist on the direction of the site with high CPF values (Gugamsetty et al., 2012; Pekney et al., 2006). CPF can be calculated through following Eq. (4)

$$CPF = \frac{m_{\Delta\Theta}}{n_{\Delta\Theta}} \quad (4)$$

In the equation, $n_{\Delta\Theta}$ is the total number of occurrences that the wind passed through direction sector ΔΘ and $m_{\Delta\Theta}$ is the number of occurrences that exceed the thresholds from direction sector ΔΘ.

In this study, the value of 22.5° was used for ΔΘ as 16 wind direction sectors were applied to CPF calculation and calm wind periods (≤ 0.5 m/sec) were excluded from the calculation (Argyropoulos et al., 2017; Du and Turner, 2015).

2.4 Potential source contribution function

The potential source contribution function (PSCF) has been widely employed for identifying potential source areas based on the conditional probability that high concentrations of a substance at a receptor site are related to the passage of air parcels which passed through some grid cells where potential source are located (Hsu et al., 2003; Lucey et al., 2001). The PSCF value for the *ij*th grid cell is expressed as PSCF (*i,j*) = m (*i,j*) / n (*i,j*).

The denominator, n (*i,j*), represents the total number of

trajectory end points which pass a certain (*ij*th) grid cell while the numerator stands for the number of end points passing the identical grid cell when the concentrations at receptors were above the criterion value.

In this study, PSCF was adopted to identify the possible locations of four sources, namely secondary nitrate, secondary sulfate, biomass burning and, soil, reported to be related to long-range transport. Backward air mass trajectories for each site were made up by the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model developed by the National Oceanic and Atmospheric Administration (NOAA), USA. Also, meteorological data with 1-degree spatial resolution was acquired from Global Data Assimilation System (GDAS) to calculate the 72-hour backward trajectories (Kumari et al., 2021; Rolph et al., 2017). The criterion values of the 75th percentile for the whole period from 2014 to 2018 were used for secondary nitrate, secondary sulfate and biomass burning sources while 90th percentile was used for soil source.

In addition, a joint PSCF (J-PSCF) was employed to locate possible source areas affecting $PM_{2.5}$ source contributions for multiple cities in common. The cities for J-PSCF analyses were determined based on the correlation coefficients of source contributions.

3. Results and discussion

3.1 Source apportionment

The number of factors was chosen based on the evaluation of model results including Q-value, residual distribution, and the coefficient of determination. Source profiles in the study cities were physically meaningful and understandable. A nine-factor solution for Daejeon and ten-factor solutions for Seoul, Gwangju, and Ulsan were drawn while source contributions varied among cities although resolved factors were almost identical. Source profiles for Seoul, Daejeon, Gwangju, and Ulsan obtained from PMF modelling are displayed in Figures 3-1, 3-3, 3-5, and 3-7, respectively along with the daily source contributions (Figures 3-2, 3-4, 3-6, and 3-8).

The first source was secondary nitrate distinguished by large contributions of NO_3^- and NH_4^+ to $PM_{2.5}$ and it showed higher contributions in winter. Its average contributions were 20.3%, 19.5%, 19.5%, and 18.9% in Seoul (6.45 ㎍/㎥), Daejeon (5.66 ㎍/㎥), Gwangju (5.24 ㎍/㎥), and Ulsan (3.57 ㎍/㎥), respectively. Secondary nitrate is mainly influenced by multiple sources related to high temperature including mobile, fuel combustion, and industry related sources. From daily

contributions during 2014-2018, higher contributions of the factor were observed in winter due to the formation mechanism of secondary nitrate. The formation of nitric acid, a precursor of secondary nitrate (Schaap et al., 2004), is favored under the conditions of high relative humidities and low temperatures (Lee et al., 2008; Ying, 2011), which are related to seasonal patterns of this factor as mentioned above.

In contrast to secondary nitrate, the contributions of secondary sulfate, identified by high concentrations of SO_4^{2-} and NH_4^+, were much higher during summer seasons. Its average contributions were 21.8%, 19.7%, 21.3%, and 23.9% in Seoul (6.92 ㎍/㎥), Daejeon (5.70 ㎍/㎥), Gwangju (5.70 ㎍/㎥), and Ulsan (4.50 ㎍/㎥), respectively. Secondary sulfate is largely formed in the atmosphere through a series of oxidative reactions of sulfur dioxide by the photochemically produced radicals (Meidan et al., 2019), which is closely related to the increase in its contributions to $PM_{2.5}$ during summer seasons. Strong photochemical reactions in summer seasons result in higher contributions of the source (Duan et al., 2020; Wang et al., 2016).

The third source was interpreted to be mobile considering high concentrations of OC, EC, NH_4^+, and NO_3^- along with medium loadings of medium loadings of Ti, Fe, Zn,

and Mn. Markers of mobile source are mostly from exhaust and non-exhaust emissions. Exhausts from gasoline and diesel fueled vehicles are dominated by OC and EC in common but the relative ratio of OC to EC is different among fuel types and individual vehicles (Charron et al., 2019). Markers of non-exhaust emissions are Ca, Ti, and Fe which are representative crustal elements contained in resuspended particles by traffic. Cu and Pb are marker species associated with vehicle's brake system (Figliuzzi et al., 2020; Na et al., 2009). The contributions of mobile sources were 22.3%, 21.7%, 20.5%, and 24.9% in Seoul (7.08 ㎍/㎥), Daejeon (6.27 ㎍/㎥), Gwangju (5.50 ㎍/㎥), and Ulsan (4.70 ㎍/㎥), respectively. Together with secondary nitrate and secondary sulfate, mobile source explained the majority of $PM_{2.5}$ mass in the study cities in common, which means alleviating ambient $PM_{2.5}$ pollution is closely associated the emission reduction from the three sources.

The fourth source, biomass burning, was explained by high K^+ concentrations and medium concentrations of OC and EC. From the combustion of wood and agricultural residue by natural wildfires and anthropogenic activities, K^+ is emitted as potassium salts, mainly in the form of KCl, K_2SO_4, and KNO_3 (Li et al., 2003). The average contributions to $PM_{2.5}$ were 4.3%, 2.7%, 3.2% and 3.6% in Seoul (1.37 ㎍/㎥), Daejeon (0.77 ㎍/㎥),

Gwangju (0.87 ㎍/㎥), and Ulsan (0.68 ㎍/㎥), respectively. This source showed a seasonal pattern of higher contribution to $PM_{2.5}$ in winter, which was thought to be the results of biomass burning for domestic heating and agricultural purposes in the Korean Peninsula and China. Open field burning of agricultural residue before cultivation (Feb-Mar) and after harvest (Oct-Nov) has been widely done in East Asia for enhancing land productivity (Ryu et al., 2007; Thepnuan et al., 2019).

The fifth source was incinerator identified by high loadings of Cl^-, NO_3^-, and NH_4^+. Cl^- is mainly emitted as hydrogen chloride in the flue gas from the incineration of municipal solid waste (MSW) or industrial materials containing plastics, especially polyvinylchloride (Wey et al., 2001). The average contributions of this factor were 8.7%, 8.9%, 12.2%, 3.7% in Seoul (2.75 ㎍/㎥), Daejeon (2.57 ㎍/㎥), Gwangju (3.26 ㎍/㎥), and Ulsan (0.70 ㎍/㎥) respectively.

Soil, the sixth source, could be distinguished by high concentrations of crustal elements such as Ca, Ti, and Fe. The contributions of the source to $PM_{2.5}$ considerably increased during spring season (Mar-May) in all cities, which might have been affected by yellow sand events mainly originating from the Gobi Desert and/or the Loess plateau located in China and Mongolia (Kim et al., 2012). Its average contributions to $PM_{2.5}$

2.6%, 4.2%, 4.2% and 5.3% in Seoul (0.81 ㎍/㎥), Daejeon (1.22 ㎍/㎥), Gwangju (1.11 ㎍/㎥), and Ulsan (1.00 ㎍/㎥), respectively.

The seventh source, industry, was represented by high concentrations of heavy metals including Fe, Mn, Cu, and Zn. Trace metals such as Mn and Zn are emitted from steel smelting processes (Querol et al., 2006) while Cu is related to smelting furnace burning (Yang et al., 2003). Pb is emitted from the production processes of steel, plastics and pigment production (Li et al., 2012). The contributions of industry source to $PM_{2.5}$ were 4.4%, 6.6%, 4.3% and 8.8% on average in Seoul (1.40 ㎍/㎥), Daejeon (1.90 ㎍/㎥), Gwangju (1.16 ㎍/㎥) and Ulsan (1.67 ㎍/㎥), respectively. The contributions of this source in Ulsan were obviously larger than the other cities, reflecting the industrial structure of the city.

Coal combustion, the eighth source, had high concentrations of As and Pb with medium loadings of OC and EC. As and Pb are mainly emitted from coal combustion due to their abundance in coal (Shah et al., 2007; Wang et al., 2021). Coal combustion source accounted for 10.7%, 10.7%, 9.7%, and 3.5% of $PM_{2.5}$ mass concentration in Seoul (3.40 ㎍/㎥), Daejeon (3.10 ㎍/㎥), Gwangju (2.59 ㎍/㎥), and Ulsan (0.67 ㎍/㎥), respectively. $PM_{2.5}$ in Seoul and Daejeon, relatively closer to

coal power plants on the western coast of Korean Peninsula, was found to be highly affected by the source.

The ninth source, oil combustion, was determined by high loadings of Ni and V and medium loadings of OC and EC. Fine particulate matter emitted from oil combustion facilities contains heavy metals such as Ni, V because the two elements are abundant in the liquid fuel (Dos Anjos, 2018; Jang et al., 2007). The average contributions of oil combustion source were 2.9%, 6.1%, 2.2% and 3.4% in Seoul (0.92 $\mu g/m^3$), Daejeon (1.76 $\mu g/m^3$), Gwangju (0.60 $\mu g/m^3$), and Ulsan (0.65 $\mu g/m^3$), respectively.

Aged sea salt source was characterized by high loadings of Na^+ with medium loadings of Cl^-. Relatively low loadings of Cl^- distinguish this factor from sea salt source because Cl^- normally depletes along with the time after fresh sea salt aerosols is formed in the atmosphere (Adachi and Buseck, 2015; Laskin et al., 2002; Yao and Zhang, 2012). Aged sea salt explained 2.1%, 2.9%, and 4.1% of $PM_{2.5}$ mass in Seoul (0.66 $\mu g/m^3$), Gwangju (0.78 $\mu g/m^3$), and Ulsan (0.74 $\mu g/m^3$), respectively.

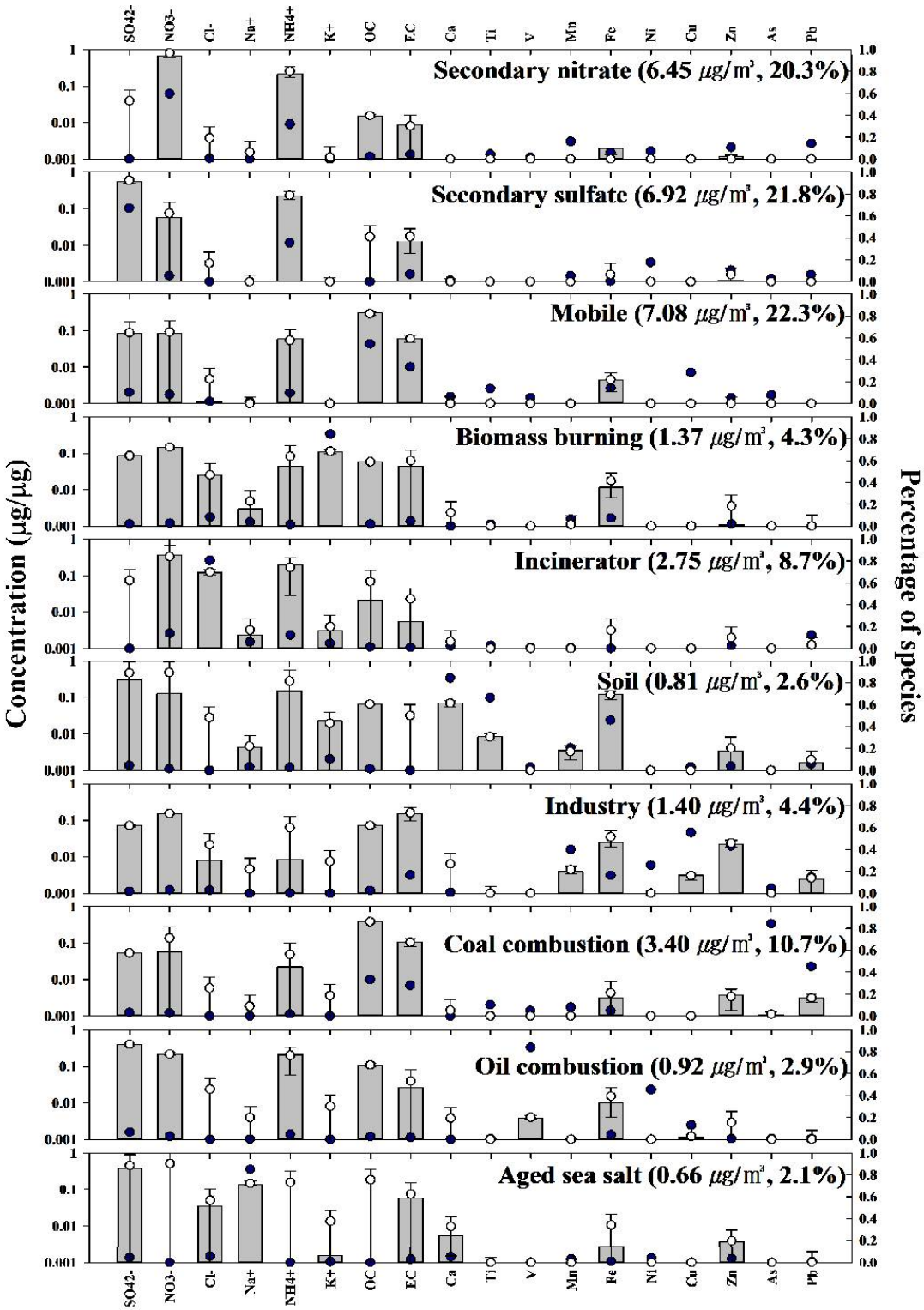


Figure 3-1 Source profiles of $PM_{2.5}$ in Seoul during 2014–2018

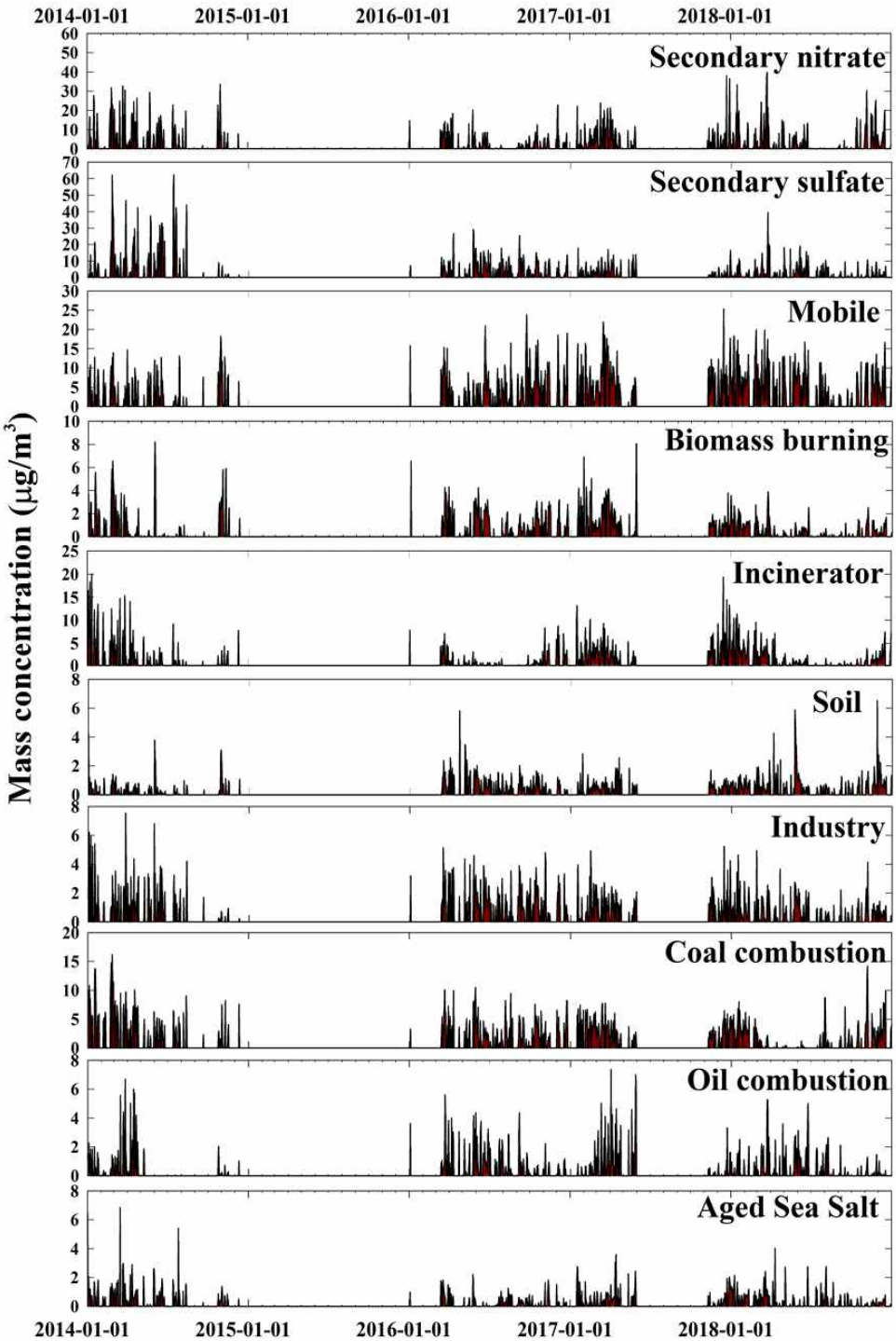


Figure 3-2 Daily source contribution plot in Seoul during 2014–2018

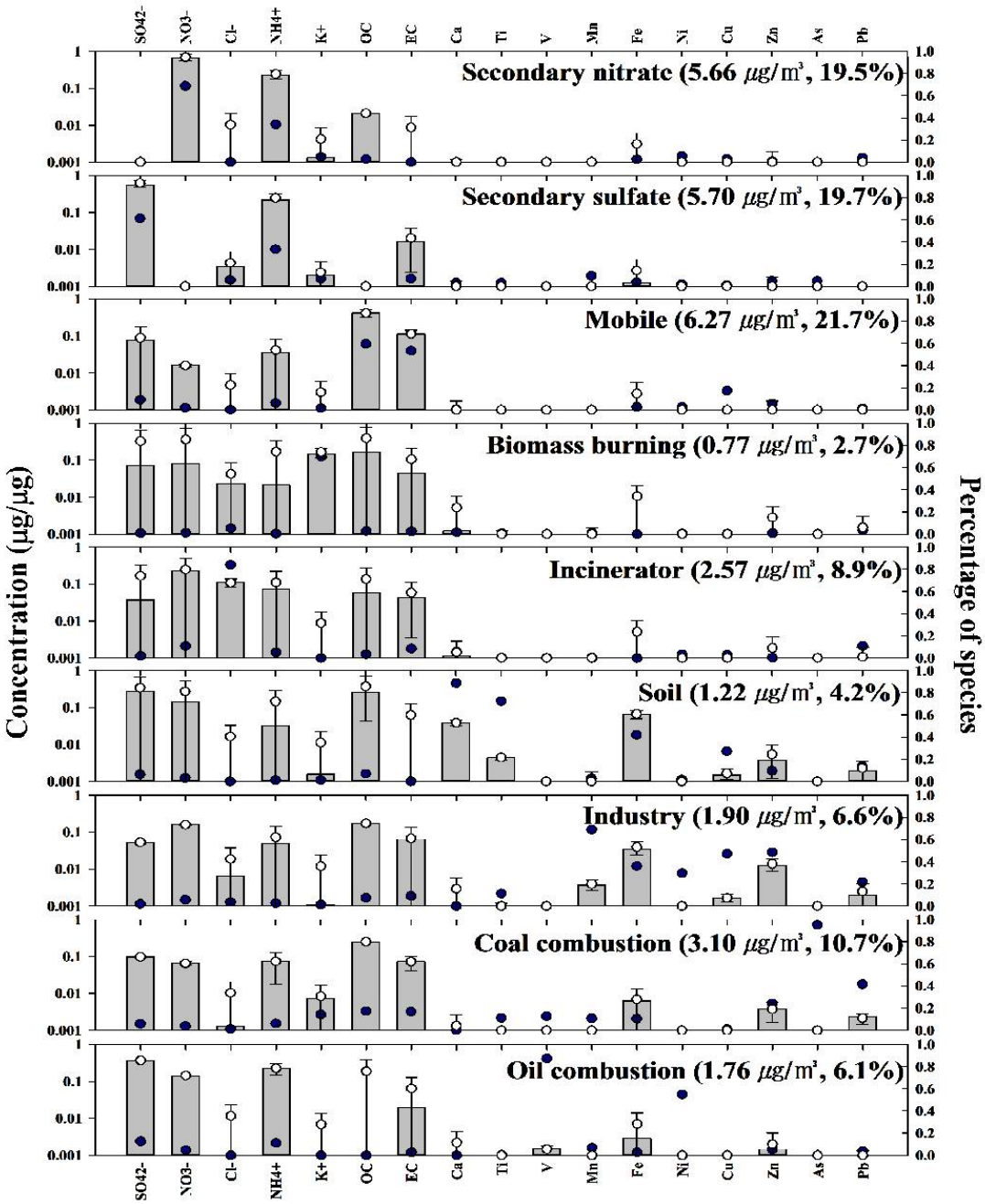


Figure 3-3 Source profiles of $PM_{2.5}$ during in Daejeon 2014–2018

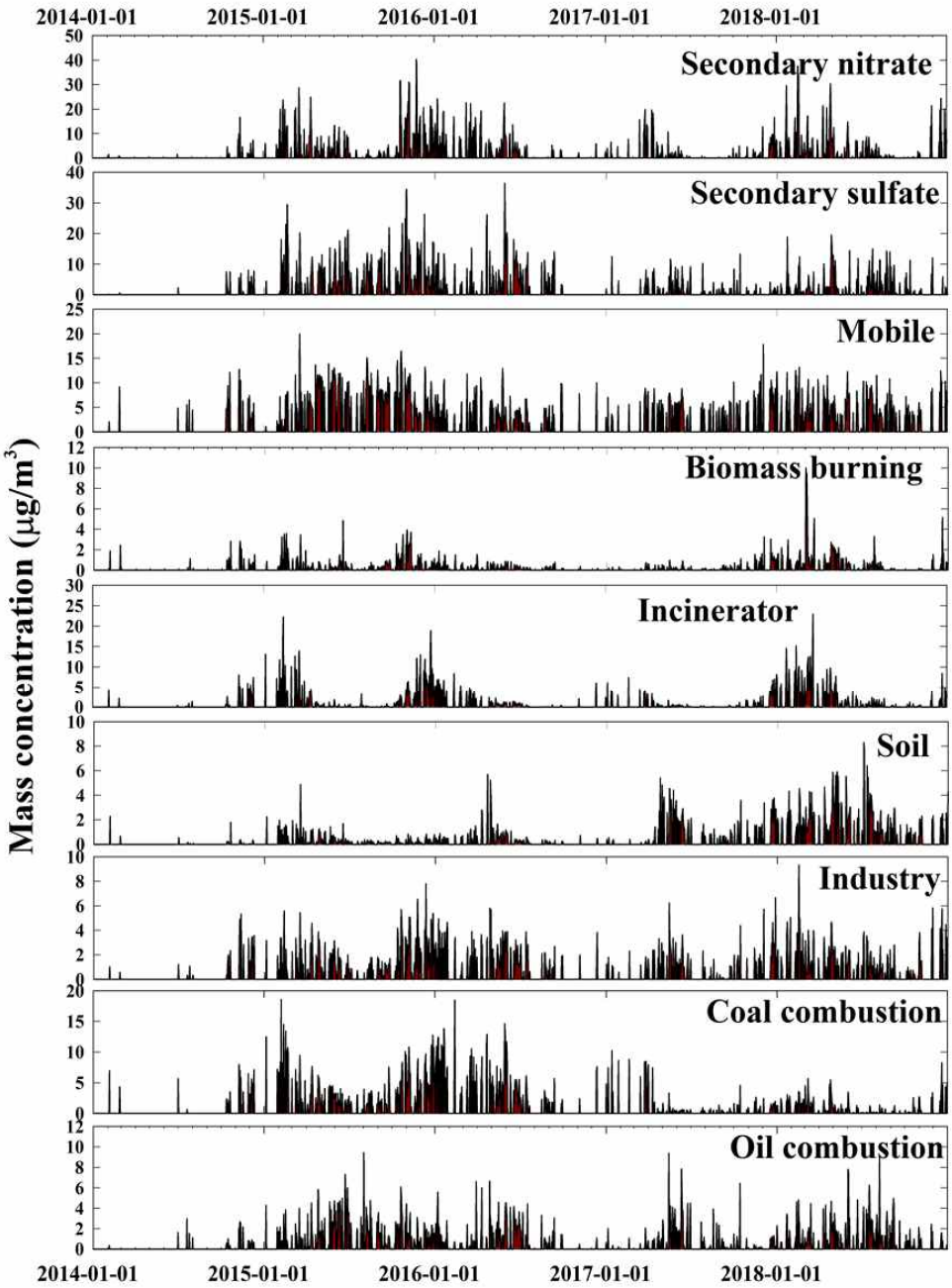


Figure 3-4 Daily source contribution plot in Daejeon during 2014–2018

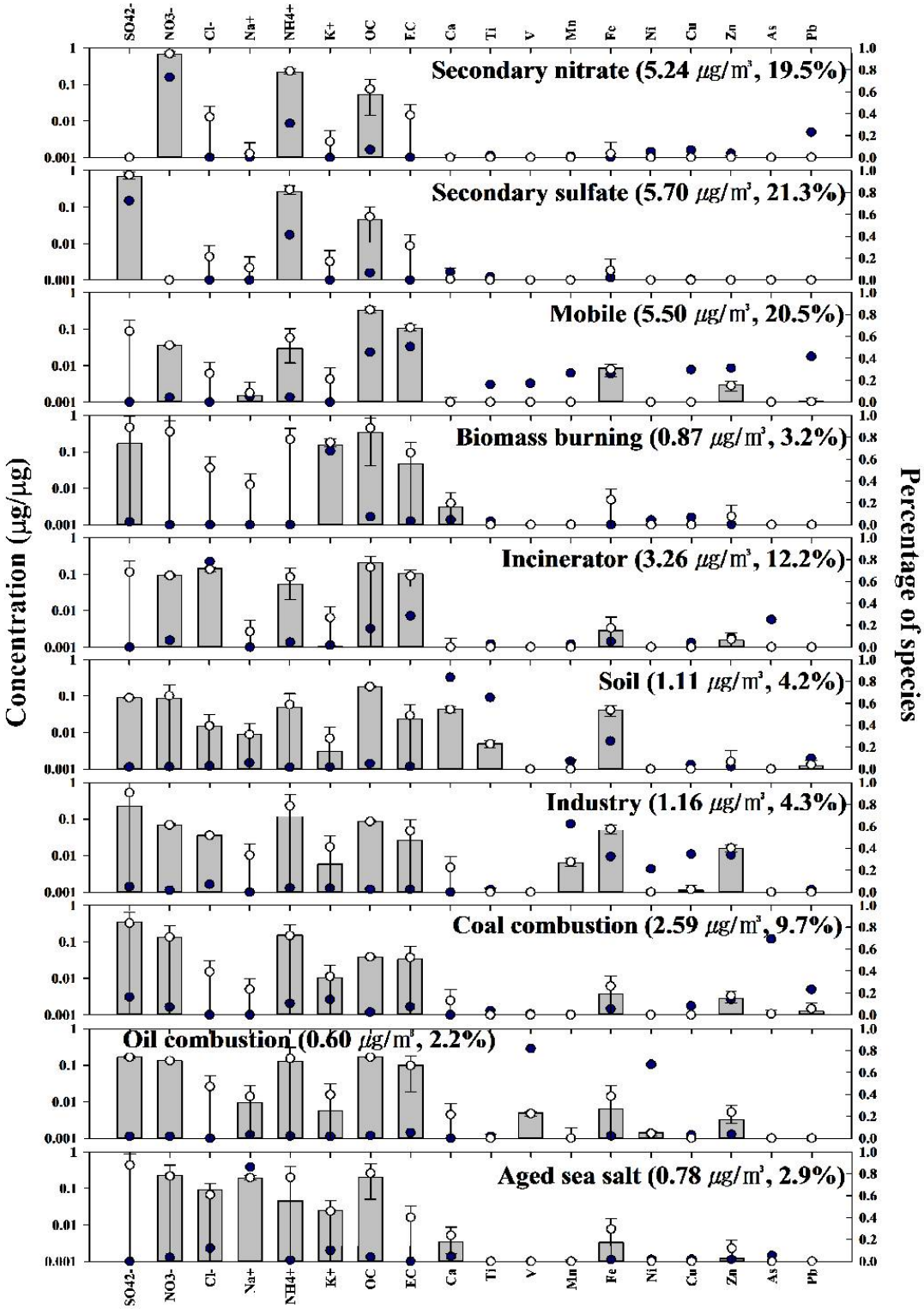


Figure 3-5 Source profiles of $PM_{2.5}$ in Gwangju during 2014–2018

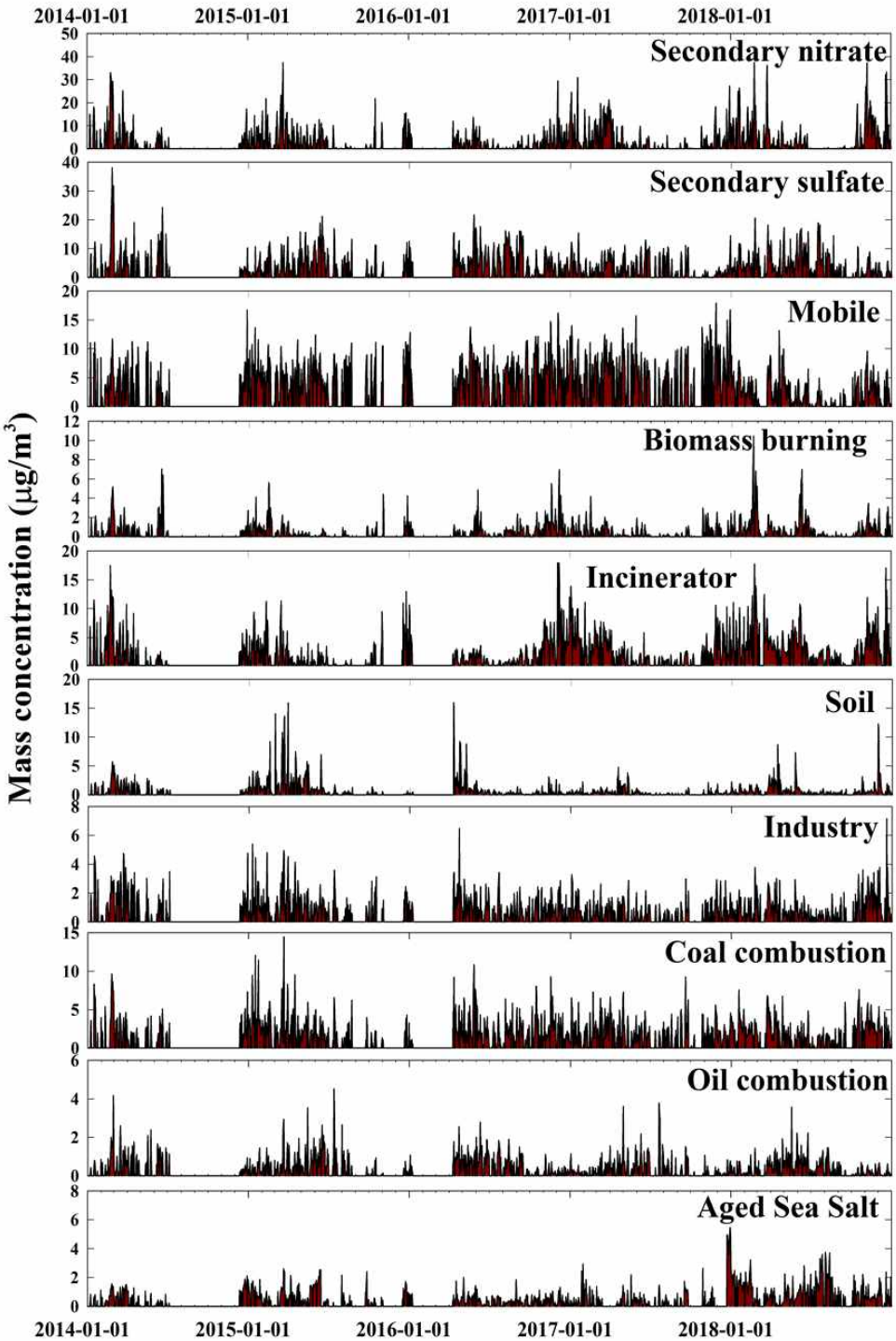


Figure 3-6 Daily source contribution plot in Gwangju during 2014–2018

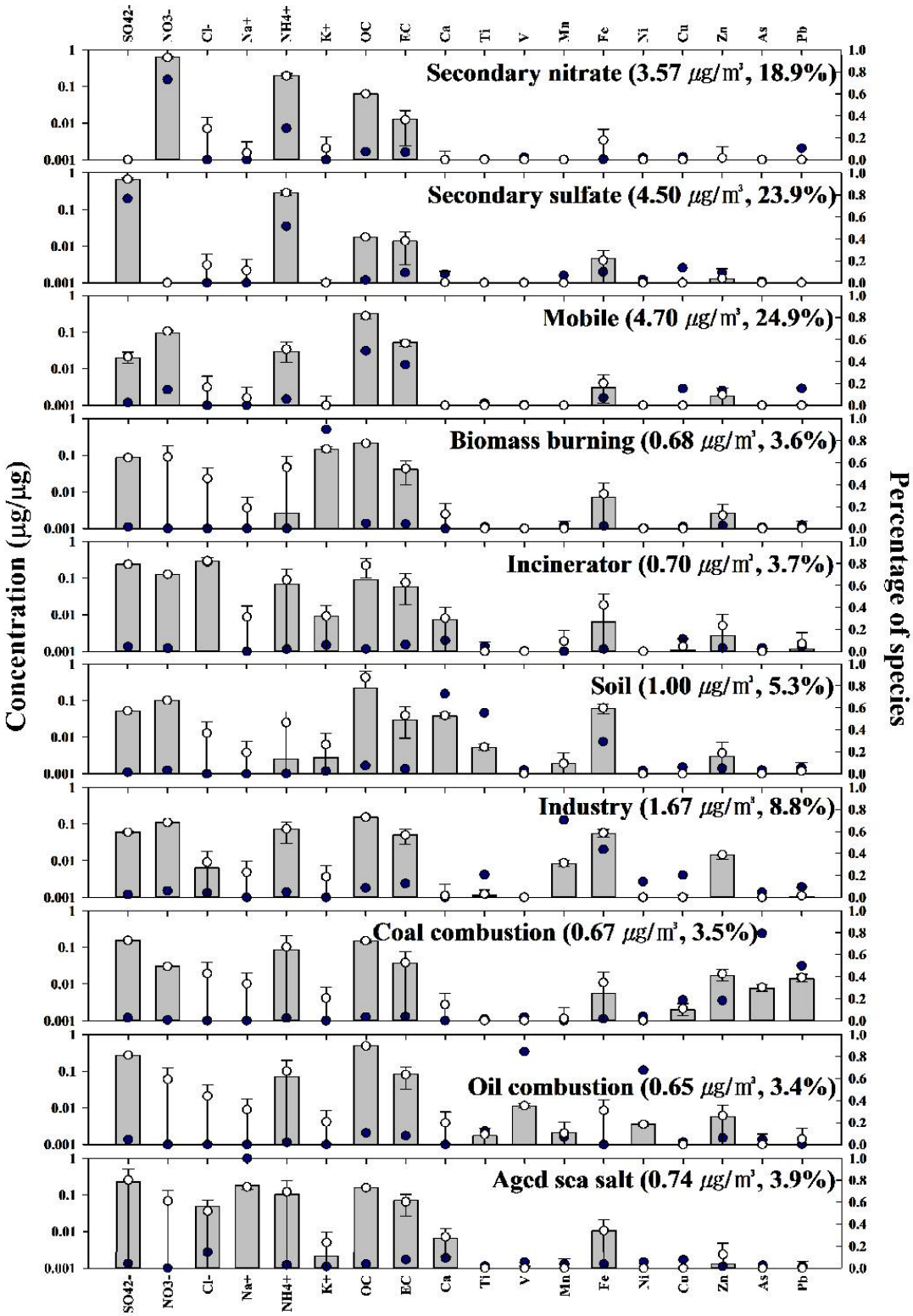


Figure 3-7 Source profiles of $PM_{2.5}$ in Ulsan during 2014–2018

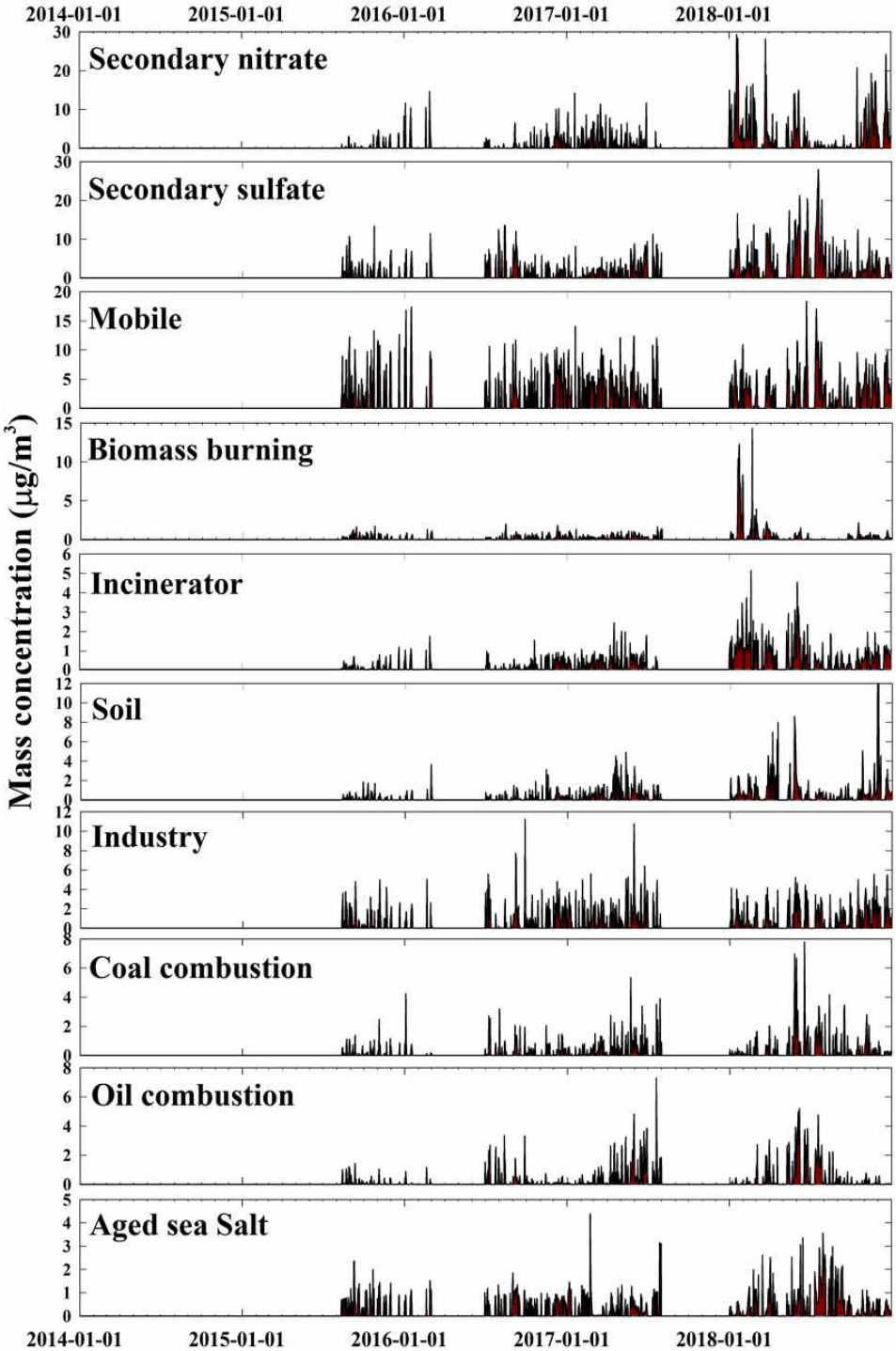


Figure 3-8 Daily source contribution plot in Ulsan during 2014–2018

3.2 Seasonal source contributions

Different from bigger particulate pollutants, $PM_{2.5}$ is mostly generated from secondary formation where multiple and chained reactions occur among gaseous precursors including SOx, NOx, NH_3, and VOCs in the atmosphere. There are various factors reported to influence the formational processes such as ambient temperature, relative humidity. In a similar context, previous studies have revealed seasonal differences in $PM_{2.5}$ composition, particularly between summer and winter seasons, which implies source contributions may also vary according to seasons (Bell et al., 2007; Xu et al., 2012).

Figure 3-9 shows the seasonal average contributions of each source in the four cities during the study period. It is notable that higher contributions of secondary nitrate during heating seasons (Nov-Mar) were observed, whereas secondary sulfate contributed more to $PM_{2.5}$ during non-heating seasons (Apr-Oct) in common. This indicates that $PM_{2.5}$ is highly dependent on meteorological conditions as well as the emission of gaseous precursors. However, secondary nitrate, secondary sulfate, and mobile sources together explained more than 50% of $PM_{2.5}$ mass regardless of seasons, which suggests they are major sources which should be controlled for reducing ambient $PM_{2.5}$ concentration in all cities.

With regard to the inter-site correlation of sources, source-specific characteristics were found depending on whether $PM_{2.5}$ from a source is locally produced or long-range transported. Considering the Pearson correlation coefficients for heating and non-heating seasons (Tables 3-1 and 3-2), it can be inferred that secondary nitrate, secondary sulfate, and soil sources influenced multiple sites through long-range transport. Secondary inorganic aerosol (SIA) including ammonium nitrate and ammonium sulfate can be transported with air masses after formed secondarily by a series of chemical reactions in the atmosphere among gaseous precursors (Voutsa et al., 2014). Soil source generally affects the whole country during the yellow sand events in spring season (Kim et al., 2007; Park et al., 2007), supported by the largest correlation coefficient during the non-heating season. Monthly variation in the standardized value of the source contributions (Figure 3-10, 3-11, and 3-12), showing similar trends throughout the year for the three sources, also supports the correlation among cities.

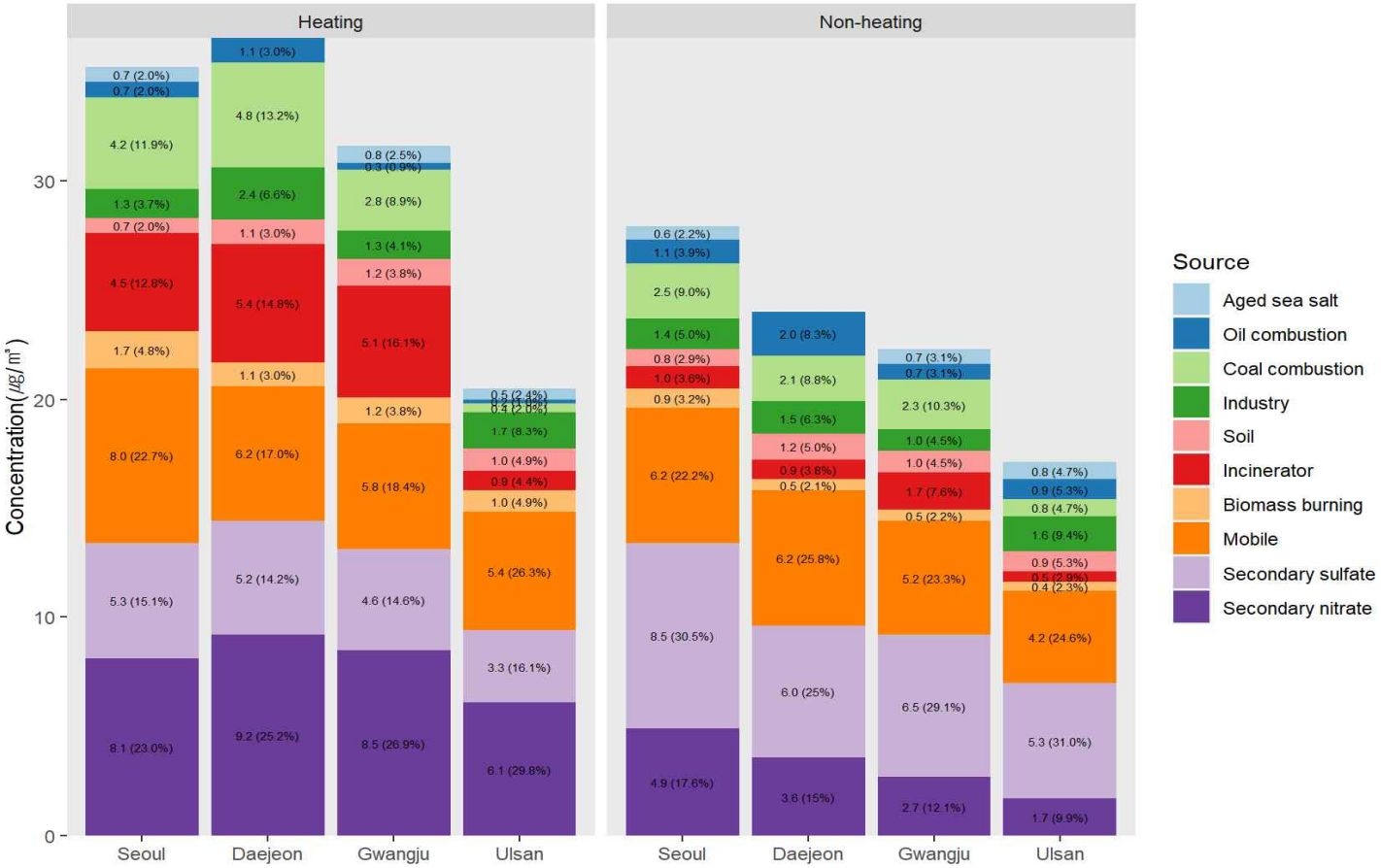


Figure 3-9 Source contributions of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during heating and non-heating seasons

Table 3-1 Inter-site correlation of the time series of the source contributions during heating seasons

Secondary nitrate	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.072	1.000		
Gwangju	0.489	-0.156	1.000	
Ulsan	0.223	-0.068	0.695	1.000

Secondary sulfate	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.048	1.000		
Gwangju	0.762	0.145	1.000	
Ulsan	0.640	0.086	0.854	1.000

Mobile	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.016	1.000		
Gwangju	0.394	-0.089	1.000	
Ulsan	0.291	-0.382	0.531	1.000

Biomass burning	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.220	1.000		
Gwangju	0.200	-0.001	1.000	
Ulsan	-0.231	0.149	0.094	1.000

Incinerator	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.409	1.000		
Gwangju	0.576	0.292	1.000	
Ulsan	0.536	0.388	0.596	1.000

Soil	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.346	1.000		
Gwangju	0.479	0.140	1.000	
Ulsan	0.239	0.105	0.867	1.000

Industry	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.280	1.000		
Gwangju	0.094	0.202	1.000	
Ulsan	0.612	-0.128	0.521	1.000

Coal combustion	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.331	1.000		
Gwangju	0.516	-0.488	1.000	
Ulsan	0.359	0.100	-0.162	1.000

Oil combustion	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.239	1.000		
Gwangju	0.542	0.093	1.000	
Ulsan	0.415	-0.054	0.045	1.000

Table 3-2 Inter-site correlation of the time series of the source contributions during non-heating seasons

Secondary nitrate	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.163	1.000		
Gwangju	0.685	-0.068	1.000	
Ulsan	0.215	0.118	0.656	1.000

Secondary sulfate	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.386	1.000		
Gwangju	0.637	0.187	1.000	
Ulsan	0.382	0.001	0.570	1.000

Mobile	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.541	1.000		
Gwangju	-0.027	-0.128	1.000	
Ulsan	0.130	-0.018	0.361	1.000

Biomass burning	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.181	1.000		
Gwangju	0.088	0.072	1.000	
Ulsan	0.557	0.004	0.515	1.000

Incinerator	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.260	1.000		
Gwangju	-0.155	0.428	1.000	
Ulsan	0.056	0.395	0.686	1.000

Soil	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.513	1.000		
Gwangju	0.877	0.592	1.000	
Ulsan	0.885	0.560	0.921	1.000

Industry	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.258	1.000		
Gwangju	0.440	-0.129	1.000	
Ulsan	0.642	0.012	0.470	1.000

Coal combustion	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	-0.084	1.000		
Gwangju	0.503	0.060	1.000	
Ulsan	-0.185	-0.012	-0.080	1.000

Oil combustion	Seoul	Daejeon	Gwangju	Ulsan
Seoul	1.000			
Daejeon	0.012	1.000		
Gwangju	0.469	-0.388	1.000	
Ulsan	0.237	0.264	0.130	1.000

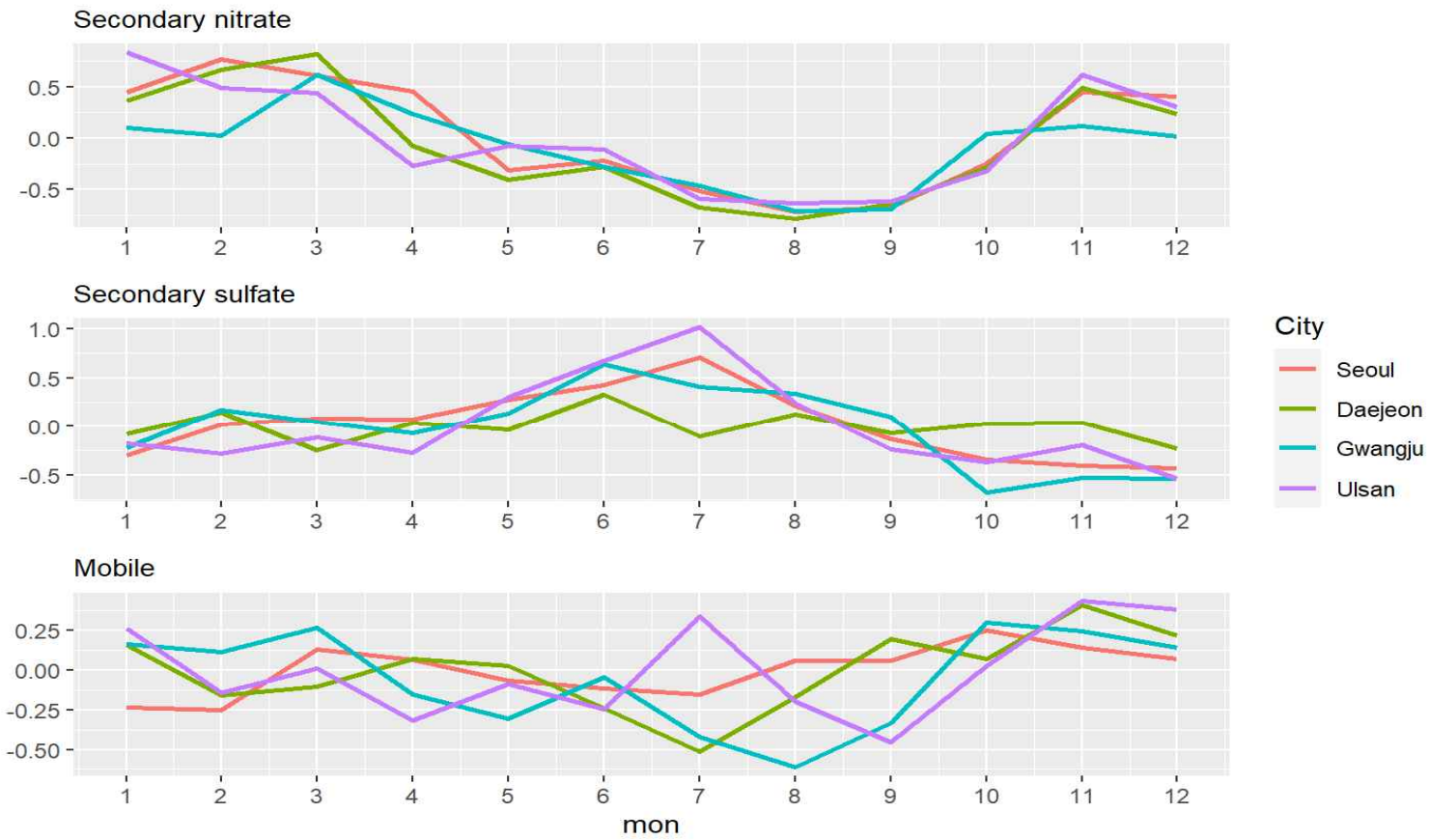


Figure 3-10 Monthly variation in the standardized value of the source contributions for secondary nitrate, secondary sulfate, and mobile sources

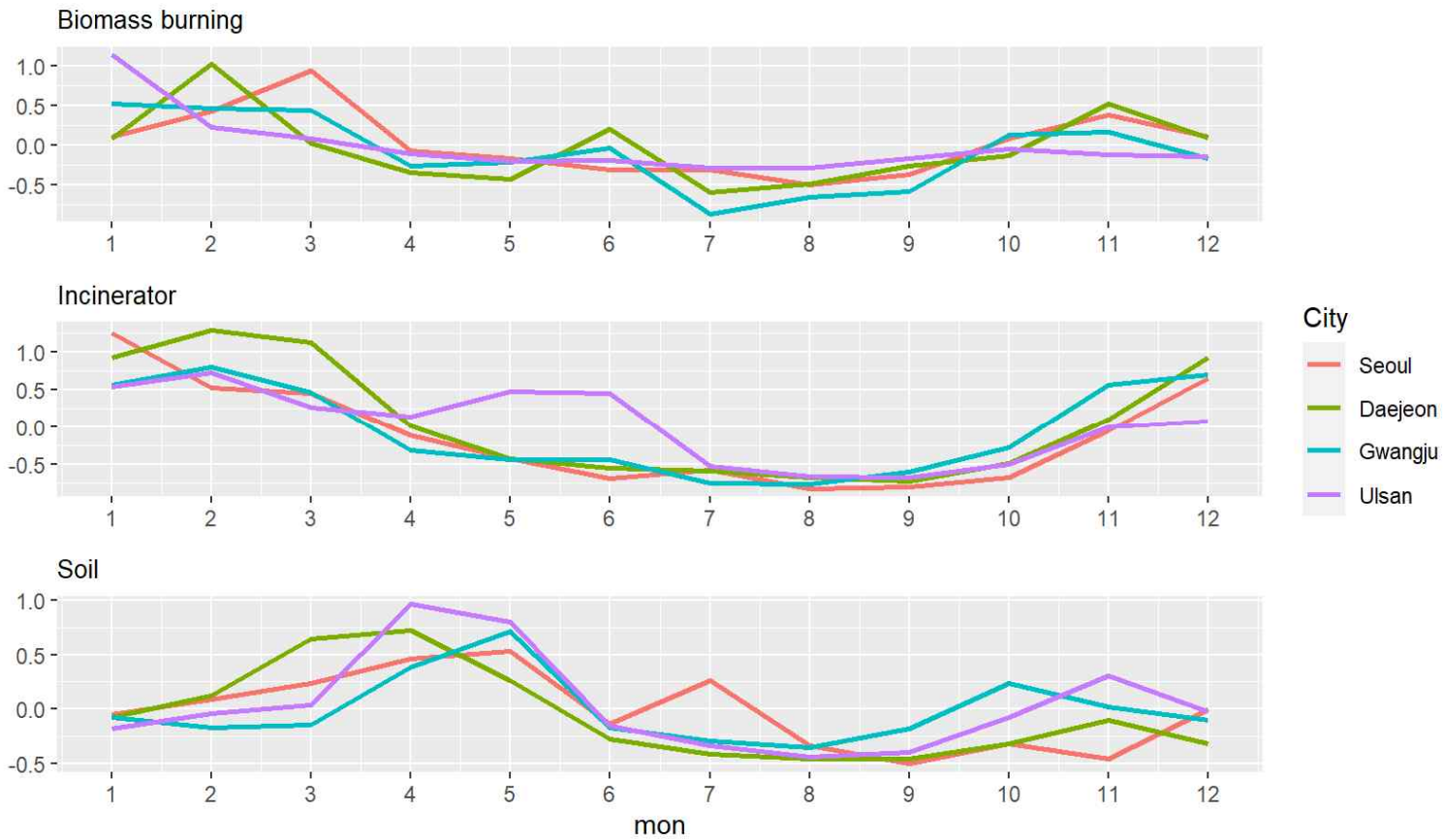


Figure 3-11 Monthly variation in the standardized value of the source contributions for biomass burning, incinerator, and soil sources

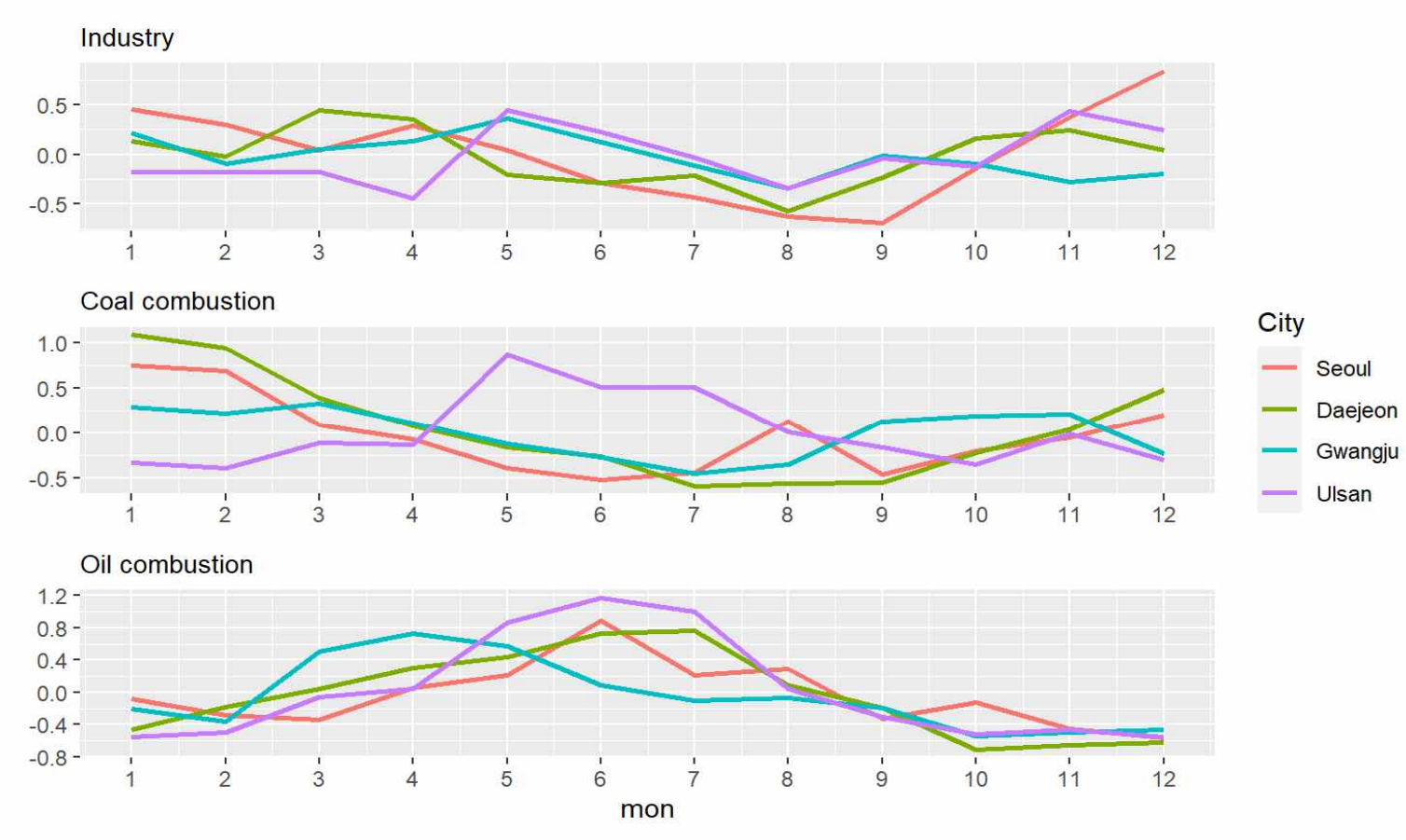


Figure 3-12 Monthly variation in the standardized value of the source contributions for industry, coal combustion, and oil combustion sources

3.3 Possible source locations

Secondary nitrate source is mainly affected by the sources with thermal processes including gasoline/diesel vehicles, coal combustion, oil combustion and incineration because of NOx formation mechanism. Among various types of NOx based on formational mechanisms, thermal NOx is known to have the largest fraction which is mainly produced by the free radical chemistry. The J-PSCF map for Seoul and Gwangju shows the potential source location of long-range transport is the cluster of Hebei, Shandong, Jiangsu and Anhui provinces. Hebei, Shandong, and Jiangsu provinces were reported as the largest NOx emitting provinces (Mijling et al., 2013). Especially, Jiangsu province is one of the provinces with the largest national share of coal power plants in terms of total capacity in China (Yuan et al., 2017). The J-PSCF map for Gwangju and Ulsan additionally suggests Shanxi is another potential source location as well as the cluster of Hebei and Shandong. Shanxi is one of the main electricity export provinces (Wang et al., 2020), implying there are huge NOx emissions that can affects other areas (Zhang et al., 2015).

The CPF results for secondary nitrate source show the possible areas of regional transport and local effects in the four cities. In Seoul, sources on southwest part of the site where

several huge coal power plants and industrial complexes exist affected secondary nitrate. The CPF plot for Daejeon indicates west winds showed high contributions for secondary nitrate. In particular, there is a 530 MW LNG-fired power plant on the northwest part of the Daejeon site. In Gwangju, it seems that regional transportation from several coal-fired power plants on the southern coast of the Korea influenced the source. The CPF results for Ulsan suggest prevailing winds from the south part of the site in which industrial complexes located showed high contributions.

Secondary sulfate source, also subject to long-range transport, is affected more directly by the combustion of sulfur contained in the fuel. The J-PSCF map for the source for Seoul and Gwangju (Figure 3-13), Gwangju and Ulsan (Figure 3-14) shows two clusters of potential source locations in China, the Anhui and Jiangsu provinces and the Shandong province. Anhui, Jiangju, and Shandong provinces were included in the top five provinces with the heaviest Se emissions in China in the mid-2000s, obvious markers of coal combustion (Tian et al., 2010). Furthermore, they were identified as the potential source regions for SO_4^{2-} and NO_3^-, which implies a high probability of potential source regions of secondary sulfate (Gao et al., 2011).

The CPF results for Seoul suggest possible source areas

are on the southwest part of the site where huge coal-fired power stations exist. In Daejeon, prevailing winds with low wind speed from east part of the site where Daejeon Industrial Complexes I and II exist showed high contributions to secondary sulfate. The CPF results for Gwangju show that secondary sulfate was locally affected by the prevailing winds from south part of the city. It seems like sulfur oxides from marine vessels in south coast had impacts on secondary sulfate in Gwangju under southerly wind condition. Marine oil is well-known for high sulfur contents, indicating coastal vessel activities can impose anthropogenic SOx emission (McLaren et al., 2012; Zetterdahl et al., 2016). In Ulsan, prevailing winds from the south direction of the site showed high contributions to the source.

Regarding possible source areas of biomass burning source, long-range transportation was investigated based on the PSCF maps as well as the estimation of regional transport and local emission using CPF results. The PSCF maps for Seoul, Daejeon, Gwangju, and Ulsan indicate there are two clusters of possible source areas, the Hebei and Shandong provinces and the Anhui and Jiangsu provinces. Several previous studies also revealed the high emissions from agricultural biomass burning originated from these provinces (Qiu et al., 2016; Xue et al.,

2014; Zhu et al., 2019).

The CPF plot of biomass burning source for Seoul indicates southwestern winds influenced the source. It seems that large agricultural areas near Seoul, Gimpo Plain, had impacts on biomass burning source. The CPF results for the other cities also indicate the source was locally affected by their agricultural neighborhood.

Mobile source is mostly influenced by local traffic rather than long-range transport. Thus, it more reasonable to use CPF results for understanding potential source areas. The CPF plot for Seoul shows that high contributions of the source originated from south part where six-lane Naebu Expressway exists as well as considerable contribution around the site by the traffic in downtown. The CPF results for Daejeon show the winds from three directions mostly contributed to mobile source. It seems that mobile source in Daejeon might have been affected by the Honam Expressway and Gyeongbu Expressway passing through the left and the right side of the city. In Gwangju, high contributions originated from the central and southwest part where Honam Expressway is closely located. The CPF results for Ulsan suggest that mobile source was mostly influenced by the winds with low speed from the south where six-lane roadways are located.

Incinerator is directly related to the combustion of municipal solid waste (MSW) or industrial waste containing a wide range of plastic products. In Seoul, there are incinerators located on the southwest from the site, consistent with the CPF results. Prevailing winds from the southwest contributed considerably to the source. In Daejeon, the CPF results show that possible source areas are located in the easterly area where Daejeon Industrial Complexes I and II exist. The CPF results for Gwangju show that high contributions occurred in the vicinity of the site. This might be resulted from the effects of a incinerator in the central part of the city which has been operated until the end of 2016. The CPF results for Ulsan indicate incinerator source was affected by the winds from three directions.

Soil source in South Korea is mainly impacted by both soil particles from long-range transport during the spring seasons from the northern part of China and Mongolia and resuspended road dust from local sources. Asian dust storm, also called yellow sand, generally occurs during spring season of the year and has been reported to contribute significantly to $PM_{2.5}$ in South Korea. Most of the dust particles originate from Gobi desert, Inner Mongolia, Gansu and Shaanxi provinces in China and Mongolia (Kang and Kim, 2014; Choi et al., 2012;

Wang et al., 2000). J-PSCF map for Seoul and Gwangju shows the northern part of Shaanxi is the cluster of possible source areas of long-range transport (Rost, 2001), also found in the results for Gwangju and Ulsan.

Industry source is highly subject to local effects by primary emission from sources. The CPF results for industry source agree well with the possible source areas in each city. Potential source areas for Seoul seem to be Sihwa and Banwol industrial complexes located in the southwest part of the site. Daejeon industrial complex I and II located on the east part from site and Hanam industrial area on the west part of the Gwangju site are thought to be source areas for Daejeon and Gwangju, respectively considering the directional apportionment patterns. On the south part of Ulsan site, there are huge industrial areas, Ulsan/Mipo and Onsan national industrial complexes. The CPF plot for Ulsan is consistent with the actual locations of the industrial complexes.

Coal combustion source is directly influenced by the several sources related to usage of coal for various purposes including generation and domestic heating. The CPF results for Seoul indicate significant contributions by regional transport with the winds speed of approximately 6 m/sec originated from the southwest where several huge coal power plants exist. In

Daejeon, the prevailing winds from the northwest showed high contributions where coal power plants on the west coastal area exist. The CPF results for Ulsan show that the high possibility that this source was affected by winds from the industrial area.

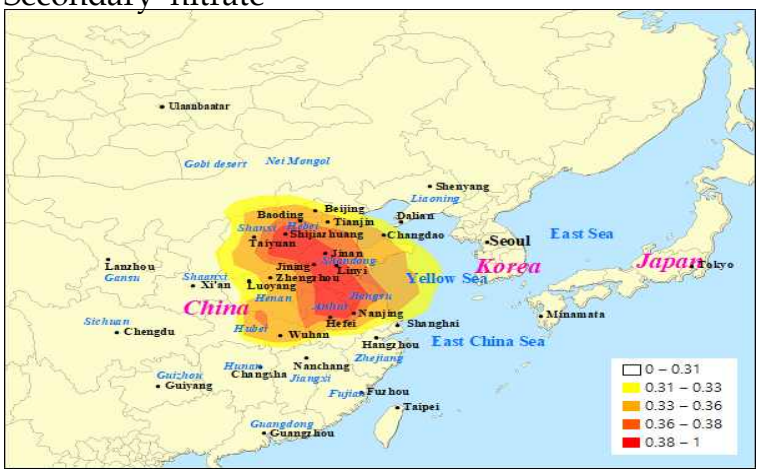
Similar to coal combustion, oil combustion source is affected by the combustion of fuel. Heavy oil, sulfur-rich fuel, is still widely used for diverse purposes (e.g. industrial boilers, marine transport). The CPF results for Seoul imply that high contributions derived from west and southwest of the site where Incheon Port, the second largest one in South Korea, exist. The winds from southeast with 2-6 m/sec speed showed high contributions in Gwangju, which imply regional transport from petrochemical-industrialized areas affected the source as well as marine activities. The CPF results for Ulsan also reflected the industrial characteristics of the city.

The CPF results for aged sea salt source for Seoul, Gwangju, and Ulsan agree well with the directional apportionment patterns. High contributions of aged sea salt were from the direction of the Yellow sea for Seoul and Gwangju and from the East Sea for Ulsan.

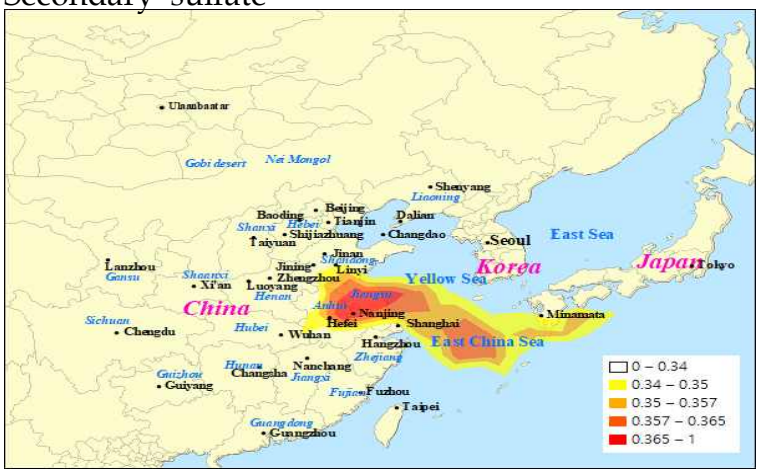
Table 3-3 Criterion values for PSCF model for Seoul, Daejeon, Gwangju, and Ulsan

Source	Criterion Value	Unit	Seoul	Daejeon	Gwangju	Ulsan
Secondary nitrate	75th percentile	$\mu g/m^3$	9.55	8.34	7.81	4.68
Secondary sulfate		$\mu g/m^3$	9.18	8.43	8.13	6.22
Biomass burning		$\mu g/m^3$	2.00	0.96	1.13	0.71
Soil	90th percentile	$\mu g/m^3$	1.50	2.90	2.61	2.21

Secondary nitrate



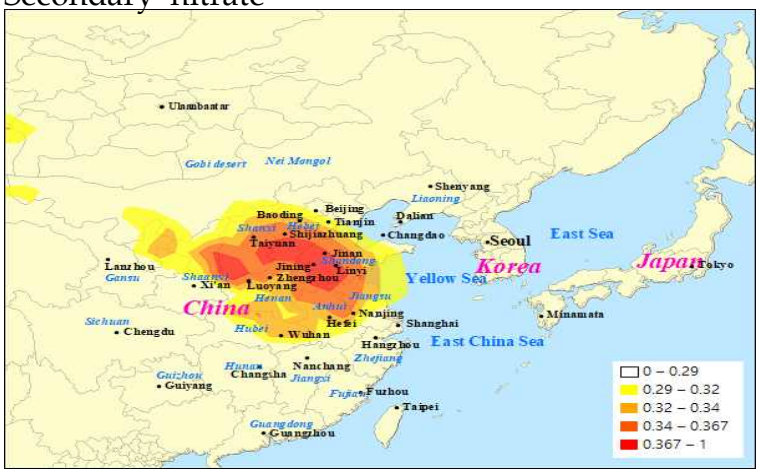
Secondary sulfate



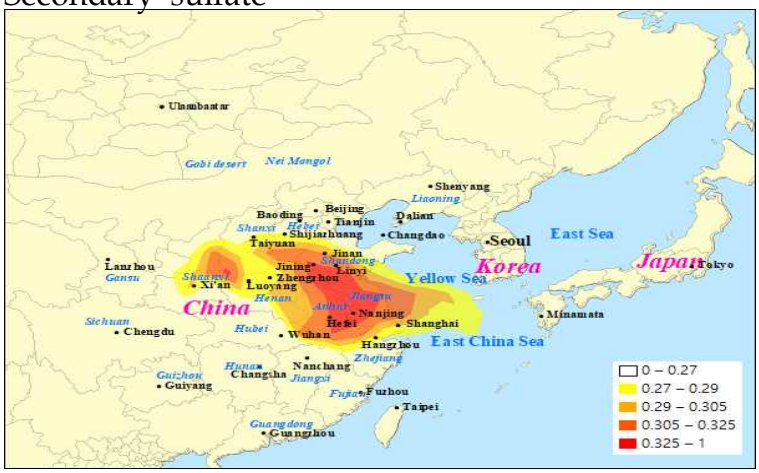
Soil

Figure 3-13 J-PSCF results for secondary nitrate, secondary sulfate, and soil sources for Seoul and Gwangju

Secondary nitrate



Secondary sulfate



Soil

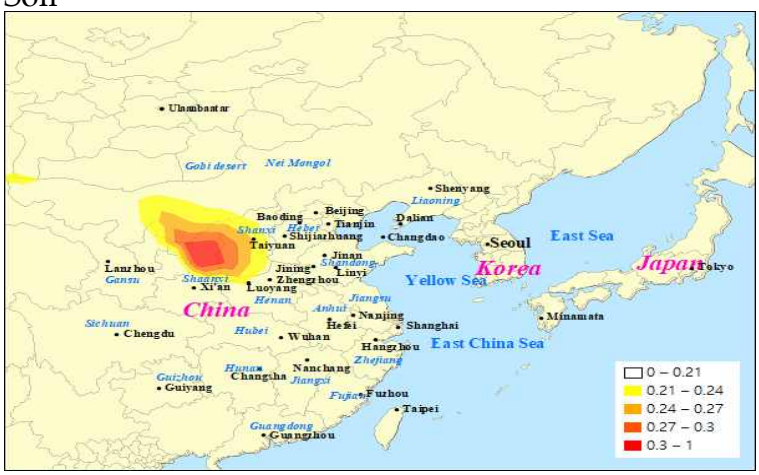
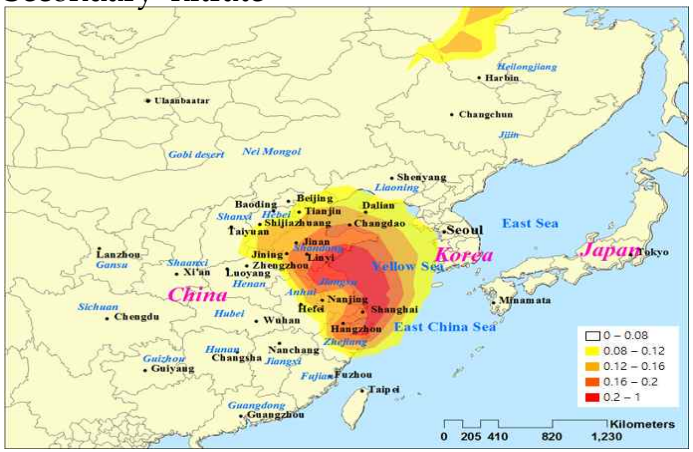
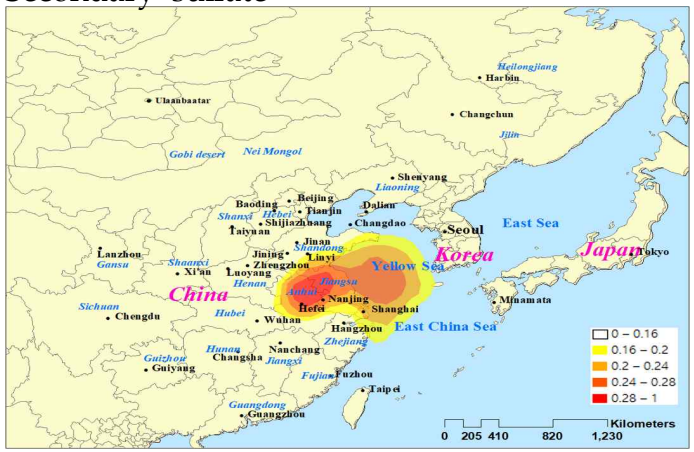


Figure 3-14 J-PSCF results for secondary nitrate, secondary sulfate, and soil sources for Gwangju and Ulsan

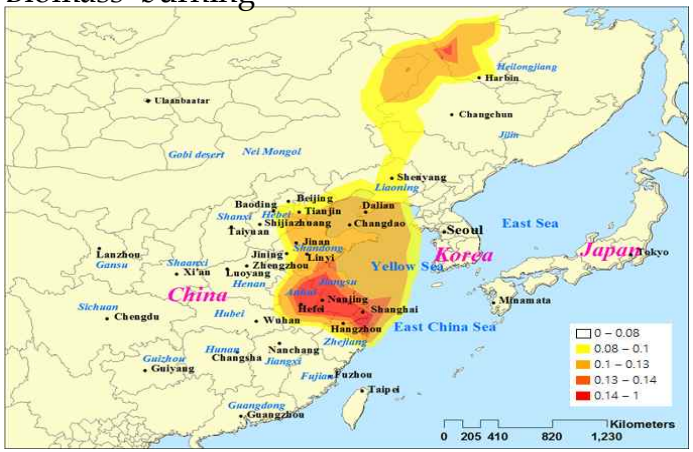
Secondary nitrate



Secondary sulfate



Biomass burning



Soil

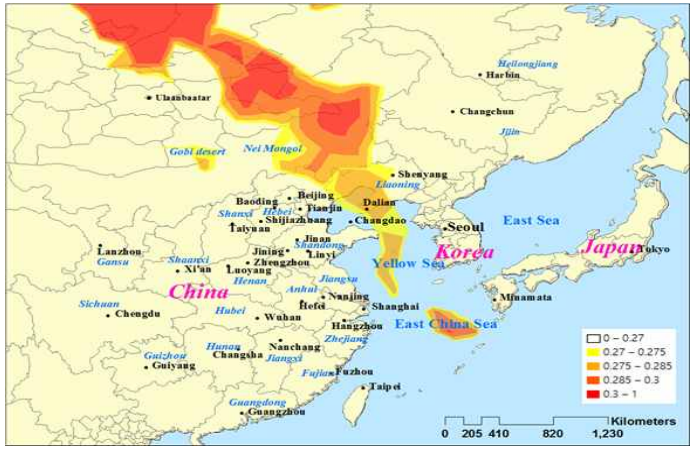


Figure 3-15 PSCF results for secondary nitrate, secondary sulfate, biomass burning, and soil sources for Seoul

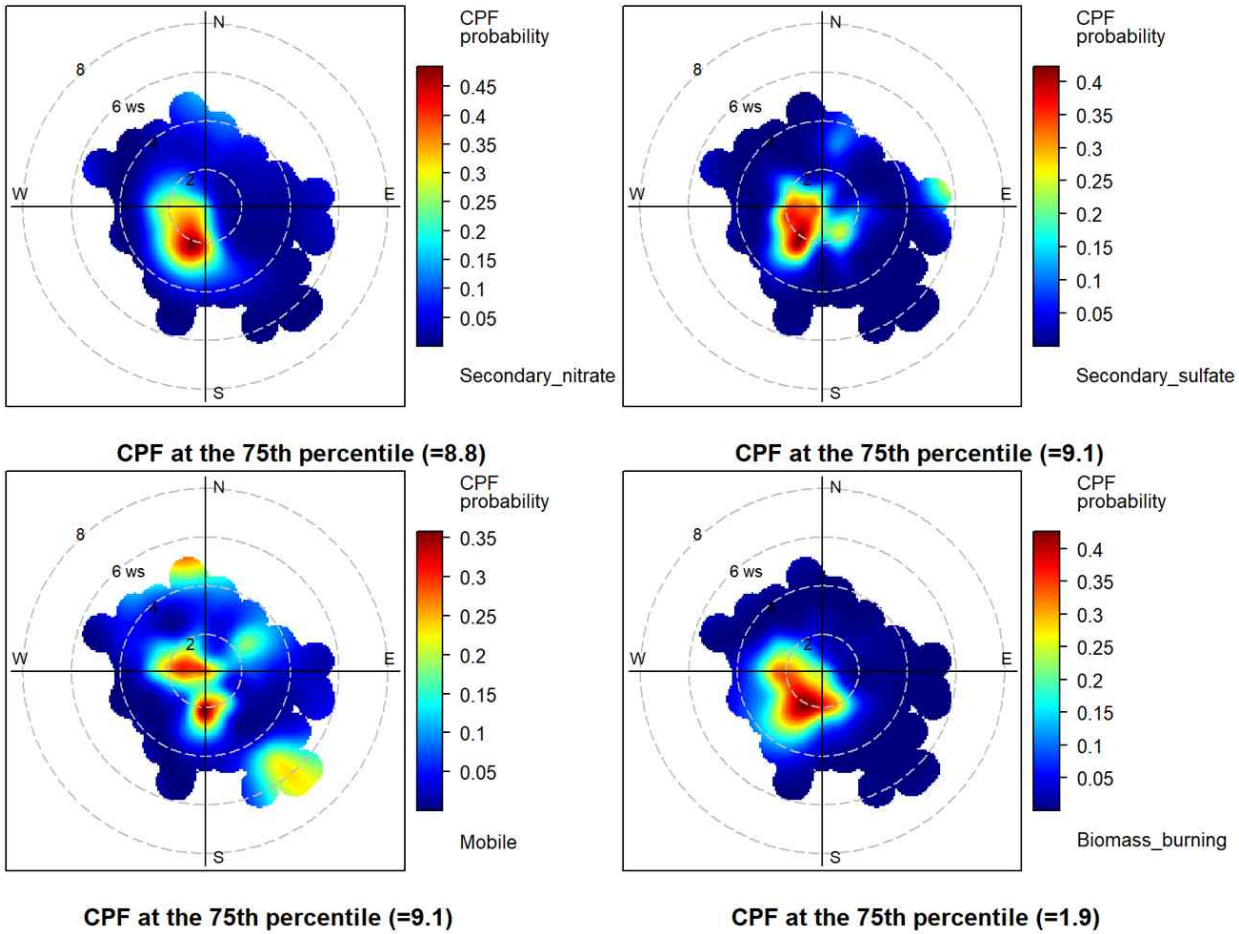


Figure 3-16 CPF results for secondary nitrate, secondary sulfate, mobile, and biomass burning sources for Seoul

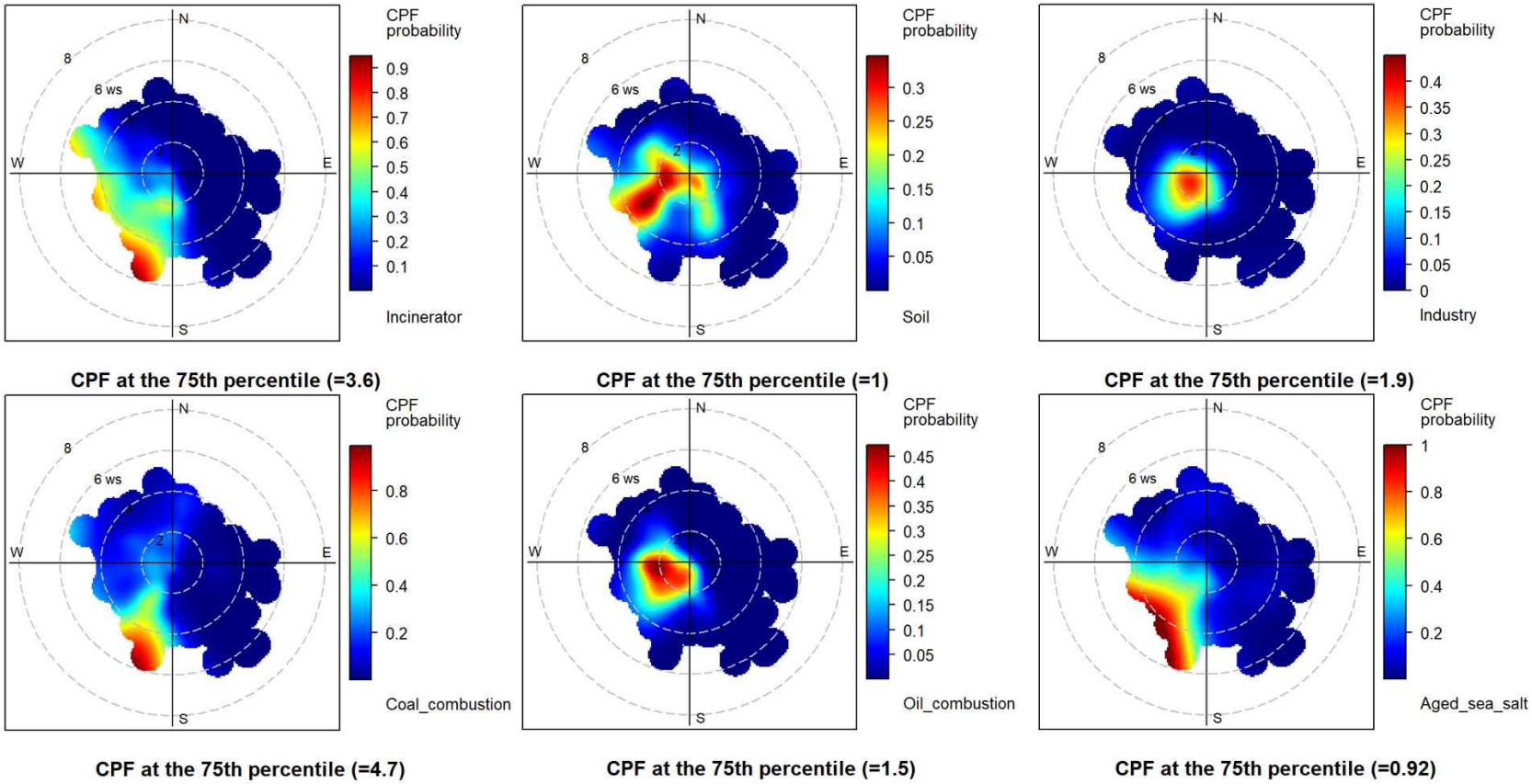
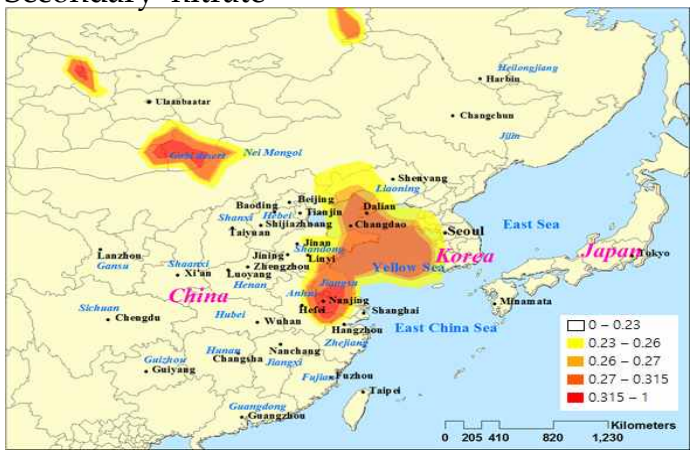
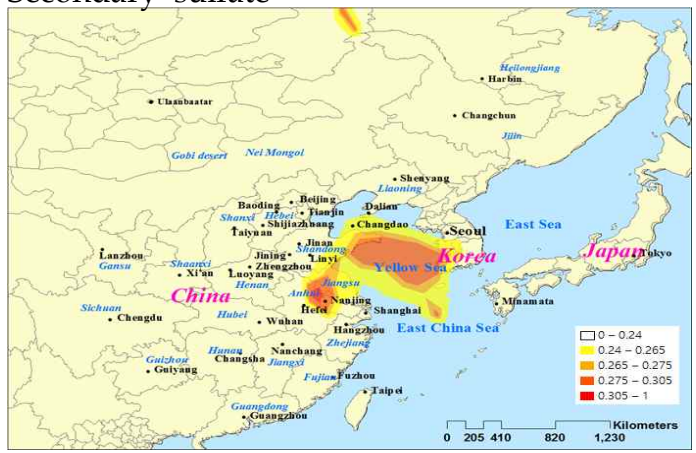


Figure 3-17 CPF results for incinerator, soil, industry, coal combustion, oil combustion, and aged sea salt sources for Seoul

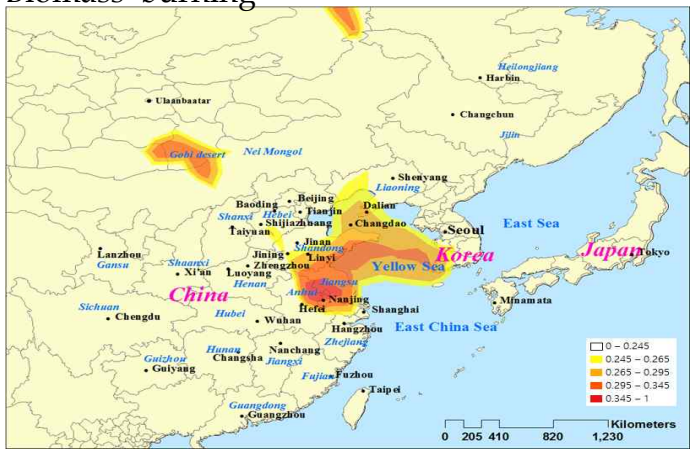
Secondary nitrate



Secondary sulfate



Biomass burning



Soil

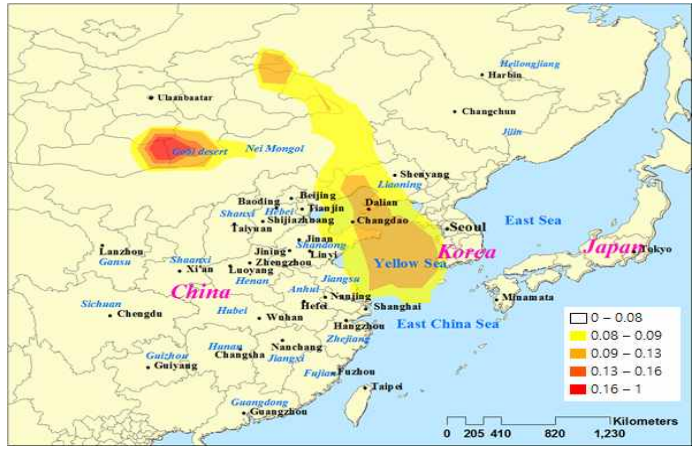


Figure 3-18 PSCF results for secondary nitrate, secondary sulfate, biomass burning, and soil sources for Daejeon

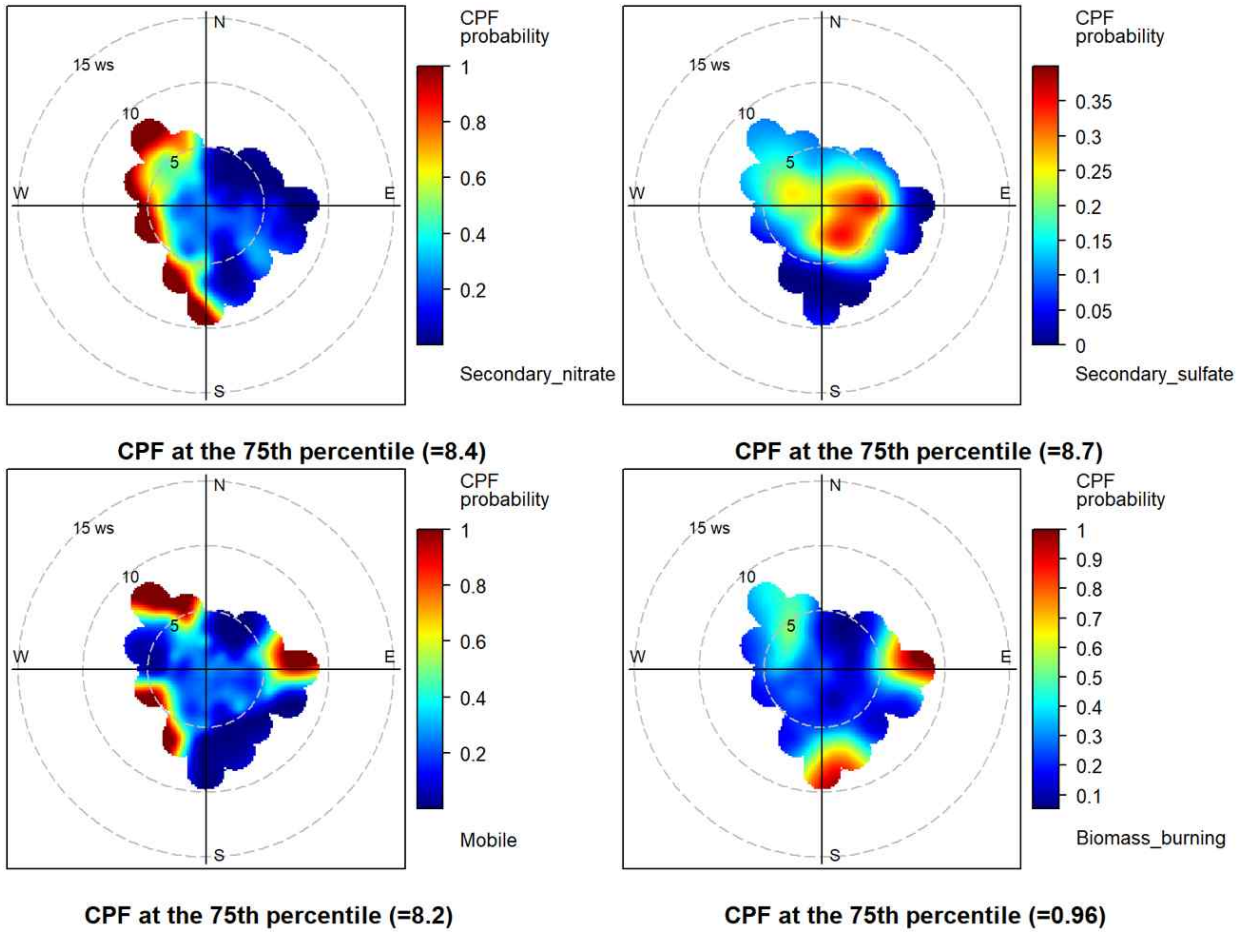


Figure 3-19 CPF results for secondary nitrate, secondary sulfate, mobile, and biomass burning sources for Daejeon

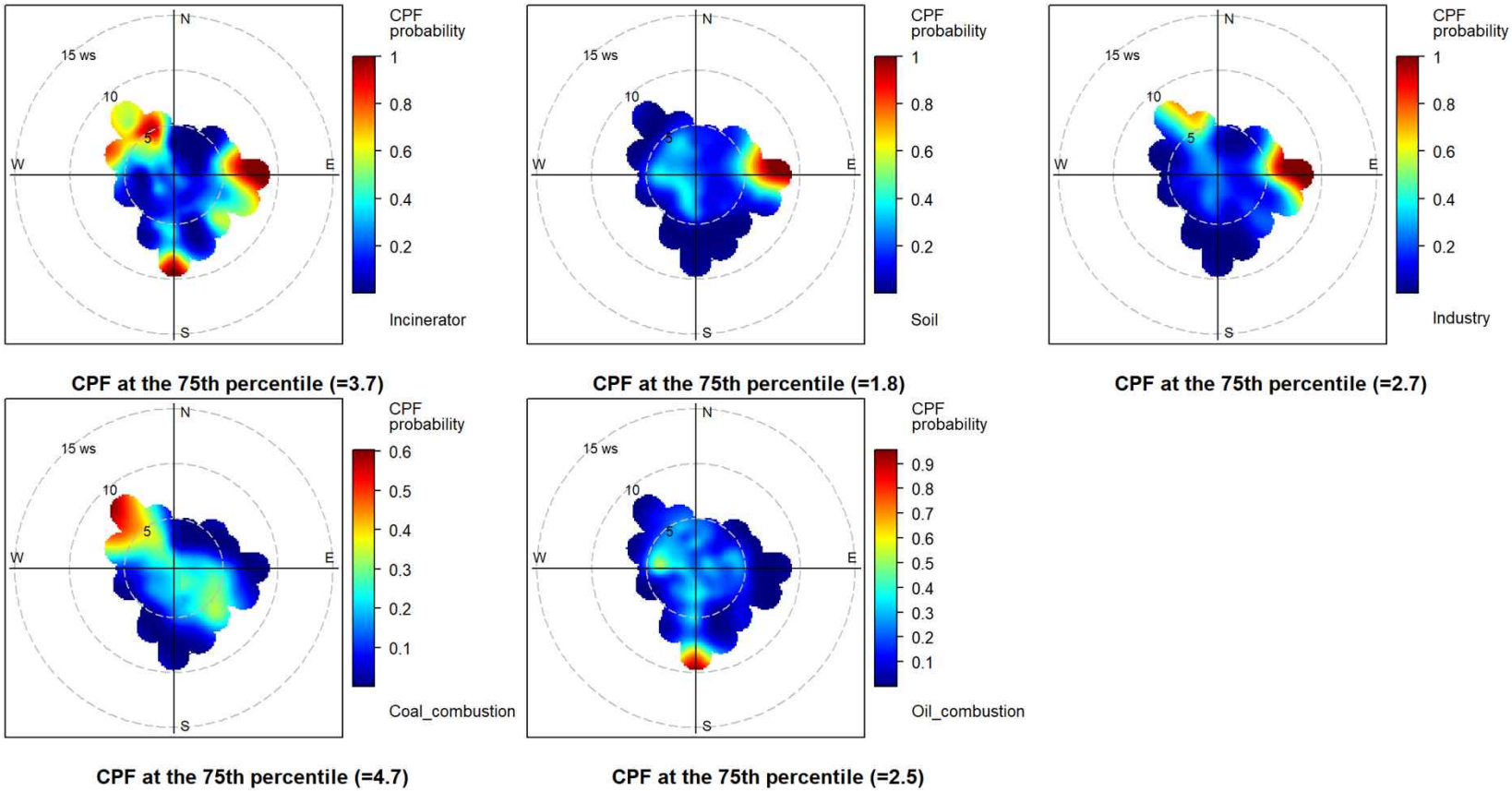
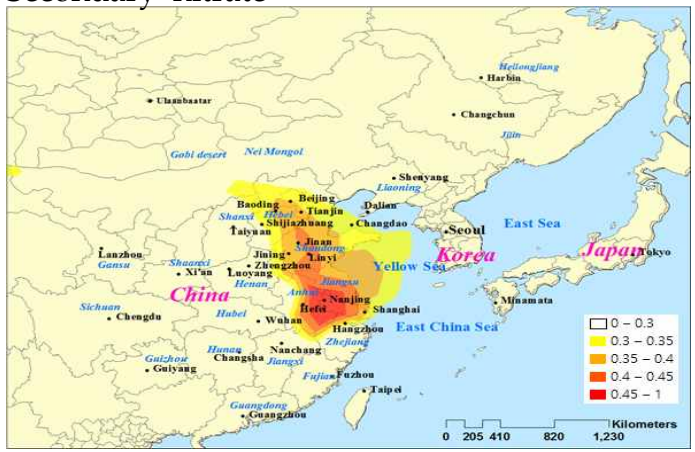


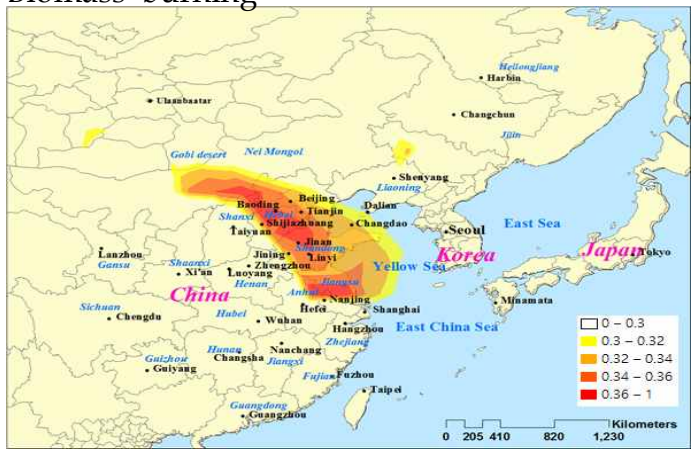
Figure 3-20 CPF results for incinerator, soil, industry, coal combustion, and oil combustion sources for Daejeon

Secondary nitrate



Secondary sulfate

Biomass burning



Soil

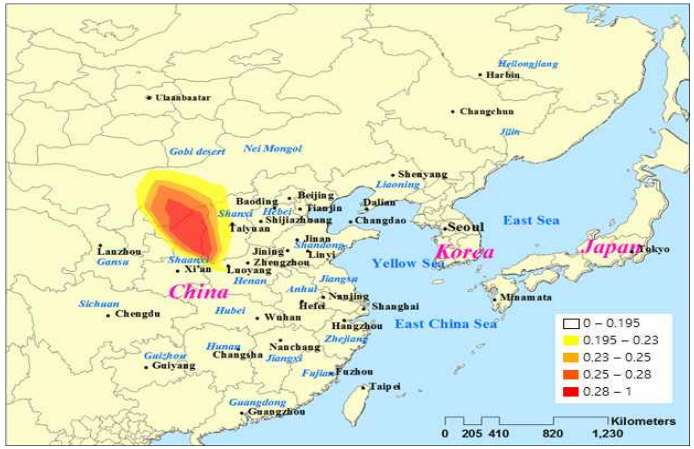


Figure 3-21 PSCF results for secondary nitrate, secondary sulfate, biomass burning, and soil sources for Gwangju

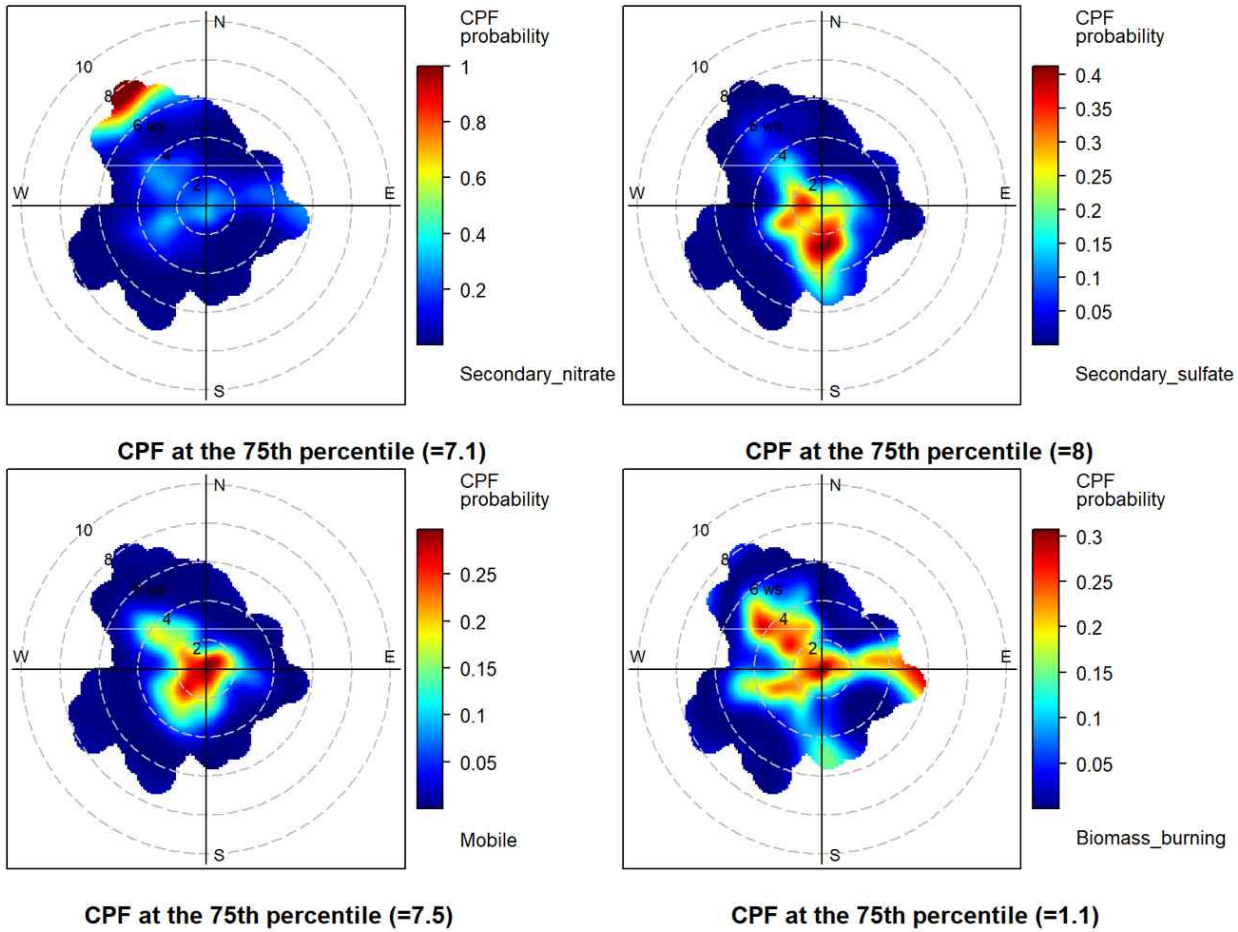


Figure 3-22 CPF results for secondary nitrate, secondary sulfate, mobile, and biomass burning sources for Gwangju

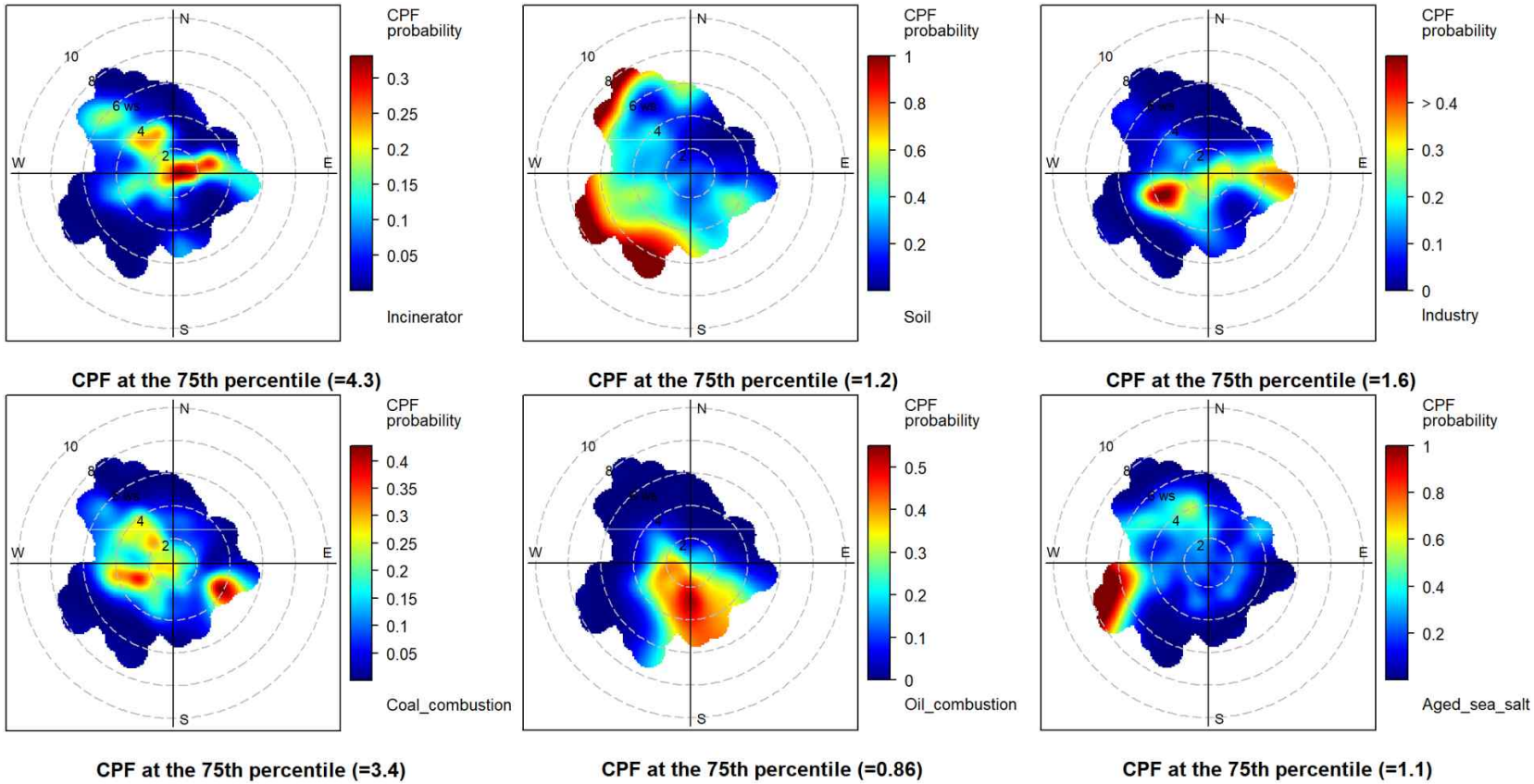
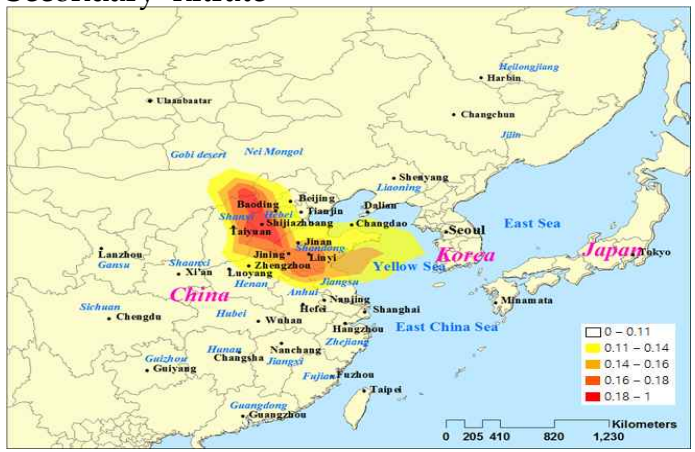
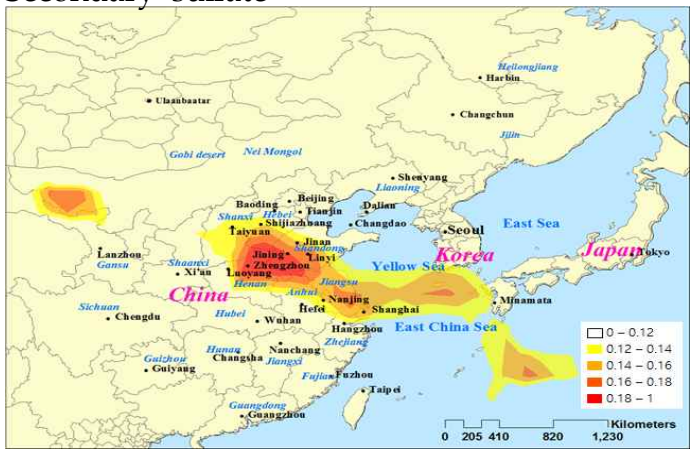


Figure 3-23 CPF results for incinerator, soil, industry, coal combustion, oil combustion, and aged sea salt sources for Gwangju

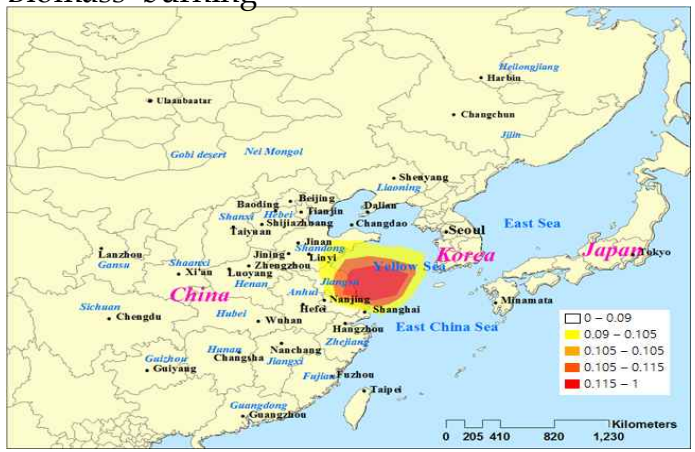
Secondary nitrate



Secondary sulfate



Biomass burning



Soil

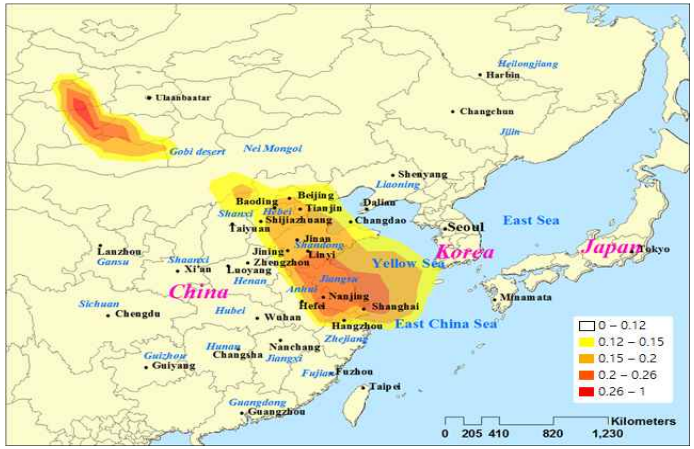


Figure 3-24 PSCF results for secondary nitrate, secondary sulfate, biomass burning, and soil sources for Ulsan

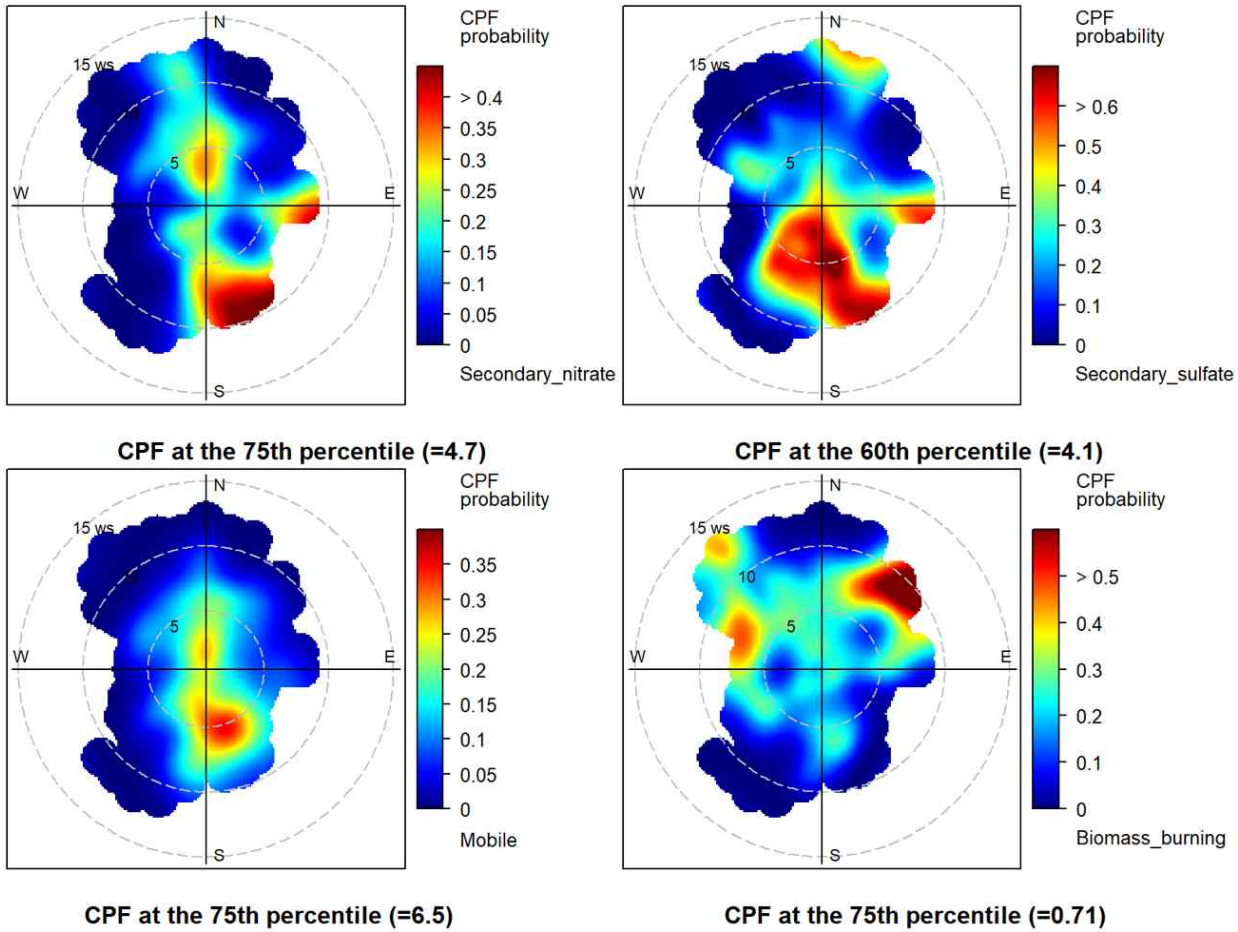


Figure 3-25 CPF results for secondary nitrate, secondary sulfate, mobile, and biomass burning sources for Ulsan

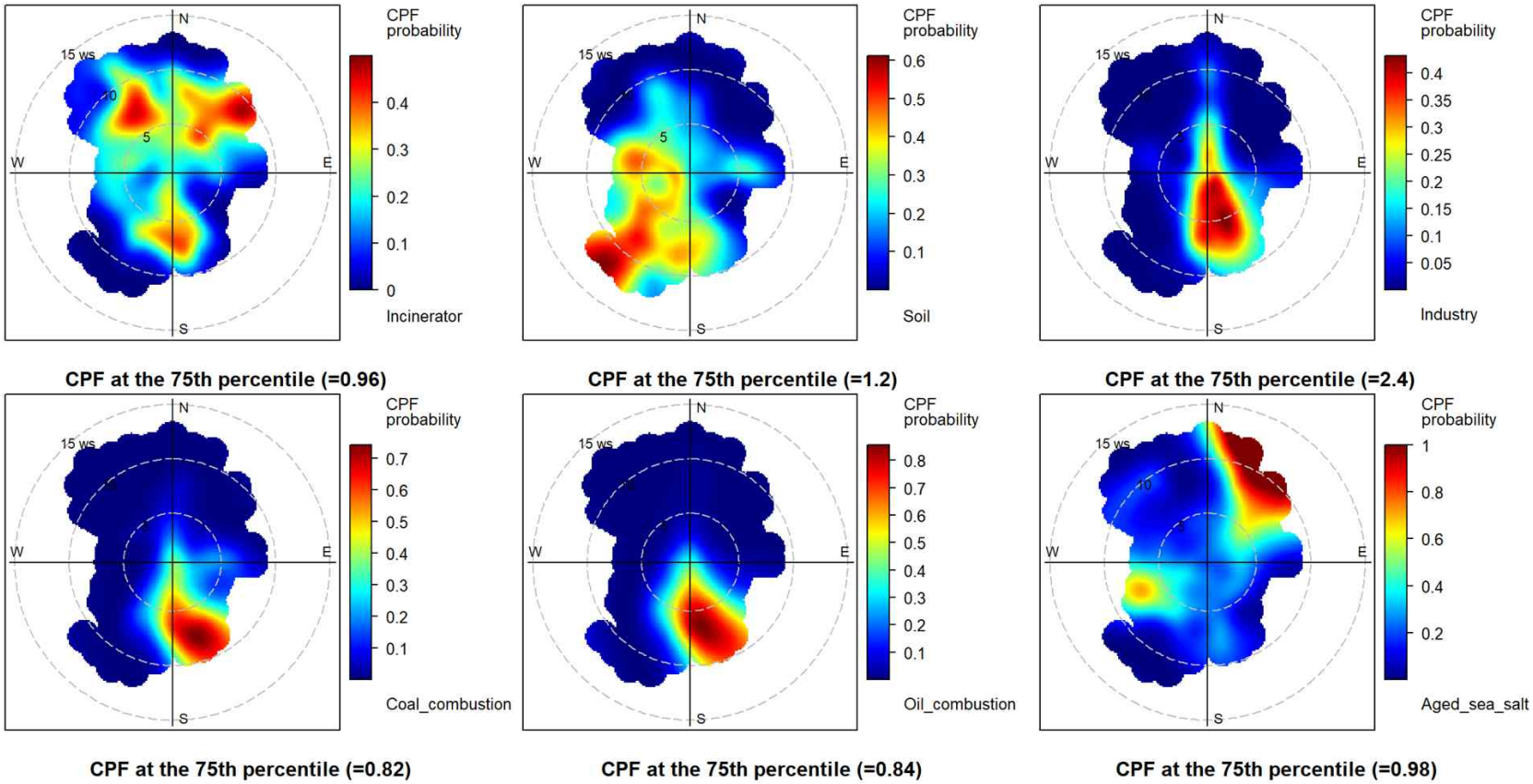


Figure 3-26 CPF results for incinerator, soil, industry, coal combustion, oil combustion, and aged sea salt sources for Ulsan

4. Conclusions

Source apportionment of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018 was conducted to identify the sources affecting to $PM_{2.5}$ in each city and to estimated their contributions. In addition, error estimation was conducted through displacement method for acquiring uncertainty estimates for each factor of the solutions.

Ten identical factors were resolved for Seoul, Gwangju and Ulsan in common while nine-factor solution was drawn for Daejeon. The absence of aged sea salt source in Daejeon seem to have derived from its geographical location. Secondary nitrate, secondary sulfate, and mobile sources accounted for the majority of $PM_{2.5}$ mass in all cities, which suggests secondary formation is a dominant factor in $PM_{2.5}$ formation. The contributions of the other sources were different across the cities, which might be a reasonable reason for the heterogeneity in $PM_{2.5}$ composition.

Possible source locations were investigated based on the results of PSCF and CPF. The clusters of possible source areas for secondary nitrate and secondary sulfate were mainly located in Hebei, Shandong, Jiangsu, and Anhui provinces where larger emissions of gaseous air pollutants were identified from previous studies. The CPF results suggest that the directions of

possible source locations were highly reasonable considering the locations of relevant sources around the study cities.

Overall, the findings of the present study show that both $PM_{2.5}$ chemical compositions and source contributions were spatially heterogeneous. This indicates region-specific policies should be made to control $PM_{2.5}$ pollution more efficiently.

References

Adachi, K. and Buseck, P. R., 2015. Changes in shape and composition of sea-salt particles upon aging in an urban atmosphere. *Atmospheric Environment*, 100, pp.1-9.

Argyropoulos, G., Samara, C., Diapouli, E., Eleftheriadis, K., Papaoikonomou, K. and Kungolos, A., 2017. Source apportionment of PM_{10} and $PM_{2.5}$ in major urban Greek agglomerations using a hybrid source-receptor modeling process. *Science of The Total Environment*, 601, pp.906-917.

Begum, B. A., Biswas, S. K. and Hopke, P. K., 2007. Source Apportionment of Air Particulate Matter by Chemical Mass Balance (CMB) and Comparison with Positive Matrix Factorization (PMF) Model. *Aerosol and Air Quality Research*, 7(4), pp.446-468.

Bell, M. L., Dominici, F., Ebisu, K., Zeger, S. L. and Samet, J. M., 2007. Spatial and temporal variation in $PM_{2.5}$ chemical composition in the United States for health effects studies. *Environmental health perspectives*, 115(7), pp.989-995.

Charron, A., Polo-Rehn, L., Besombes, J. L., Golly, B., Buisson, C., Chanut, H., Marchand, N., Guillaud, G. and Jaffrezo, J. L., 2019. Identification and quantification of particulate tracers of exhaust and non-exhaust vehicle emissions. *Atmospheric Chemistry and Physics*, 19(7), pp.5187-5207.

Choi, J. K., Heo, J. B., Ban, S. J., Yi, S. M. and Zoh, K. D., 2012.

Chemical characteristics of $PM_{2.5}$ aerosol in Incheon, Korea. *Atmospheric environment*, 60, pp.583-592.

Dos Anjos, S. L., Alves, J. C., Soares, S. A. R., Araujo, R. G., de Oliveira, O. M., Queiroz, A. F. and Ferreira, S. L., 2018. Multivariate optimization of a procedure employing microwave-assisted digestion for the determination of nickel and vanadium in crude oil by ICP OES. *Talanta*, 178, pp. 842-846.

Du, L. and Turner, J., 2015. Using $PM_{2.5}$ lanthanoid elements and nonparametric wind regression to track petroleum refinery FCC emissions. *Science of the Total Environment*, 529, pp.65-71.

Duan, J., Huang, R. J., Li, Y., Chen, Q., Zheng, Y., Chen, Y., Lin, C., Ni, H., Wang, M., Ovadnevaite, J., Ceburnis, D., Chen, C., Worsnop, D. R., Hoffmann, T., O'Dowd, C. and Cao, J., 2020. Summertime and wintertime atmospheric processes of secondary aerosol in Beijing. *Atmospheric Chemistry and Physics*, 20(6), pp.3793-3807.

Figliuzzi, M., Tironi, M., Longaretti, L., Mancini, A., Teoldi, F., Sangalli, F. and Remuzzi, A., 2020. Copper-dependent biological effects of particulate matter produced by brake systems on lung alveolar cells. *Archives of Toxicology*, 94(9), pp.2965-2979.

Gao, X., Yang, L., Cheng, S., Gao, R., Zhou, Y., Xue, L., Shou, Y., Wang, J., Wang, X., Nie, W., Xu, P. and Wang, W.,

2011. Semi-continuous measurement of water-soluble ions in $PM_{2.5}$ in Jinan, China: temporal variations and source apportionments. *Atmospheric Environment*, 45(33), pp.6048-6056.

Gugamsetty, B., Wei, H., Liu, C. N., Awasthi, A., Hsu, S. C., Tsai, C. J., Roam G. D., Wu, Y. C. and Chen, C. F. 2012. Source characterization and apportionment of PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ by using positive matrix factorization. *Aerosol and Air Quality Research*, 12(4), pp.476-491.

Guo, H., Wang, T. and Louie, P. K. K., 2004. Source apportionment of ambient non-methane hydrocarbons in Hong Kong: Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. *Environmental Pollution*, 129(3), pp.489-498.

Hopke, P. K., 2003. Recent developments in receptor modeling. *Journal of Chemometrics: A Journal of the Chemometrics Society*, 17(5), pp.255-265.

Hsu, Y. K., Holsen, T. M. and Hopke, P. K., 2003. Comparison of hybrid receptor models to locate PCB sources in Chicago. *Atmospheric environment*, 37(4), pp.545-562.

Jang, H. N., Seo, Y. C., Lee, J. H., Hwang, K. W., Yoo, J. I., Sok, C. H. and Kim, S. H., 2007. Formation of fine particles enriched by V and Ni from heavy oil combustion: Anthropogenic sources and drop-tube furnace experiments. *Atmospheric Environment*, 41(5), pp.1053-1063.

Kang, D. and Kim, J. E., 2014. Fine, ultrafine, and yellow dust:

Emerging health problems in Korea. *Journal of Korean medical science*, 29(5), pp.621-622.

Ke, L., Liu, W., Wang, Y., Russell, A. G., Edgerton, E. S. and Zheng, M., 2008. Comparison of $PM_{2.5}$ source apportionment using positive matrix factorization and molecular marker-based chemical mass balance. *Science of the Total Environment*, 394(2-3), pp.290-302.

Kim, H. S., Huh, J. B., Hopke, P. K., Holsen, T. M. and Yi, S. M., 2007. Characteristics of the major chemical constituents of $PM_{2.5}$ and smog events in Seoul, Korea in 2003 and 2004. *Atmospheric Environment*, 41(32), pp.6762-6770.

Kim, H. S., Chung, Y. S. and Lee, S. G., 2012. Characteristics of aerosol types during large-scale transport of air pollution over the Yellow Sea region and at Cheongwon, Korea, in 2008. *Environmental monitoring and assessment*, 184(4), pp.1973-1984.

Krishna, T. R., Reddy, M. K., Reddy, R. C. and Singh, R. N., 2005. Impact of an industrial complex on the ambient air quality: Case study using a dispersion model. *Atmospheric Environment*, 39(29), pp.5395-5407.

Kumari, S., Verma, N., Lakhani, A. and Kumari, K. M., 2021. Severe haze events in the Indo-Gangetic Plain during post-monsoon: Synergetic effect of synoptic meteorology and crop residue burning emission. *Science of The Total Environment*, 768, 145479.

Langner, C., and Klemm, O., 2011. A comparison of model performance between AERMOD and AUSTAL2000. *Journal of the Air & Waste Management Association*, 61(6), pp.640-646.

Laskin, A., Iedema, M. J. and Cowin, J. P. 2002. Quantitative time-resolved monitoring of nitrate formation in sea salt particles using a CCSEM/EDX single particle analysis. *Environmental science & technology*, 36(23), pp.4948-4955.

Lee, T., Yu, X. Y., Kreidenweis, S. M., Malm, W. C. and Collett, J. L., 2008. Semi-continuous measurement of $PM_{2.5}$ ionic composition at several rural locations in the United States. *Atmospheric Environment*, 42(27), pp.6655-6669.

Li, J., Posfai, M., Hobbs, P. V. and Buseck, P. R., 2003. Individual aerosol particles from biomass burning in southern Africa: 2, Compositions and aging of inorganic particles. *Journal of Geophysical Research: Atmospheres*, 108(D13).

Li, Q., Cheng, H., Zhou, T., Lin, C. and Guo, S., 2012. The estimated atmospheric lead emissions in China, 1990–2009. *Atmospheric Environment*, 60, pp.1-8.

Lucey, D., Hadjiiski, L., Hopke, P. K., Scudlark, J. R. Church, T., 2001. Identification of sources of pollutants in precipitation measured at the mid-Atlantic US coast using potential source contribution function (PSCF). *Atmospheric Environment*, 35(23), pp.3979-3986.

Manousakas, M., Papaefthymiou, H., Diapouli, E., Migliori, A., Karydas, A. G., Bogdanovic-Radovic, I. and Eleftheriadis, K., 2017. Assessment of $PM_{2.5}$ sources and their corresponding level of uncertainty in a coastal urban area using EPA PMF 5.0 enhanced diagnostics. *Science of the Total Environment*, 574, pp.155-164.

McLaren, R., Wojtal, P., Halla, J. D., Mihele, C. and Brook, J. R., 2012. A survey of NO_2: SO_2 emission ratios measured in marine vessel plumes in the Strait of Georgia. *Atmospheric environment*, 46, pp.655-658.

Meidan, D., Holloway, J. S., Edwards, P. M., Dubé, W. P., Middlebrook, A. M., Liao, J., Welti, A., Graus, M., Warneke, C., Ryerson, T. B., Pollack, I. B., Brown, S. S. and Rudich, Y., 2019. Role of criegee intermediates in secondary sulfate aerosol formation in nocturnal power plant plumes in the Southeast US. *ACS Earth and Space Chemistry*, 3(5), pp.748-759.

Mijling, B., Van Der A, R. J. and Zhang, Q., 2013. Regional nitrogen oxides emission trends in East Asia observed from space. *Atmospheric Chemistry and Physics*, 13(23), pp.12003-12012.

Na, K. and Cocker III, D. R., 2009. Characterization and source identification of trace elements in $PM_{2.5}$ from Mira Loma, Southern California. *Atmospheric Research*, 93(4), pp.793-800.

Norris, G., Duvall, R., Brown, S., Bai, S., 2008. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide.

Prepared for the US Environmental Protection Agency Office of Research and Development, Washington, DC. DC EPA/600/R-14/108.

Park, S. S., Kim, Y. J., Cho, S. Y. and Kim, S. J., 2007. Characterization of $PM_{2.5}$ aerosols dominated by local pollution and Asian dust observed at an urban site in Korea during aerosol characterization experiments (ACE)-Asia Project. *Journal of the Air & Waste Management Association*, 57(4), pp.434-443.

Pekney, N. J., Davidson, C. I., Zhou, L. and Hopke, P. K., 2006. Application of PSCF and CPF to PMF-modeled sources of $PM_{2.5}$ in Pittsburgh. *Aerosol Science and Technology*, 40(10), pp.952-961.

Qiu, X., Duan, L., Chai, F., Wang, S., Yu, Q. and Wang, S., 2016. Deriving high-resolution emission inventory of open biomass burning in China based on satellite observations. *Environmental science & technology*, 50(21), pp.11779-11786.

Querol, X., Zhuang, X., Alastuey, A., Viana, M., Lv, W., Wang, Y., Lopez, A., Zhu, Z., Wei, H. and Xu, S., 2006. Speciation and sources of atmospheric aerosols in a highly industrialised emerging mega-city in Central China. *Journal of Environmental Monitoring*, 8(10), pp.1049-1059.

Rolph, G., Stein, A. and Stunder, B., 2017. Real-time environmental applications and display system: READY. *Environmental Modelling & Software*, 95, pp.210-228.

Rost, K. T., 2001. Late Holocene loess deposits and dust accumulation in the alpine meadow belt of the Wutai Shan, China. *Quaternary International*, 76, pp.85-92.

Ryu, S. Y., Kwon, B. G., Kim, Y. J., Kim, H. H. and Chun, K. J., 2007. Characteristics of biomass burning aerosol and its impact on regional air quality in the summer of 2003 at Gwangju, Korea. *Atmospheric Research*, 84(4), pp.362-373.

Scerri, M. M., Kandler, K., Weinbruch, S., Yubero, E., Galindo, N., Prati, P., Caponi, L. and Massabò, D., 2018. Estimation of the contributions of the sources driving $PM_{2.5}$ levels in a Central Mediterranean coastal town. *Chemosphere*, 211, pp.465-481.

Schaap, M., Loon, M. V., Ten Brink, H. M., Dentener, F. J. and Builtjes, P. J. H., 2004. Secondary inorganic aerosol simulations for Europe with special attention to nitrate. *Atmospheric Chemistry and Physics*, 4(3), pp.857-874.

Shah, P., Strezov, V., Stevanov, C. and Nelson, P. F., 2007. Speciation of arsenic and selenium in coal combustion products. *Energy & fuels*, 21(2), pp.506-512.

Teixeira, E. C., Agudelo-Castañeda, D. M. and Mattiuzi, C. D. P., 2015. Contribution of polycyclic aromatic hydrocarbon (PAH) sources to the urban environment: a comparison of receptor models. *Science of the Total Environment*, 538, pp.212-219.

Thepnuan, D., Chantara, S., Lee, C. T., Lin, N. H. and Tsai, Y. I., 2019. Molecular markers for biomass burning associated with the characterization of $PM_{2.5}$ and component sources during dry season haze episodes in Upper South East Asia. *Science of the Total Environment*, 658, pp.708-722.

Tian, H. Z., Wang, Y., Xue, Z. G., Cheng, K., Qu, Y. P., Chai, F. H. and Hao, J. M., 2010. Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980–2007. *Atmospheric Chemistry and Physics*, 10(23), pp.11905-11919.

Voutsa, D., Samara, C., Manoli, E., Lazarou, D. and Tzoumaka, P., 2014. Ionic composition of $PM_{2.5}$ at urban sites of northern Greece: secondary inorganic aerosol formation. *Environmental Science and Pollution Research*, 21(7), pp.4995-5006.

Wang, L., Yu, Y., Huang, K., Zhang, Z. and Li, X., 2020. The inharmonious mechanism of CO_2, NO_x, SO_2, and $PM_{2.5}$ electric vehicle emission reductions in Northern China. *Journal of Environmental Management*, 274, 111236.

Wang, Y., Yu, J., Wang, Z., Liu, Y. and Zhao, Y., 2021. A review on arsenic removal from coal combustion: Advances, challenges and opportunities. *Chemical Engineering Journal*, 128785.

Wang, D., Zhou, B., Fu, Q., Zhao, Q., Zhang, Q., Chen, J., Yang, X., Duan, Y. and Li, J., 2016. Intense secondary aerosol

formation due to strong atmospheric photochemical reactions in summer: observations at a rural site in eastern Yangtze River Delta of China. *Science of the Total Environment*, 571, pp.1454-1466.

Wang, Z., Ueda, H. and Huang, M., 2000. A deflation module for use in modeling long-range transport of yellow sand over East Asia. *Journal of Geophysical Research: Atmospheres*, 105(D22), pp.26947-26959.

Watson, J. G., Antony Chen, L. W., Chow, J. C., Doraiswamy, P. and Lowenthal, D. H., 2008. Source apportionment: findings from the US supersites program. *Journal of the Air & Waste Management Association*, 58(2), pp.265-288.

Wey, M. Y., Ou, W. Y., Liu, Z. S., Tseng, H. H., Yang, W. Y. and Chiang, B. C., 2001. Pollutants in incineration flue gas. *Journal of hazardous materials*, 82(3), pp.247-262.

Xu, L., Chen, X., Chen, J., Zhang, F., He, C., Zhao, J. and Yin, L., 2012. Seasonal variations and chemical compositions of $PM_{2.5}$ aerosol in the urban area of Fuzhou, China. *Atmospheric Research*, 104, pp.264-272.

Xue, Y., Xu, H., Guang, J., Mei, L., Guo, J., Li, C., Mikusauskas, R. and He, X., 2014. Observation of an agricultural biomass burning in central and east China using merged aerosol optical depth data from multiple satellite missions. *International Journal of Remote Sensing*, 35(16), pp.5971-5983.

Yang, F., He, K., Ma, Y., Chen, X., Cadle, S. H., Tai, C. and Mulawa,

P. A., 2003. Characteristics and sources of trace elements in ambient $PM_{2.5}$ in Beijing. *Huan Jing ke Xue=Huanjing Kexue*, 24(6), pp.33-37.

Yao, X. and Zhang, L., 2012. Chemical processes in sea-salt chloride depletion observed at a Canadian rural coastal site. *Atmospheric environment*, 46, pp.189-194.

Ying, Q., 2011. Physical and chemical processes of wintertime secondary nitrate aerosol formation. *Frontiers of Environmental Science & Engineering in China*, 5(3), 348.

Yuan, J., Wang, Y., Zhang, W., Zhao, C., Liu, Q., Shen, X., Zhang K. and Dong, L., 2017. Will recent boom in coal power lead to a bust in China. A micro-economic analysis. *Energy Policy*, 108, pp.645-656.

Zetterdahl, M., Moldanova, J., Pei, X., Pathak, R. K. and Demirdjian, B., 2016. Impact of the 0.1% fuel sulfur content limit in SECA on particle and gaseous emissions from marine vessels. *Atmospheric Environment*, 145, pp.338-345.

Zhang, Z. Y., Wong, M. S. and Lee, K. H., 2015. Estimation of potential source regions of $PM_{2.5}$ in Beijing using backward trajectories. *Atmospheric Pollution Research*, 6(1), pp.173-177.

Zhu, B., Zhang, Y., Chen, N. and Quan, J., 2019. Assessment of air pollution aggravation during straw burning in Hubei, Central China. *International journal of environmental research and public health*, 16(8), 1446.

Chapter 4.

Associations of $PM_{2.5}$ chemical constituents and source contributions with mortality

Abstract

$PM_{2.5}$ exposure is known to cause adverse health effects, especially impacts on respiratory and cardiovascular system of human body through various biological mechanisms such as oxidative stress and inflammation. However, the negative health effects of $PM_{2.5}$ exposure have been reported to vary spatially due to the region-specific compositional characteristics of $PM_{2.5}$. Thus, the associations of $PM_{2.5}$ exposure with health outcomes need to be understood to manage $PM_{2.5}$ pollution efficiently.

The associations of $PM_{2.5}$ chemical constituents and source contributions with cause-specific mortality in Seoul, Daejeon, Gwangju, and Ulsan during 2014-2018 were investigated. The GLM with natural spline function was applied to daily mortality data. In addition, meteorological parameters were also included the model to be controlled.

Overall, IQR increases in the concentration of $PM_{2.5}$ chemical species and source contribution affected the risks of mortality. However, the significance and strength of the associations were different among cities, which implies the heterogeneity in the health effects of $PM_{2.5}$ exposure. The findings suggest region-specific effects of $PM_{2.5}$ components and sources should be assessed to protect public health.

1. Introduction

Along with the aggravation of air pollution, there are growing concerns about the associations of $PM_{2.5}$ exposure with adverse health effects on human body. Although many epidemiologic studies revealed the close associations between $PM_{2.5}$ and mortality, the significance and strength of the associations are not solely determined by the $PM_{2.5}$ mass concentration. This implies that chemical constituents-specific effects exist because the proportion of each constituent in $PM_{2.5}$ varies depending on the locations even though $PM_{2.5}$ mass concentrations are identical.

$PM_{2.5}$ is mostly composed of diverse chemical species which have their own mechanisms and target organs in toxicity. Principal pathways of effects on respiratory and cardiovascular system are $PM_{2.5}$-induced oxidative stress and inflammation causing dysfunction of the organs. Despite the understanding of pathological injury by $PM_{2.5}$, there still remains uncertainty about which chemical constituents of $PM_{2.5}$ are more detrimental to the public health. Thus, region-specific health effects regarding $PM_{2.5}$ need to be evaluated.

The aim of this chapter is to investigate the effects of the chemical constituents of $PM_{2.5}$ and source contributions on cause-specific mortality for identifying the components and

sources of concern in each city, which might be fundamentals of controlling $PM_{2.5}$ from the public health perspective.

2. Materials and methods

2.1 Data

2.1.1 Daily mortality

Various health related parameters including daily mortality, hospital emergency department visits, out-of-hospital cardiac arrest (OHCA) have been widely used to estimate the adverse effects of PM exposure on human health in many epidemiological studies (Maheswaran et al., 2005; Qiao et al., 2014; Pradeau et al., 2015). In the present study, cause-specific daily mortality data was adopted as health outcomes for analyzing the health effects of $PM_{2.5}$ exposure. The study populations were all residents of Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018.

Daily death counts were obtained from MicroData Integrated Service (https://mdis.kostat.go.kr) operated by the Statistics Korea. A death for a resident in each city was included as mortality data after classified into all-cause (A00-R99), cardiovascular diseases (CVD, I00-I99), and respiratory diseases (RD, J00-J99) mortality based on the 10th version of

International Classification of Disease (ICD-10). This study was approved by the Seoul National University Institutional Review Board (IRB No: E2101/003-001).

2.1.2 $PM_{2.5}$ constituents and meteorological data

$PM_{2.5}$ chemical compositional data for PMF modelling was used for the analyses of health effects. With regard to source contributions, PMF-modeled data was added to the statistical model for the consistency with the analyses of the effects of $PM_{2.5}$ chemical composition on mortality.

Meteorological parameters are also important factors affecting human health such as temperature, relative humidity and they should be included in the health effect model to be controlled (Allen and Sheridan, 2014; Wang et al., 2019). Daily mean temperature, relative humidity (RH) and barometric pressure (BP) data for the same period of air pollution data was acquired from Weather Data Service (https://data.kma.go.kr) of Korea Meteorological Administration.

2.2 Statistical model

Health effects can be expressed as the strength of the associations between $PM_{2.5}$ constituents and health outcomes via

time-series analyses using various statistical models. Many previous studies have revealed the effects of fine particulate matter on health related outcomes including mortality, morbidity using generalized linear model (GLM), generalized additive model (GAM), and other statistical models (Phung et al., 2018; Janssen et al., 2013; Pascal et al., 2014; Cai et al., 2019).

In this study, 15 chemical species were selected and GLM with a natural spline (ns) was used for the investigation of the adverse effects of both $PM_{2.5}$ constituents and sources on daily death counts. Death counts were modeled with either Poisson distribution or over-dispersed Poisson distribution based on their distribution of each study city. Natural spline function of time and temperature was used to control both long-term and seasonal trends of death counts and $PM_{2.5}$ mass concentration was also added as a covariate for the adjustment of the effects by $PM_{2.5}$ mass. To determine the degrees of freedom (df) of natural spline, sensitivity analyses were conducted while changing df from 2 to 10 per year and they were selected to minimize the Akaike Information Criterion (Akaike, 1974). In addition, delayed effects, single-lag effect from on the day of exposure (lag 0) to seven days (lag 7) after exposure, were examined to get the greatest risk estimates because lagging effects of the exposure to $PM_{2.5}$ have been

reported (Chai et al., 2019; Li et al., 2021). The final model was constructed as Eq (1).

$$\ln(E[Y_t]) = \beta_0 + \beta_1 \cdot X_{t-l} + \beta_2 \cdot PM_{2.5} + \beta_3 \cdot RH + \beta_4 \cdot BP + \beta_5 \cdot DOW + ns(time, df) + ns(temperature, df) + \varepsilon \quad (1)$$

where, Yt is the observed daily death counts on the day t, X_{t-l} represents the daily mean concentration of $PM_{2.5}$ constituents at day t to l (l=0, 1, 2, ..., 7); RH, BP, and DOW stand for daily average relative humidity, barometric pressure, and day of week, respectively; β_1-β_5 is the coefficient of Xt, $PM_{2.5}$, RH, BP, DOW. After drawing β_1 through Eq. (1), the relative risk (RR) was calculated by the following Eq. (2).

$$RR = e^{\beta 1 * IQR} \quad (2)$$

Furthermore, multi-pollutant models including multiple $PM_{2.5}$ constituents simultaneously were applied to estimate the RR of each constituent under the control for other components. (Heo et al., 2014). Generally, the other constituents were included as well as target species into the model with the following exceptions due to the formation or emission characteristics. First, NH_4^+ was excluded in the models for NO_3^-

and SO_4^{2-} because NH_4^+ mostly exists as ionic compounds with NO_3^- or SO_4^{2-} in the form of NH_4NO_3, $(NH_4)_2SO_4$ (Zhang et al., 2021). Thus, NH_4^+ is closely correlated with NO_3^- or SO_4^{2-}, implying NO_3^- and SO_4^{2-} need to be controlled to estimate the coefficient of NH_4^+. In the same context, NH_4^+ was removed in the multi-pollutant models for NO_3^- and SO_4^{2-}. Soil-related constituents, especially crustal elements, are also so correlated that their effects need to be adjusted. Thus, Ti was excluded when the model for Fe was constructed and vice versa. All analyses were performed by using 'mgcv' package in statistical software R (http://www.R-project.org).

3. Results and discussion

Based on the PMF-modeled source contributions as well as $PM_{2.5}$ speciation data, adverse health effects on mortality were investigated. Largely, IQR (Table 4-1) increases in the concentration of $PM_{2.5}$ chemical constituents influenced all types of cause-specific mortality, whereas only a few components were significantly associated with mortality with different strength depending on the city and cause of mortality, which indicates risk heterogeneity among $PM_{2.5}$ constituents. The impacts of source contributions on mortality also varied among

the cities. The associations of cause-specific mortality with $PM_{2.5}$ chemical constituents and source contributions are summarized in Tables from 4-3 to 4-14.

Table 4-1 Interquartile range of $PM_{2.5}$ constituents concentration

Constituent	unit	Seoul	Daejeon	Gwangju	Ulsan
SO_4^{2-}	$\mu g/m^3$	4.79	4.73	4.44	3.49
NO_3^-	$\mu g/m^3$	7.65	6.39	5.07	3.03
NH_4^+	$\mu g/m^3$	3.67	3.38	2.76	2.20
K^+	$\mu g/m^3$	0.18	0.13	0.17	0.08
OC	$\mu g/m^3$	2.49	2.62	2.92	2.36
EC	$\mu g/m^3$	0.88	0.96	0.68	0.49
Ti	ng/m^3	6.72	6.45	6.31	7.56
V	ng/m^3	5.69	2.96	3.55	9.36
Mn	ng/m^3	11.35	7.93	9.16	18.90
Fe	ng/m^3	127.59	132.54	116.14	163.79
Ni	ng/m^3	1.98	1.26	1.18	3.36
Cu	ng/m^3	7.26	5.49	3.09	4.99
Zn	ng/m^3	57.78	35.86	42.63	56.49
As	ng/m^3	4.18	3.07	2.54	6.37
Pb	ng/m^3	17.53	15.52	19.92	18.16

In Seoul, chemical constituents with significant associations were as follows: K^+ (RR 1.016, 95% CI 1.002-1.031), EC (1.015, 1.000-1.031), Ti (1.011, 1.003-1.019), and Fe (1.010, 1.000-1.021) with all-cause mortality, Ti (1.016, 1.001-1.032), Fe (1.023, 1.003-1.044), and As (1.030, 1.003-1.058) with CVD

mortality, Pb (1.071, 1.013-1.128) with RD mortality. Ti and Fe, representative transition metals, are known to generate reactive oxygen species (ROS) which lead to cell damage (Moreno et al., 2019). As and Pb, markers of coal combustion, are toxic even at low levels and they are reported as carcinogen to human by International Agency for Research on Cancer. Significant associations of mortality with sources were mostly found for CVD mortality: incinerator (1.032, 1.007-1.057), coal combustion (1.034, 1.003-1.065), soil (1.016, 1.000-1.032).

Notably, mobile source showed no significant associations with any cause-specific mortality solely in Seoul, thought to be the results of several administrative policies implemented from the mid-2000s to improve the air quality in metropolitan area. Above all, "Special act on the improvement of air quality in Seoul Metropolitan Area" played an important role in reducing the emission in mobile sector through relevant programs such as the dissemination of low-pollution motor vehicles and the subsidiary support for installing exhaust gas reduction device. Overall, the results for Seoul show that the health effects were closely linked to heavy metals from both natural and anthropogenic sources. Heavy metals have been continuously reported to have impacts on cardiovascular via both direct and indirect pathways inducing oxidative stress and inflammation

(Mills et al., 2009). In addition, respiratory system is subject to damage by transition metals which trigger oxidative stress in lung alveoli (Hamad et al., 2016).

In Daejeon, $PM_{2.5}$ constituents increased the RR of all types of cause-specific mortality while most of the significant associations were related to CVD mortality. Chemical constituents with significant associations were EC (1.051, 1.004-1.100) and Fe (1.039, 1.009-1.069) for all-cause mortality, OC (1.146, 1.057-1.239), V (1.080, 1.007-1.154), Mn (1.097, 1.027-1.167), Ni (1.042, 1.005-1.080), Zn (1.076, 1.005-1.148), and Pb (1.091, 1.006-1.177) for CVD mortality and OC (1.219, 1.090-1.354), and As (1.190, 1.007-1.384) for RD mortality. Beside heavy metals mentioned above, OC and EC have been consistently reported to influence the various indicators of cardiovascular diseases such as blood pressure, heart rate variability (Huang et al., 2012; Schneider et al., 2012; Wu et al., 2013) which can lead to cardiovascular health outcomes (Bell et al., 2009; Ito et al., 2011). Similarly, sources of which marker species are carbonaceous species and transition metals (e.g. mobile, industry, and oil combustion) also showed significant associations with mortality in Daejeon.

Significant associations of $PM_{2.5}$ constituents and sources with mortality in Gwangju were mostly found for RD mortality,

which was unique among the four cities. Chemical species of significant association with RD mortality included ionic species such as SO_4^{2-} (1.085, 1.009-1.163), NH_4^+ (1.071, 1.000-1.143) as well as transition metals including Ti (1.048, 1.009-1.088), V (1.109, 1.040-1.179), Fe (1.061, 1.001-1.120), Ni (1.100, 1.033-1.170), and Zn (1.078, 1.010-1.146). While several previous studies revealed the significant association SO_4^{2-} and NH_4^+ with mortality risk, there are not explicit biological mechanisms of adverse health effects of them (Ueda et al., 2016). Nevertheless, some plausible theories have been suggested to explain the positive association of SO_4^{2-} with adverse health effects. First, particle acidity by sulfate may change the pulmonary toxicity of other $PM_{2.5}$ constituents or physical properties from their own toxicity (Dreher, 2000). Second, catalyzation of metals into more bioavailable forms is another possible explanation for the high associations of sulfate with adverse effects. For source-mortality relationships, sources of the species with significant association (e.g. oil combustion, mobile, and soil) were consistently revealed to increase the RD mortality in Gwangju.

In Ulsan, SO_4^{2-} (1.047, 1.004-1.091), OC (1.056, 1.001-1.113), and Mn (1.060, 1.018-1.103) for all-cause mortality while OC (1.126, 1.009-1.248) increased the CVD mortality risk significantly. Regarding source-mortality relationships, secondary

sulfate (1.053, 1.007-1.099), mobile (1.054, 1.009-1.099), and industry (1.059, 1.016-1.102) sources were strongly associated with all-cause mortality. These results are consistent with the PMF modelling results for the city identifying higher contributions of mobile and secondary sulfate. The compositional characteristics of the highest SO_4^{2-}/NO_3^- ratio among the four cities also support the health effects of $PM_{2.5}$ sources in the city.

The associations of mortality with $PM_{2.5}$ constituents obtained from multi-pollutant models were largely consistent with those from single-pollutant models. However, some differences were also observed due to the control of the effects caused by other species. First, EC and Fe for all-cause mortality in Seoul didn't show significant relationships compared to single-pollutant model. This suggests Ti is a more important element for all-cause mortality regarding the effects of soil source. The chemical constituents (i.e. Ti, Fe, and As) of significant associations with CVD mortality identically showed strong relationships from multi-pollutant models. A representative element from coal combustion, As, is an important factor on cardiovascular health outcomes as well as other heavy metallic elements. None of chemical species were

revealed to be significantly associated with RD mortality, supporting that $PM_{2.5}$ health effects in Seoul were mainly related to all-cause and CVD mortality caused by transition metals. In Daejeon, no significant associations between $PM_{2.5}$ components with all-cause mortality were observed and the number of constituents closely related to CVD mortality decreased from the results of multi-pollutant models. However, it is notable that NO_3^- showed significant associations with RD mortality, considered to be influenced by the control of NH_4^+ in the model. This explains source-mortality relationships more clearly where secondary nitrate was significantly associated with RD mortality. The results of multi-pollutant models for Gwangju were quite similar to those from single-pollutant models while $PM_{2.5}$ chemicals significantly associated with RD mortality were reduced. Remarkably, Ni and V were closely related to RD mortality from multi-pollutant models as well as single-pollutant models, suggesting primary emission from oil combustion source had effects on the respiratory system of the population in Gwangju. The results of multi-pollutant models for Ulsan consistently shows that SO_4^{2-}, OC, and Mn were important species for the adverse health effects observed in the city.

Table 4-2 Summary of daily mortality and meteorological conditions during 2014–2018

City		Avg. (S.D.)	Min.	P_{25}	P_{50}	P_{75}	Max.
Seoul	Daily mortality						
	All-cause	108 (14)	69	98	107	115	182
	CVD	11 (4)	2	8	10	13	29
	RD	24 (6)	8	20	23	27	44
	Meteorological parameters						
	Temp	13.3 (10.8)	-14.8	3.7	14.7	22.7	33.7
	RH	59.1 (14.7)	21.8	48.4	59.1	69.1	99.0
	BP	1006.3 (7.9)	981.0	999.8	1006.7	1012.6	1026.8
Daejeon	Daily mortality						
	All-cause	19 (5)	8	16	18	22	35
	CVD	3 (2)	0	1	2	3	11
	RD	4 (3)	0	3	4	6	13
	Meteorological parameters						
	Temp	13.9 (9.3)	-9.5	5.7	14.5	22.3	31.5
	RH	68.3 (15.0)	23.9	57.4	69.6	78.6	99.0
	BP	1008.7 (7.7)	987.9	1002.4	1009	1014.9	1027.6
Gwangju	Daily mortality						
	All-cause	18 (5)	5	14	17	20	33
	CVD	2 (2)	0	1	2	3	8
	RD	4 (2)	0	2	4	5	11
	Meteorological parameters						
	Temp	13.4 (10.2)	-12.7	4.3	14.1	22.2	33.4
	RH	69.3 (13.8)	27.5	59.4	70.5	78.8	99.3
	BP	1008.9 (8.0)	985.7	1002.3	1009.3	1015.2	1029.1
Ulsan	Daily mortality						
	All-cause	13 (4)	2	9	12	14	27
	CVD	2 (2)	0	0	1	2	6
	RD	4 (2)	0	2	3	4	10
	Meteorological parameters						
	Temp	13.8 (8.5)	-8.2	6.9	14.3	20.8	31.0
	RH	64.5 (19.1)	18.0	49.3	66.5	80.0	98.0
	BP	1009.5 (7.9)	982.5	1003.6	1009.7	1015.2	1030.0

Table 4-3 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from single-pollutant models in Seoul

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.011 (2) (0.999, 1.023)	1.015 (2) (0.991, 1.039)	1.024 (4) (0.987, 1.059)
NO_3^-	1.005 (1) (0.992, 1.018)	1.008 (2) (0.982, 1.034)	1.025 (0) (0.942, 1.110)
NH_4^+	1.008 (2) (0.995, 1.020)	1.012 (2) (0.987, 1.036)	1.022 (4) (0.984, 1.058)
K^+	1.016* (7) (1.002, 1.031)	1.017 (7) (0.989, 1.049)	1.044 (0) (0.992, 1.112)
OC	1.012 (2) (0.997, 1.027)	1.023 (2) (0.994, 1.053)	1.030 (6) (0.986, 1.074)
EC	1.015* (2) (1.000, 1.031)	1.021 (7) (0.992, 1.050)	1.032 (7) (0.990, 1.076)
Ti	1.011* (7) (1.003, 1.019)	1.016* (7) (1.001, 1.032)	1.017 (7) (0.993, 1.041)
V	1.008 (1) (0.995, 1.021)	1.008 (1) (0.983, 1.034)	1.033 (0) (0.990, 1.077)
Mn	1.004 (3) (0.991, 1.016)	1.017 (7) (0.994, 1.040)	1.034 (0) (0.985, 1.082)
Fe	1.010* (7) (1.000, 1.021)	1.023* (7) (1.003, 1.044)	1.022 (0) (0.982, 1.063)
Ni	1.004 (1) (0.991, 1.017)	1.008 (7) (0.985, 1.032)	1.024 (4) (0.987, 1.062)
Cu	1.009 (2) (0.996, 1.021)	1.021 (1) (0.995, 1.048)	1.023 (0) (0.973, 1.073)
Zn	1.008 (2) (0.995, 1.020)	1.015 (2) (0.990, 1.040)	1.038 (0) (0.979, 1.098)
As	1.004 (2) (0.990, 1.018)	1.030* (1) (1.003, 1.058)	1.027 (6) (0.985, 1.069)
Pb	1.009 (2) (0.997, 1.022)	1.017 (7) (0.993, 1.041)	1.071* (0) (1.013, 1.128)

* : significant at 95% CI

Table 4-4 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from multi-pollutant models in Seoul

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.018 (0) (0.992, 1.044)	1.016 (2) (0.992, 1.040)	1.030 (4) (0.994, 1.065)
NO_3^-	1.009 (0) (0.978, 1.040)	1.010 (0) (0.947, 1.073)	1.032 (0) (0.938, 1.127)
NH_4^+	1.022 (0) (0.982, 1.063)	1.025 (0) (0.944, 1.107)	1.041 (0) (0.922, 1.165)
K^+	1.016*(7) (1.001, 1.031)	1.015 (7) (0.987, 1.047)	1.031 (0) (0.976, 1.104)
OC	1.012 (2) (0.997, 1.028)	1.024 (2) (0.994, 1.054)	1.067 (0) (0.981, 1.156)
EC	1.020 (0) (0.988, 1.053)	1.019 (7) (0.990, 1.049)	1.040 (7) (0.997, 1.085)
Ti	1.010* (7) (1.003, 1.018)	1.017* (7) (1.001, 1.032)	1.015 (3) (0.990, 1.041)
V	1.007 (1) (0.994, 1.020)	1.015 (0) (0.956, 1.076)	1.073 (0) (0.984, 1.163)
Mn	1.003 (3) (0.990, 1.015)	1.018 (2) (0.993, 1.043)	1.065 (0) (0.977, 1.153)
Fe	1.011 (0) (0.992, 1.031)	1.023* (7) (1.002, 1.044)	1.019 (3) (0.984, 1.053)
Ni	1.003 (2) (0.990, 1.016)	1.007 (7) (0.983, 1.031)	1.025 (4) (0.988, 1.063)
Cu	1.009 (2) (0.996, 1.021)	1.020 (1) (0.993, 1.047)	1.011 (2) (0.974, 1.048)
Zn	1.009 (0) (0.983, 1.035)	1.016 (2) (0.991, 1.042)	1.024 (2) (0.986, 1.062)
As	1.005 (2) (0.991, 1.019)	1.032* (1) (1.003, 1.060)	1.028 (6) (0.985, 1.070)
Pb	1.010 (2) (0.998, 1.023)	1.019 (2) (0.993, 1.045)	1.076 (0) (0.997, 1.156)

* : significant at 95% CI

Table 4-5 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in source contribution in Seoul

Source	All-cause	CVD	RD
Secondary sulfate	1.009 (0.998, 1.020)	1.012 (0.992, 1.033)	1.024 (0.992, 1.057)
Secondary nitrate	1.005 (0.992, 1.017)	1.004 (0.979, 1.030)	1.024 (0.986, 1.061)
Incinerator	1.009 (0.996, 1.021)	1.032* (1.007, 1.057)	1.016 (0.980, 1.052)
Coal combustion	1.009 (0.993, 1.026)	1.034* (1.003, 1.065)	1.043 (0.995, 1.092)
Mobile	1.009 (0.996, 1.022)	1.018 (0.993, 1.044)	1.012 (0.975, 1.050)
Biomass burning	1.012 (0.998, 1.026)	1.012 (0.981, 1.044)	1.039 (0.989, 1.091)
Industry	1.005 (0.993, 1.017)	1.014 (0.990, 1.039)	1.008 (0.972, 1.044)
Oil combustion	1.008 (0.996, 1.020)	1.007 (0.984, 1.030)	1.025 (0.986, 1.063)
Soil	1.010* (1.002, 1.018)	1.016* (1.000, 1.032)	1.024 (0.998, 1.052)
Aged sea salt	1.007 (0.996, 1.018)	1.020 (0.998, 1.043)	1.029 (0.996, 1.064)

* : significant at 95% CI

Table 4-6 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from single-pollutant models in Daejeon

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.018 (2) (0.984, 1.051)	1.049 (1) (0.977, 1.123)	1.059 (5) (0.954, 1.165)
NO_3^-	1.026 (1) (0.990, 1.062)	1.041 (1) (0.963, 1.119)	1.070 (1) (0.965, 1.177)
NH_4^+	1.016 (1) (0.980, 1.053)	1.054 (1) (0.975, 1.134)	1.093 (0) (0.834, 1.372)
K^+	1.015 (4) (0.981, 1.059)	1.049 (1) (0.973, 1.184)	1.123 (5) (0.981, 1.443)
OC	1.024 (4) (0.983, 1.066)	1.146* (4) (1.057, 1.239)	1.219* (5) (1.091, 1.354)
EC	1.051* (2) (1.004, 1.100)	1.060 (4) (0.955, 1.177)	1.189 (0) (0.978, 1.447)
Ti	1.022 (2) (0.999, 1.045)	1.026 (0) (0.975, 1.079)	1.056 (2) (0.994, 1.118)
V	1.025 (3) (0.991, 1.060)	1.080* (1) (1.007, 1.154)	1.080 (2) (0.976, 1.186)
Mn	1.027 (1) (0.995, 1.059)	1.097* (1) (1.027, 1.167)	1.075 (2) (0.981, 1.171)
Fe	1.039* (2) (1.009, 1.069)	1.026 (1) (0.957, 1.095)	1.070 (2) (0.984, 1.156)
Ni	1.018 (2) (0.999, 1.038)	1.042* (1) (1.005, 1.080)	1.039 (2) (0.984, 1.097)
Cu	1.038 (1) (0.999, 1.076)	1.064 (1) (0.978, 1.151)	1.098 (5) (0.979, 1.219)
Zn	1.021 (1) (0.989, 1.053)	1.076* (1) (1.005, 1.148)	1.079 (5) (0.979, 1.179)
As	1.040 (1) (0.995, 1.086)	1.091 (1) (0.992, 1.194)	1.190* (0) (1.007, 1.384)
Pb	1.033 (1) (0.995, 1.071)	1.091* (1) (1.006, 1.177)	1.146 (0) (0.955, 1.339)

* : significant at 95% CI

Table 4-7 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from multi-pollutant models in Daejeon

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.025 (7) (0.985, 1.065)	1.065 (7) (0.980, 1.151)	1.114 (0) (0.854, 1.39)
NO_3^-	1.022 (1) (0.978, 1.066)	1.048 (1) (0.954, 1.144)	1.155* (5) (1.028, 1.285)
NH_4^+	1.032 (0) (0.915, 1.153)	1.071 (1) (0.972, 1.173)	1.321 (0) (0.940, 1.746)
K^+	1.019 (4) (0.980, 1.072)	1.051 (1) (0.964, 1.217)	1.161 (5) (0.988, 1.587)
OC	1.033 (7) (0.992, 1.074)	1.104 (2) (0.994, 1.219)	1.242* (5) (1.081, 1.413)
EC	1.056 (2) (0.995, 1.12)	1.204 (0) (0.944, 1.538)	1.143 (3) (0.943, 1.386)
Ti	1.026 (2) (0.998, 1.053)	1.058 (0) (0.972, 1.145)	1.050 (6) (0.968, 1.134)
V	1.018 (3) (0.977, 1.06)	1.089* (1) (1.004, 1.177)	1.068 (2) (0.936, 1.206)
Mn	1.031 (1) (0.993, 1.07)	1.092* (1) (1.011, 1.173)	1.075 (2) (0.961, 1.19)
Fe	1.035 (2) (0.999, 1.072)	1.073 (0) (0.922, 1.224)	1.134 (0) (0.912, 1.356)
Ni	1.013 (6) (0.989, 1.037)	1.036 (1) (0.990, 1.084)	1.058 (2) (0.988, 1.132)
Cu	1.039 (1) (0.993, 1.085)	1.065 (4) (0.958, 1.174)	1.167* (5) (1.019, 1.319)
Zn	1.037 (1) (0.995, 1.078)	1.114* (1) (1.026, 1.202)	1.118 (5) (0.992, 1.245)
As	1.042 (1) (0.982, 1.102)	1.096 (1) (0.969, 1.227)	1.341* (0) (1.049, 1.661)
Pb	1.063 (0) (0.953, 1.173)	1.129 (0) (0.896, 1.366)	1.217 (0) (0.889, 1.553)

* : significant at 95% CI

Table 4-8 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in source contribution in Daejeon

Source	All-cause	CVD	RD
Secondary sulfate	1.019 (0.986, 1.052)	1.040 (0.967, 1.114)	1.104* (1.005, 1.204)
Secondary nitrate	1.034* (1.003, 1.065)	1.060 (0.991, 1.130)	1.126* (1.040, 1.214)
Incinerator	1.037* (1.000, 1.074)	1.129* (1.049, 1.212)	1.092 (0.984, 1.204)
Coal combustion	1.020 (0.974, 1.067)	1.061 (0.960, 1.164)	1.078 (0.941, 1.219)
Mobile	1.030 (0.991, 1.070)	1.125* (1.038, 1.214)	1.102 (0.980, 1.227)
Biomass burning	1.018 (0.991, 1.046)	1.044 (0.994, 1.098)	1.068 (0.998, 1.158)
Industry	1.032 (0.998, 1.067)	1.095* (1.016, 1.176)	1.078 (0.979, 1.181)
Oil combustion	1.031* (1.002, 1.061)	1.038 (0.975, 1.103)	1.086 (0.999, 1.176)
Soil	1.034 (0.990, 1.079)	1.029 (0.933, 1.133)	1.127 (0.989, 1.276)

* : significant at 95% CI

Table 4-9 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from single-pollutant models in Gwangju

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.004 (1) (0.977, 1.032)	1.029 (7) (0.981, 1.077)	1.085* (1) (1.009, 1.163)
NO_3^-	1.014 (6) (0.989, 1.038)	1.072 (0) (0.989, 1.156)	1.047 (1) (0.980, 1.114)
NH_4^+	1.011 (1) (0.986, 1.037)	1.030 (2) (0.977, 1.085)	1.071* (1) (1.000, 1.143)
K^+	1.008 (7) (0.990, 1.027)	1.023 (7) (0.986, 1.068)	1.047 (5) (0.983, 1.138)
OC	1.018 (2) (0.990, 1.045)	1.035 (5) (0.978, 1.092)	1.056 (2) (0.979, 1.134)
EC	1.012 (6) (0.985, 1.039)	1.057 (0) (0.970, 1.157)	1.048 (7) (0.983, 1.120)
Ti	1.015* (3) (1.001, 1.029)	1.018 (0) (0.991, 1.044)	1.048* (5) (1.009, 1.088)
V	1.015 (7) (0.992, 1.038)	1.034 (4) (0.981, 1.087)	1.109* (1) (1.040, 1.179)
Mn	1.012 (5) (0.989, 1.035)	1.022 (0) (0.961, 1.084)	1.036 (1) (0.970, 1.102)
Fe	1.017 (5) (0.997, 1.038)	1.037 (0) (0.992, 1.081)	1.061* (5) (1.001, 1.120)
Ni	1.011 (7) (0.990, 1.032)	1.034 (2) (0.986, 1.084)	1.100* (1) (1.033, 1.170)
Cu	1.008 (2) (0.988, 1.029)	1.033 (0) (0.983, 1.083)	1.032 (1) (0.973, 1.091)
Zn	1.016 (1) (0.992, 1.04)	1.030 (6) (0.980, 1.080)	1.078* (1) (1.010, 1.146)
As	1.015 (1) (0.993, 1.039)	1.026 (5) (0.979, 1.074)	1.058 (1) (0.994, 1.124)
Pb	1.015 (0) (0.986, 1.043)	1.019 (0) (0.960, 1.079)	1.069 (1) (0.999, 1.140)

* : significant at 95% CI

Table 4-10 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from multi-pollutant models in Gwangju

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.004 (1) (0.977, 1.032)	1.027 (7) (0.979, 1.075)	1.124 (0) (0.977, 1.276)
NO_3^-	1.015 (0) (0.968, 1.061)	1.053 (0) (0.956, 1.151)	1.088 (0) (0.958, 1.221)
NH_4^+	1.014 (0) (0.949, 1.080)	1.032 (2) (0.978, 1.087)	1.105 (0) (0.922, 1.300)
K^+	1.007 (7) (0.989, 1.027)	1.026 (7) (0.988, 1.073)	1.049 (5) (0.984, 1.142)
OC	1.020 (2) (0.992, 1.048)	1.031 (2) (0.973, 1.090)	1.168 (0) (0.998, 1.347)
EC	1.013 (2) (0.986, 1.042)	1.042 (2) (0.985, 1.105)	1.043 (7) (0.977, 1.115)
Ti	1.014* (3) (1.001, 1.028)	1.026 (0) (0.994, 1.058)	1.046* (5) (1.006, 1.086)
V	1.014 (7) (0.991, 1.038)	1.035 (4) (0.982, 1.088)	1.104* (1) (1.034, 1.175)
Mn	1.011 (2) (0.988, 1.035)	1.023 (6) (0.976, 1.070)	1.068 (0) (0.889, 1.251)
Fe	1.016 (5) (0.995, 1.037)	1.067* (0) (1.000, 1.134)	1.061* (5) (1.001, 1.121)
Ni	1.014 (0) (0.965, 1.065)	1.056 (0) (0.955, 1.166)	1.092* (1) (1.024, 1.164)
Cu	1.008 (2) (0.988, 1.029)	1.027 (6) (0.985, 1.069)	1.032 (1) (0.973, 1.093)
Zn	1.016 (1) (0.991, 1.040)	1.030 (6) (0.980, 1.080)	1.073* (1) (1.003, 1.143)
As	1.017 (1) (0.994, 1.041)	1.024 (4) (0.976, 1.072)	1.054 (1) (0.988, 1.121)
Pb	1.020 (0) (0.985, 1.055)	1.024 (0) (0.952, 1.097)	1.063 (1) (0.992, 1.135)

* : significant at 95% CI

Table 4-11 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in source contribution in Gwangju

Source	All-cause	CVD	RD
Secondary sulfate	1.008 (0.977, 1.040)	1.036 (0.980, 1.091)	1.085 (0.995, 1.176)
Secondary nitrate	1.016 (0.990, 1.041)	1.076 (0.996, 1.157)	1.041 (0.970, 1.112)
Incinerator	1.017 (0.989, 1.045)	1.044 (0.986, 1.103)	1.047 (0.979, 1.115)
Coal combustion	1.012 (0.991, 1.034)	1.020 (0.977, 1.065)	1.063* (1.003, 1.125)
Mobile	1.016 (0.985, 1.048)	1.034 (0.969, 1.100)	1.114* (1.026, 1.204)
Biomass burning	1.007 (0.988, 1.025)	1.022 (0.985, 1.060)	1.035 (0.985, 1.087)
Industry	1.014 (0.992, 1.037)	1.018 (0.976, 1.062)	1.033 (0.969, 1.100)
Oil combustion	1.013 (0.988, 1.038)	1.031 (0.979, 1.087)	1.108* (1.036, 1.188)
Soil	1.013* (1.001, 1.025)	1.019 (0.996, 1.042)	1.040* (1.006, 1.074)
Aged sea salt	1.030 (0.997, 1.064)	1.055 (0.987, 1.129)	1.085* (1.007, 1.171)

* : significant at 95% CI

Table 4-12 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from single-pollutant models in Ulsan

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.047* (4) (1.004, 1.091)	1.049 (5) (0.958, 1.142)	1.077 (7) (0.968, 1.190)
NO_3^-	1.024 (5) (0.988, 1.060)	1.040 (4) (0.968, 1.114)	1.074 (0) (0.937, 1.218)
NH_4^+	1.050 (0) (0.960, 1.145)	1.100 (0) (0.914, 1.303)	1.065 (4) (0.936, 1.202)
K^+	1.008 (0) (0.995, 1.024)	1.028 (4) (0.997, 1.071)	1.028 (7) (0.990, 1.087)
OC	1.056* (4) (1.001, 1.113)	1.126* (4) (1.009, 1.248)	1.121 (0) (0.878, 1.391)
EC	1.029 (4) (0.981, 1.081)	1.066 (0) (0.911, 1.279)	1.105 (4) (0.964, 1.289)
Ti	1.017 (6) (0.987, 1.047)	1.039 (4) (0.980, 1.099)	1.056 (2) (0.968, 1.144)
V	1.027 (5) (0.999, 1.055)	1.046 (0) (0.982, 1.110)	1.043 (7) (0.976, 1.110)
Mn	1.060* (0) (1.018, 1.103)	1.062 (0) (0.973, 1.151)	1.101 (2) (0.996, 1.207)
Fe	1.036 (0) (0.989, 1.083)	1.065 (0) (0.970, 1.161)	1.073 (7) (0.970, 1.177)
Ni	1.027 (5) (0.996, 1.059)	1.046 (0) (0.973, 1.122)	1.048 (7) (0.972, 1.125)
Cu	1.020 (1) (0.983, 1.056)	1.037 (4) (0.964, 1.111)	1.086 (7) (0.990, 1.184)
Zn	1.040 (0) (0.990, 1.091)	1.099 (0) (0.995, 1.203)	1.090 (6) (0.975, 1.207)
As	1.015 (1) (0.991, 1.038)	1.017 (3) (0.969, 1.067)	1.048 (7) (0.986, 1.111)
Pb	1.026 (4) (0.992, 1.060)	1.039 (4) (0.969, 1.110)	1.044 (6) (0.949, 1.140)

* : significant at 95% CI

Table 4-13 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents from multi-pollutant models in Ulsan

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.052* (4) (1.009, 1.095)	1.036 (4) (0.945, 1.131)	1.094 (0) (0.847, 1.359)
NO_3^-	1.020 (5) (0.984, 1.056)	1.040 (4) (0.967, 1.115)	1.090 (0) (0.929, 1.261)
NH_4^+	1.060 (0) (0.958, 1.166)	1.110 (0) (0.899, 1.341)	1.080 (0) (0.793, 1.408)
K^+	1.008 (0) (0.994, 1.025)	1.025 (6) (0.995, 1.066)	1.036 (7) (0.994, 1.104)
OC	1.060* (4) (1.005, 1.116)	1.135* (4) (1.018, 1.258)	1.330* (0) (1.007, 1.696)
EC	1.030 (4) (0.983, 1.082)	1.030 (4) (0.936, 1.146)	1.091 (4) (0.955, 1.269)
Ti	1.011 (4) (0.981, 1.041)	1.053 (4) (0.993, 1.113)	1.047 (2) (0.959, 1.137)
V	1.117 (0) (0.902, 1.337)	1.438 (0) (0.981, 1.918)	1.047 (7) (0.977, 1.118)
Mn	1.125* (0) (1.040, 1.211)	1.105 (0) (0.927, 1.284)	1.098 (0) (0.847, 1.352)
Fe	1.011 (4) (0.969, 1.053)	1.064 (4) (0.978, 1.150)	1.071 (7) (0.967, 1.176)
Ni	1.029 (5) (0.997, 1.061)	1.041 (4) (0.974, 1.109)	1.344 (0) (0.608, 2.264)
Cu	1.018 (4) (0.982, 1.054)	1.039 (4) (0.966, 1.113)	1.093 (7) (0.994, 1.193)
Zn	1.030 (4) (0.987, 1.074)	1.113 (0) (0.930, 1.296)	1.072 (6) (0.953, 1.191)
As	1.015 (4) (0.991, 1.038)	1.017 (3) (0.968, 1.066)	1.051 (7) (0.987, 1.116)
Pb	1.137* (0) (1.035, 1.239)	1.137 (0) (0.917, 1.360)	1.235 (0) (0.942, 1.532)

* : significant at 95% CI

Table 4-14 The highest RR and 95% CI of cause-specific mortality associated with IQR increases in source contribution in Ulsan

Source	All-cause	CVD	RD
Secondary sulfate	1.053* (1.007, 1.099)	1.051 (0.956, 1.148)	1.093 (0.977, 1.211)
Secondary nitrate	1.022 (0.988, 1.057)	1.036 (0.946, 1.128)	1.045 (0.924, 1.170)
Incinerator	1.026 (0.990, 1.064)	1.030 (0.952, 1.117)	1.089 (0.988, 1.204)
Coal combustion	1.016 (0.994, 1.039)	1.009 (0.965, 1.057)	1.036 (0.979, 1.099)
Mobile	1.054* (1.009, 1.099)	1.056 (0.963, 1.150)	1.042 (0.911, 1.176)
Biomass burning	1.006 (0.995, 1.017)	1.019 (0.996, 1.043)	1.021 (0.991, 1.052)
Industry	1.059* (1.016, 1.102)	1.049 (0.962, 1.140)	1.116* (1.007, 1.231)
Oil combustion	1.029 (0.999, 1.061)	1.048 (0.985, 1.115)	1.043 (0.972, 1.120)
Soil	1.015 (0.992, 1.038)	1.029 (0.982, 1.079)	1.048 (0.992, 1.107)
Aged sea salt	1.023 (0.981, 1.067)	1.047 (0.960, 1.147)	1.098 (0.990, 1.223)

* : significant at 95% CI

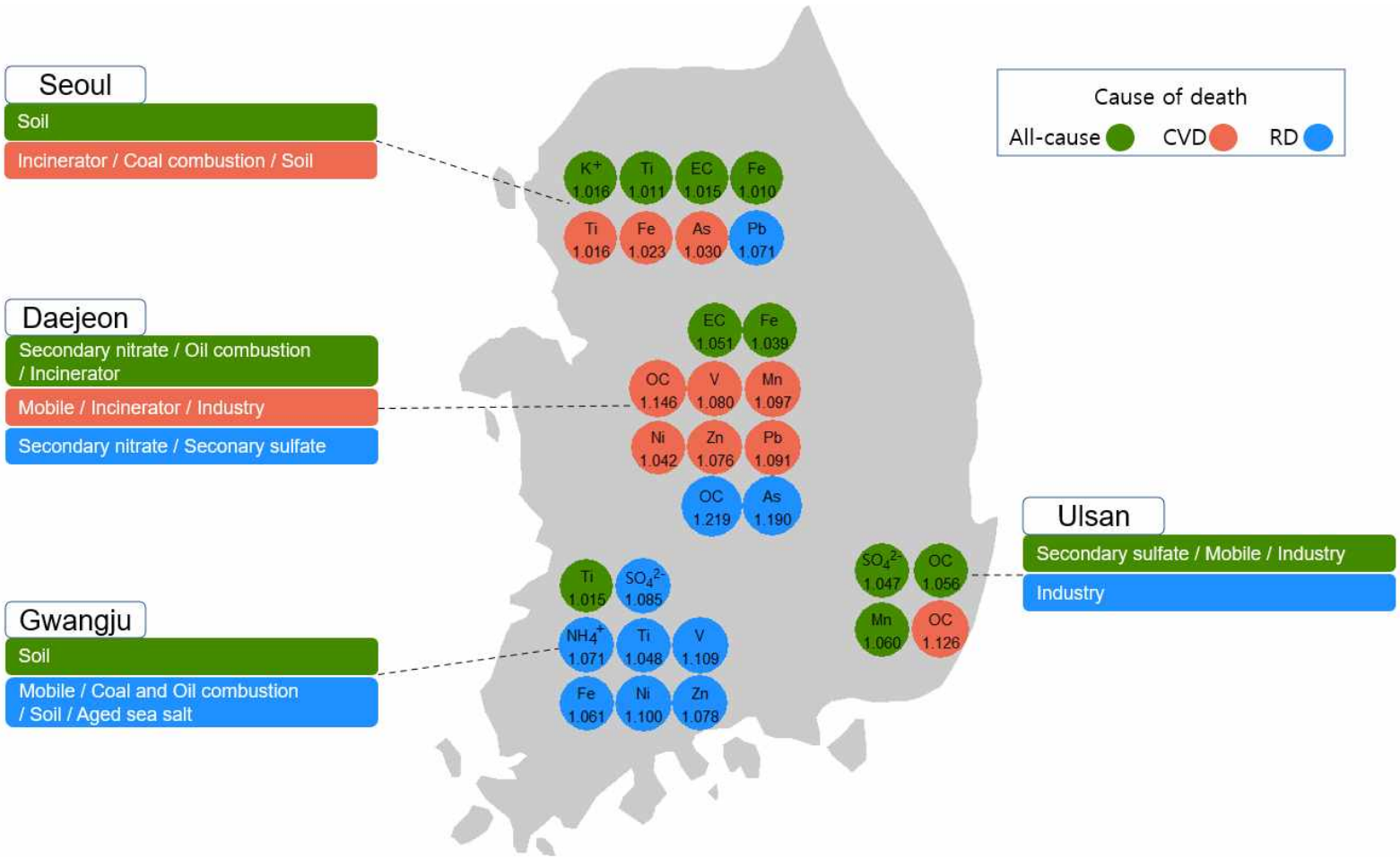


Figure 4-1 $PM_{2.5}$ constituents and sources significantly associated with mortality in Seoul, Daejeon, Gwangju, and Ulsan

4. Conclusions

The associations of $PM_{2.5}$ chemical constituents and source contributions with cause-specific mortality were investigated. Daily death counts, a parameter for the health effects of $PM_{2.5}$ exposure, were modeled with either Poisson distribution or over-dispersed Poisson distribution based on the data distribution of each city.

Overall, IQR increases in the concentration of $PM_{2.5}$ chemical constituents and source contribution resulted in increased RR for three types of cause-specific mortality. However, the significance and strength of associations were different among the cities, which shows the heterogeneity of the adverse health effects of $PM_{2.5}$ exposure.

In Seoul, significant associations were found for all cause-specific mortality which were mainly associated with heavy metals and related to sources including soil and coal combustion. In Daejeon, most of the significant associations were found for CVD mortality with constituents from combustion related sources including mobile and industry. Different from Daejeon, most of significant associations in Gwangju were found for RD mortality with constituents related to secondary formation (i.e. SO_4^{2-}, NH_4^+) and heavy metals. The

significant associations in Ulsan were closely related to SO_4^{2-}, OC and Mn, which is considered to reflect the characteristic of the city where large heavy and chemical industry complexes exist.

The findings of the present study suggest that the risks of cause-specific mortality increased by $PM_{2.5}$ chemical constituents and source contributions were quite heterogeneous. Thus, identification of $PM_{2.5}$ chemical constituents and sources affecting health outcomes significantly in the region of interest should take priority in designing policies to manage $PM_{2.5}$ efficiently.

References

Akaike H, 1974. A new look at the statistical model identification. *IEEE transactions on automatic control*. 19, pp.716-723.

Allen, M. J. and Sheridan, S. C., 2014. High-mortality days during the winter season: comparing meteorological conditions across 5 US cities. *International journal of biometeorology*, 58(2), pp.217-225.

Bell, M. L., Ebisu, K., Peng, R. D., Samet, J. M. and Dominici, F., 2009. Hospital admissions and chemical composition of fine particle air pollution. *American journal of respiratory and critical care medicine*, 179(12), pp.1115-1120.

Cai, J., Peng, C., Yu, S., Pei, Y., Liu, N., Wu, Y., Fu, Y. and Cheng, J., 2019. Association between $PM_{2.5}$ exposure and all-cause, non-accidental, accidental, different respiratory diseases, sex and age mortality in Shenzhen, China. *International journal of environmental research and public health*, 16(3), 401.

Chai, G., He, H., Sha, Y., Zhai, G. and Zong, S., 2019. Effect of $PM_{2.5}$ on daily outpatient visits for respiratory diseases in Lanzhou, China. *Science of the Total Environment*, 649, pp.1563-1572.

Donaldson, K., Beswick, P. H. and Gilmour, P. S., 1996. Free radical activity associated with the surface of particles: a unifying factor in determining biological activity. *Toxicology letters*, 88(1-3), pp.293-298.

Dreher, K. L., 2000. Particulate matter physicochemistry and toxicology: In search of causality—A critical perspective. *Inhalation Toxicology*, 12(sup3), 45-57.

Heo, J., Schauer, J. J., Yi, O., Paek, D., Kim, H. and Yi, S. M., 2014. Fine particle air pollution and mortality: importance of specific sources and chemical species. *Epidemiology*, pp.379-388.

Huang, W., Zhu, T., Pan, X., Hu, M., Lu, S. E., Lin, Y., Wang, T., Zhang, Y. and Tang, X., 2012. Air pollution and autonomic and vascular dysfunction in patients with cardiovascular disease: interactions of systemic inflammation, overweight, and gender. *American journal of epidemiology*, 176(2), pp.117-126.

Ito, K., Mathes, R., Ross, Z., Nádas, A., Thurston, G. and Matte, T., 2011. Fine particulate matter constituents associated with cardiovascular hospitalizations and mortality in New York City. *Environmental health perspectives*, 119(4), pp.467-473.

Janssen, N. A. H., Fischer, P., Marra, M., Ameling, C. and Cassee, F. R., 2013. Short-term effects of $PM_{2.5}$, PM_{10} and $PM_{2.5-10}$ on daily mortality in the Netherlands. *Science of the Total Environment*, 463, pp.20-26.

Li, B., Yang, J., Dong, H., Li, M., Cai, D., Yang, Z., Zhang C., Wang, H., Hu, J., Bergmann, S., Lin, G. and Wang, B., 2021. $PM_{2.5}$ constituents and mortality from a spectrum of causes in Guangzhou, China. *Ecotoxicology and Environmental Safety*, 222, 112498.

Maheswaran, R., Haining, R. P., Brindley, P., Law, J., Pearson, T.,

Fryers, P. R., Wise, S. and Campbell, M. J., 2005. Outdoor air pollution, mortality, and hospital admissions from coronary heart disease in Sheffield, UK: a small-area level ecological study. *European heart journal*, 26(23), pp.2543-2549.

Mills, N. L., Donaldson, K., Hadoke, P. W., Boon, N. A., MacNee, W., Cassee, F. R., Sandström, T., Blomberg, A. and Newby, D. E., 2009. Adverse cardiovascular effects of air pollution. *Nature clinical practice Cardiovascular medicine*, 6(1), pp.36-44.

Moreno, T., Trechera, P., Querol, X., Lah, R., Johnson, D., Wrana, A. and Williamson, B. 2019. Trace element fractionation between PM_{10} and $PM_{2.5}$ in coal mine dust: Implications for occupational respiratory health. *International Journal of Coal Geology*, 203, pp.52-59.

Pascal, M., Falq, G., Wagner, V., Chatignoux, E., Corso, M., Blanchard, M., Host, S., Pascal, L. and Larrieu, S., 2014. Short-term impacts of particulate matter (PM_{10}, $PM_{10-2.5}$, $PM_{2.5}$) on mortality in nine French cities. *Atmospheric Environment*, 95, pp.175-184.

Phung, V. L. H., Ueda, K., Kasaoka, S., Seposo, X., Tasmin, S., Yonemochi, S., Phosri, A., Honda, A., Takano, H., Michikawa, T. and Nitta, H., 2018. Acute effects of ambient $PM_{2.5}$ on all-cause and cause-specific emergency ambulance dispatches in Japan. *International journal of environmental research and public health*, 15(2), 307.

Pradeau, C., Rondeau, V., Lévèque, E., Guernion, P. Y., Tentillier, E., Thicoipé, M. and Brochard, P., 2015. Air pollution and

activation of mobile medical team for out-of-hospital cardiac arrest. *The American journal of emergency medicine*, 33(3), pp.367-372.

Qiao, L., Cai, J., Wang, H., Wang, W., Zhou, M., Lou, S., Chen, R., Dai, H., Chen, C. and Kan, H., 2014. $PM_{2.5}$ constituents and hospital emergency-room visits in Shanghai, China. *Environmental science & technology*, 48(17), pp.10406-10414.

Schneider, A., Hampel, R., Ibald-Mulli, A., Zareba, W., Schmidt, G., Schneider, R., Rückerl, R., Couderc, J. P., Mykins B., Oberdörster, G., Wölke, G., Pitz, M., Wichmann H. E. and Peters, A., 2010. Changes in deceleration capacity of heart rate and heart rate variability induced by ambient air pollution in individuals with coronary artery disease. *Particle and fibre toxicology*, 7(1), pp.1-12.

Ueda, K., Yamagami, M., Ikemori, F., Hisatsune, K. and Nitta, H., 2016. Associations between fine particulate matter components and daily mortality in Nagoya, Japan. *Journal of epidemiology*, JE20150039.

Wang, Y., Shi, Z., Shen, F., Sun, J., Huang, L., Zhang, H., Chen, C., Li, T. and Hu, J., 2019. Associations of daily mortality with short-term exposure to $PM_{2.5}$ and its constituents in Shanghai, China. *Chemosphere*, 233, pp.879-887.

Wu, S., Deng, F., Huang, J., Wang, H., Shima, M., Wang, X., Qin, Y., Zheng, C., Wei, H., Hao, Y., Lv, H., Lu, X. and Guo, X., 2013. Blood pressure changes and chemical constituents of particulate air pollution: results from the healthy volunteer

natural relocation (HVNR) study. *Environmental health perspectives*, 121(1), pp.66-72.

Zhang, T., Shen, Z. X., Su, H., Liu, S. X., Zhou, J. M., Zhao, Z. Z., Wang, Q. Y., Prévôt, A. S. H. and Cao, J. J., 2021. Effects of Aerosol Water Content on the formation of secondary inorganic aerosol during a Winter Heavy $PM_{2.5}$ Pollution Episode in Xi'an, China. *Atmospheric Environment*, 252, 118304.

Chapter 5.

Associations of $PM_{2.5}$ chemical constituents and source contributions with morbidity

Abstract

$PM_{2.5}$ exposure has been reported to be closely related to adverse health effects, especially respiratory and cardiovascular diseases via various biological mechanisms such as oxidative stress and inflammation. However, the negative health impacts have been revealed to vary depending on the location of a receptor because the compositional characteristics of $PM_{2.5}$ are very region-specific. Thus, the associations between $PM_{2.5}$ exposure with health outcomes need to be understood for reducing the adverse effects of $PM_{2.5}$.

In the present study, the associations of $PM_{2.5}$ chemical constituents and source contributions with cause-specific morbidity in major metropolitan cities were evaluated. Daily emergency department visits (EDVs) in the study areas during 2014-2018 were modeled with the daily concentrations of $PM_{2.5}$ chemical constituents and source contributions in each city using the generalized linear model (GLM) while meteorological parameters were controlled.

Overall, IQR increases in the concentrations of $PM_{2.5}$ chemical species and source contribution mostly showed positive relations with EDVs risks. However, the significance and strength of the associations were different among cities, implying heterogeneous health effects of $PM_{2.5}$ exposure.

1. Introduction

Air pollution is one of the driving risk factors linked to adverse health impacts on not only respiratory system but also cardiovascular and neurological system (Dabass et al., 2016; Fu et al., 2019; Jo et al., 2018). Among various air pollutants such as NO_2, SO_2, and O_3, there have been growing concerns about the health risks of exposure to particulate matters. A research on risk factors of human health around the world, Global Burden of Disease (GBD) 2019, revealed that ambient particulate matter pollution was the seventh leading risk factor for attributable disability-adjusted life years (DALYs) for all ages in 2019 (GBD 2019 Risk Factors Collaborators, 2020).

Although the associations of ambient $PM_{2.5}$ with diverse illnesses have been identified, there is little consistent evidence regarding the magnitude of the associations. This may derive from the heterogeneous characteristics of $PM_{2.5}$ composition. $PM_{2.5}$ comprises a number of chemical constituents including nitrate, sulfate, ammonium, organic carbon, elemental carbon, and other trace elements because $PM_{2.5}$ is mostly generated from the reactions among precursors in the atmosphere rather than primarily emitted from sources. Moreover, the complicated reactions among precursors are also affected by the meteorological parameters such as temperature, relative

humidity. Thus, $PM_{2.5}$ compositional characteristics are so dependent on the location of receptors that the associations of $PM_{2.5}$ composition and source contribution with health outcomes in the region of interest need to be investigated. In the present study, region-specific associations were assessed and compared to draw evidence for managing $PM_{2.5}$–induced morbidity more properly from a public health perspective.

2. Materials and methods

2.1 Data

2.1.1 Daily morbidity

Morbidity is one of the widely used indicators for evaluating the adverse health effects of the exposure to air pollution. Various parameters can stand for morbidity including emergency department visits (EDVs), out-of-hospital cardiac arrest (OCHA), and hospital admissions (De Marco et al., 2018; Qiao et al., 2014; Sielski et al., 2021). In the present study, cause-specific EDVs were adopted as a morbidity parameter to analyze the health effects of $PM_{2.5}$ exposure. The study populations were all residents in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018.

Daily EDVs were obtained from National Emergency Department Information System (NEDIS) operated by National Medical Center, Korea. EDVs in the four cities were included as morbidity data after classified into all-cause (A00-R99), cardiovascular diseases (CVD, I00-I99), and respiratory diseases (RD, J00-J99) morbidity according to the 10th version of International Classification of Disease (ICD-10). This study was approved by the Seoul National University Institutional Review Board (IRB No: E2101/003-001).

2.1.2 $PM_{2.5}$ constituents and meteorological data

$PM_{2.5}$ speciation data in Seoul, Daejeon, Gwangju, and Ulsan during 2014-2018 was used for the analyses of health effects. With regard to source contributions, PMF-modeled data was added to the statistical models for the consistency with the analyses of the health effects of $PM_{2.5}$ chemical compounds on morbidity.

Meteorological parameters are also important factors affecting human health such as temperature, relative humidity and they should be included in the health effect model to be controlled (Allen and Sheridan, 2014; Wang et al., 2019). Daily mean temperature, relative humidity (RH), and barometric

pressure (BP) data was obtained from Weather Data Service (https://data.kma.go.kr) of Korea Meteorological Administration.

2.2 Statistical model

Adverse health effects of air pollution can be expressed as the strength of the associations between the unit increase in the pollutants concentration exposed to human body and health outcomes based on time-series analyses using various statistical models. Generalized linear model (GLM) and generalized additive model (GAM) have been used for examining short-term effects of air pollution on health parameters such as mortality or morbidity (He et al., 2006).

In the present study, quasi-Poisson regression models with GLM were applied to estimate the associations of both $PM_{2.5}$ constituents and sources with morbidity considering the presence of overdispersion in daily EDVs. Natural spline function of time and temperature was used to control both long-term and seasonal trends of EDVs and $PM_{2.5}$ mass concentration was also included as a covariate for adjustment of the effects by mass concentration. To determine the degrees of freedom (df) of natural spline, sensitivity analyses were conducted by changing df from 2 to 10 per year and they were

selected to minimize the QAIC, a modification of Akaike Information Criterion for overdispersed count data (Kim et al., 2014). In addition, delayed effects, single-lag effect from on the day of exposure (lag 0) to three days (lag 3) after exposure, were examined because the health outcomes of $PM_{2.5}$ are likely to be lagged after exposure (Kim et al., 2012; Qiu et al., 2020). The final model was constructed as Eq. (1).

$$\ln(E[Y_t]) = \beta_0 + \beta_1 \cdot X_{t-l} + \beta_2 \cdot PM_{2.5} + \beta_3 \cdot RH + \beta_4 \cdot BP + \beta_5 \cdot DOW + ns(time, df) + ns(temperature, df) + \varepsilon \quad (1)$$

where, Yt is the observed EDVs on the day t, X_{t-l} represents the daily average concentration of $PM_{2.5}$ constituents at day t to l (l=0, 1, 2, 3); RH, BP, and DOW stand for daily average relative humidity, barometric pressure, and day of week, respectively; β_1-β_5 is the coefficient of Xt, $PM_{2.5}$, RH, BP, DOW. After drawing β_1 through Eq. (1), the relative risk (RR) was calculated by the following Eq. (2).

$$RR = e^{\beta 1 * IQR} \quad (2)$$

All analyses were performed by using 'mgcv' package in statistical software R (http://www.R-project.org).

3. Results and discussion

During the study period, more than six million patients visited hospital emergency departments and were diagnosed with non-accidental illnesses in Seoul, Daejeon, Gwangju, and Ulsan. Descriptive statistics of cause-specific EDVs and meteorological conditions during 2014-2018 in each study city are shown Table in 5-2.

In summary, IQR increases in the concentration of $PM_{2.5}$ chemical constituents (Table 5-1) largely influenced cause-specific EDVs, whereas only a few constituents were significantly associated with different strength depending on the city and cause of disease, implying risk heterogeneity among various $PM_{2.5}$ constituents. IQR increases in source contribution also influenced cause-specific EDVs with different strength among the cities. The associations of cause-specific EDVs with $PM_{2.5}$ chemical constituents and source contributions are summarized in Tables from 5-3 to 5-10 respectively.

In Seoul, significant associations of $PM_{2.5}$ chemical constituents with EDVs were found for cardiovascular and respiratory disease. First, Zn (RR 1.021, 95% CI 1.002-1.040) increased the risks of cardiovascular EDVs. Exposure to PM containing Zn can lead cardiac injury directly or indirectly through several pathways such as lung inflammation and/or

systemic endothelial activation (Godleski, 2006; Kodavanti et al., 2008), supported by the previous studies which revealed significant associations between Zn and cardiovascular EDVs (Bell et al., 2014; Campen et al., 2001; Ostro et al., 2007).

Table 5-1 Interquartile range of $PM_{2.5}$ constituents concentration

Constituent	unit	Seoul	Daejeon	Gwangju	Ulsan
SO_4^{2-}	$\mu g/m^3$	4.79	4.73	4.44	3.49
NO_3^-	$\mu g/m^3$	7.65	6.39	5.07	3.03
NH_4^+	$\mu g/m^3$	3.67	3.38	2.76	2.20
K^+	$\mu g/m^3$	0.18	0.13	0.17	0.08
OC	$\mu g/m^3$	2.49	2.62	2.92	2.36
EC	$\mu g/m^3$	0.88	0.96	0.68	0.49
Ti	ng/m^3	6.72	6.45	6.31	7.56
V	ng/m^3	5.69	2.96	3.55	9.36
Mn	ng/m^3	11.35	7.93	9.16	18.90
Fe	ng/m^3	127.59	132.54	116.14	163.79
Ni	ng/m^3	1.98	1.26	1.18	3.36
Cu	ng/m^3	7.26	5.49	3.09	4.99
Zn	ng/m^3	57.78	35.86	42.63	56.49
As	ng/m^3	4.18	3.07	2.54	6.37
Pb	ng/m^3	17.53	15.52	19.92	18.16

Second, Mn (1.025, 1.000-1.050) and Cu (1.028, 1.002-1.054) showed significant associations with respiratory EDVs. Transition metals have been widely known to affect

human body through several pathways inducing oxidative stress and inflammation (Mills et al., 2009). After deposited in respiratory system, transition metals can produce free radicals such as hydroxy radical, hydrogen peroxide, superoxide anion radical via Fenton type reaction and act as catalysts as well as induce inflammatory cytokines (Donaldson et al., 1996; Greenwell et al., 2002; Risom et al., 2005; Wu et al., 2018). Subsequently, these radicals cause oxidative damage on epithelial cells, which leads to DNA injury or apoptosis (Gao et al., 2016; Liu et al., 2020). Moreover, inflammatory cytokine and/or ROS produced on the epithelial cells of respiratory system also affect cardiovascular system through systemic circulation. Several inflammatory mediators such as interleukin 6 (IL-6), tumor necrosis factor-α (TNF-α) can spread into systemic circulation after released from lung cells (Martinelli et al., 2013), resulting in atherosclerosis, a basic step of many cardiovascular illnesses (Sun et al., 2005; Tian et al., 2021). Regarding source effects, industry (1.030, 1.005-1.055) source was significantly associated with daily EDVs for respiratory disease in Seoul. This source was characterized by the high loadings of heavy metals which strongly affect respiratory system.

In Daejeon, $PM_{2.5}$ chemical constituents also largely influenced the EDVs risk and significant associations were

found for all types of cause-specific EDVs. In particular, SO_4^{2-} and As affected both non-accidental and respiratory EDVs. Other components showing significant associations were Fe (1.028, 1.001-1.055) and Pb (1.063, 1.000-1.126) for cardiovascular EDVs, Ti (1.034, 1.012-1.057) for respiratory EDVs, respectively. SO_4^{2-} was reported to be strongly related to respiratory hospitalization (Jones et al., 2015), particularly in summer seasons when the constituent becomes predominant in $PM_{2.5}$ composition due to the formation mechanism favored by high temperature and relative humidity (Cao et al., 2017; Liu et al., 2005). Although significant associations between SO_4^{2-} and hospital admissions have been found for respiratory disease (Burnett et al., 1995; Jones et al., 2015), there are not explicit biological mechanisms of adverse health effects of them (Ueda et al., 2016). Nevertheless, some plausible theories have been suggested to explain the positive associations of SO_4^{2-} with adverse health effects. First, particle acidity by SO_4^{2-} may change the pulmonary toxicity of other $PM_{2.5}$ constituents or physical properties from their own toxicity (Dreher, 2000). Second, catalyzation of metals into more bioavailable forms is another possible explanation for the high associations of SO_4^{2-} with adverse effects.

For source-morbidity relationships, the sources of which

marker species were significantly associated with morbidity mostly had impacts on cause-specific EDVs. It is notable that secondary sulfate influenced all types of EDVs, which implies secondary sulfate was one of the important factors causing the burden of EDVs in Daejeon. This seemed to originate from the geographical location deep inland, facilitating the formation of secondary inorganic aerosols in the atmosphere. The percentage of calm conditions, where the wind speed is below 0.5 m/sec, in Daejeon during the study period was 12.5% which was much higher than those in Seoul (3.8%) and Ulsan (6.2%).

In Gwangju, $PM_{2.5}$ chemical constituents were largely associated with daily EDVs while the significance and strength of the associations varied among the components. As, known as highly toxic, affected both non-accidental (1.029, 1.002-1.056) and respiratory (1.056, 1.009-1.103) morbidity. Source-morbidity relationships also show coal combustion source, explained by high loadings of As, was significantly associated with non-accidental and respiratory EDVs. These results demonstrate As emitted from the source had negative health effects in Gwangju. In addition, K^+ (1.019, 1.003-1.036) and EC (1.023, 1.003-1.043) significantly influenced cardiovascular morbidity. Gwangju is surrounded by wide agricultural areas where open field burning of crop waste is periodically done for enhancing

land productivity. Accordingly, the marker species of biomass burning source seem to have affected cardiovascular EDVs.

In Ulsan, the significant associations between $PM_{2.5}$ constituents and the risk of EDVs were dominant for respiratory illnesses. Among them, OC (1.142, 1.001-1.291) showed the largest value of EDVs risk. OC is one of the $PM_{2.5}$ constituents which has been continuously reported to be linked to negative impacts on human body (Delfino et al., 2003; Peel et al., 2005; Sinclair and Tolsma, 2004) where the toxicity mechanisms, the oxidative stress and inflammation, are similar to other components. A representative pathway is to mimic the dioxin mechanism mediated aryl hydrocarbon receptor (Kennedy, 2007). Aryl hydrocarbon receptor (AhR) is a transcriptional factor that is involved in adaptive xenobiotic response (Hao and Whitelaw, 2013). $PM_{2.5}$ exposure can down-regulate the expression of AhR, which is known to induce inflammatory responses (Feng et al., 2019). For source effects on EDVs risk, coal combustion source affected both cardiovascular (1.035, 1.008-1.063) and respiratory (1.044, 1.012-1.077) diseases. These results are in line with the $PM_{2.5}$ constituents-EDVs risk relationship given that As and Pb are marker species of coal combustion source. Previous studies also revealed that coal-related $PM_{2.5}$ is particularly important in terms of toxicity (Park et al., 2018; Sun et al., 2015).

Table 5-2 Summary of daily EDVs and meteorological conditions during 2014–2018

City		Avg. (S.D.)	Min	P_{25}	P_{50}	P_{75}	Max.
Seoul	Daily EDVs						
	All-cause	2637 (601)	1284	2260	2498	2865	6875
	CVD	151 (24)	73	134	149	164	262
	RD	412 (263)	137	269	335	461	3150
	Meteorological parameters						
	Temp, ℃	13.3 (10.8)	-14.8	3.7	14.7	22.7	33.7
	RH,%	59.1 (14.7)	21.8	48.4	59.1	69.1	99.0
	BP, hPa	1006.3 (7.9)	981.0	999.8	1006.7	1012.6	1026.8
Daejeon	Daily EDVs						
	All-cause	401 (98)	138	335	383	447	945
	CVD	30 (8)	7	25	29	34	55
	RD	71 (42)	15	46	60	81	409
	Meteorological parameters						
	Temp, ℃	13.9 (9.3)	-9.5	5.7	14.5	22.3	31.5
	RH,%	68.3 (15.0)	23.9	57.4	69.6	78.6	99.0
	BP, hPa	1008.7 (7.7)	987.9	1002.4	1009	1014.9	1027.6
Gwangju	Daily EDVs						
	All-cause	367 (189)	148	252	298	435	2330
	CVD	32 (8)	7	26	31	36	65
	RD	76 (78)	12	39	55	84	1246
	Meteorological parameters						
	Temp, ℃	13.4 (10.2)	-12.7	4.3	14.1	22.2	33.4
	RH,%	69.3 (13.8)	27.5	59.4	70.5	78.8	99.3
	BP, hPa	1008.9 (8.0)	985.7	1002.3	1009.3	1015.2	1029.1
Ulsan	Daily EDVs						
	All-cause	175 (71)	81	132	158	194	981
	CVD	8 (4)	1	5	7	10	25
	RD	26 (30)	3	13	19	28	538
	Meteorological parameters						
	Temp, ℃	13.8 (8.5)	-8.2	6.9	14.3	20.8	31.0
	RH,%	64.5 (19.1)	18.0	49.3	66.5	80.0	98.0
	BP, hPa	1009.5 (7.9)	982.5	1003.6	1009.7	1015.2	1030.0

Table 5-3 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents in Seoul

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.017 (0) (0.998, 1.037)	1.001 (0) (0.983, 1.020)	1.004 (2) (0.978, 1.031)
NO_3^-	1.001 (2) (0.987, 1.014)	1.003 (3) (0.992, 1.015)	1.009 (2) (0.982, 1.036)
NH_4^+	1.008 (0) (0.974, 1.042)	1.001 (1) (0.989, 1.013)	1.006 (2) (0.980, 1.032)
K^+	1.010 (2) (0.994, 1.027)	1.009 (3) (0.995, 1.023)	1.028 (2) (0.993, 1.071)
OC	1.004 (1) (0.988, 1.019)	1.010 (3) (0.997, 1.023)	1.013 (1) (0.980, 1.045)
EC	1.002 (1) (0.985, 1.018)	1.017 (0) (0.993, 1.041)	1.003 (1) (0.969, 1.038)
Ti	1.004 (1) (0.995, 1.013)	1.007 (0) (0.998, 1.015)	1.012 (1) (0.993, 1.030)
V	1.004 (1) (0.990, 1.018)	1.008 (1) (0.995, 1.021)	1.009 (3) (0.982, 1.036)
Mn	1.007 (3) (0.995, 1.019)	1.007 (0) (0.991, 1.023)	1.025* (3) (1.000, 1.050)
Fe	1.006 (3) (0.996, 1.017)	1.009 (0) (0.996, 1.022)	1.021 (3) (0.999, 1.044)
Ni	1.001 (1) (0.987, 1.015)	1.006 (0) (0.991, 1.022)	1.012 (3) (0.986, 1.038)
Cu	1.003 (3) (0.991, 1.016)	1.005 (0) (0.988, 1.021)	1.028* (3) (1.002, 1.054)
Zn	1.004 (3) (0.992, 1.016)	1.021* (0) (1.002, 1.040)	1.019 (3) (0.994, 1.045)
As	1.009 (0) (0.993, 1.025)	1.006 (0) (0.991, 1.021)	1.028 (0) (0.994, 1.061)
Pb	1.002 (3) (0.990, 1.014)	1.006 (3) (0.994, 1.018)	1.007 (3) (0.982, 1.031)

* : significant at 95% CI

Table 5-4 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in source contribution in Seoul

Source	All-cause	CVD	RD
Secondary sulfate	1.013 (0.997, 1.029)	1.001 (0.987, 1.016)	1.034 (0.999, 1.069)
Secondary nitrate	1.001 (0.987, 1.014)	1.004 (0.992, 1.016)	1.010 (0.983, 1.037)
Incinerator	0.999 (0.986, 1.013)	1.002 (0.988, 1.017)	1.001 (0.975, 1.026)
Coal combustion	1.013 (0.994, 1.032)	1.007 (0.992, 1.022)	1.031 (0.991, 1.071)
Mobile	1.001 (0.988, 1.015)	1.002 (0.988, 1.016)	1.007 (0.978, 1.036)
Biomass burning	1.010 (0.994, 1.027)	1.009 (0.995, 1.022)	1.029 (0.995, 1.065)
Industry	1.005 (0.994, 1.017)	1.008 (0.994, 1.023)	1.030* (1.005, 1.055)
Oil combustion	1.003 (0.991, 1.016)	1.008 (0.996, 1.019)	1.008 (0.984, 1.033)
Soil	1.005 (0.997, 1.013)	1.004 (0.995, 1.013)	1.011 (0.994, 1.029)
Aged sea salt	1.004 (0.993, 1.014)	1.008 (0.998, 1.018)	1.008 (0.984, 1.033)

* : significant at 95% CI

Table 5-5 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents in Daejeon

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.058*(0) (1.027, 1.090)	1.025(2) (0.995, 1.055)	1.134*(0) (1.070, 1.199)
NO_3^-	0.998(2) (0.978, 1.017)	1.013(3) (0.980, 1.047)	1.005(2) (0.967, 1.043)
NH_4^+	1.006(2) (0.987, 1.025)	1.020(2) (0.987, 1.053)	1.012(2) (0.973, 1.051)
K^+	1.002(0) (0.974, 1.038)	1.020(2) (0.989, 1.058)	1.045(0) (0.977, 1.155)
OC	0.998(3) (0.979, 1.017)	1.017(0) (0.960, 1.075)	1.003(2) (0.962, 1.045)
EC	0.998(3) (0.976, 1.021)	1.020(0) (0.953, 1.091)	1.010(2) (0.965, 1.057)
Ti	1.006(1) (0.995, 1.018)	1.019(3) (0.999, 1.040)	1.034*(1) (1.012, 1.057)
V	1.000(2) (0.983, 1.016)	1.017(2) (0.988, 1.047)	1.011(2) (0.975, 1.048)
Mn	1.002(2) (0.987, 1.017)	1.013(3) (0.986, 1.041)	1.021(1) (0.989, 1.053)
Fe	1.000(1) (0.985, 1.015)	1.028*(3) (1.001, 1.055)	1.027(1) (0.997, 1.058)
Ni	0.995(2) (0.986, 1.004)	0.997(2) (0.980, 1.014)	0.997(2) (0.978, 1.017)
Cu	0.995(2) (0.976, 1.015)	1.013(0) (0.963, 1.064)	1.011(2) (0.972, 1.049)
Zn	0.993(2) (0.978, 1.009)	1.017(3) (0.989, 1.046)	0.998(1) (0.964, 1.031)
As	1.039*(0) (1.007, 1.072)	1.019(1) (0.978, 1.061)	1.139*(0) (1.073, 1.208)
Pb	1.002(2) (0.985, 1.020)	1.063*(0) (1.000, 1.126)	1.022(2) (0.985, 1.059)

* : significant at 95% CI

Table 5-6 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in source contribution in Daejeon

Source	All-cause	CVD	RD
Secondary sulfate	1.018* (1.001, 1.034)	1.032* (1.002, 1.062)	1.046* (1.013, 1.079)
Secondary nitrate	1.013 (0.998, 1.029)	1.029* (1.001, 1.057)	1.026 (0.996, 1.056)
Incinerator	1.023* (1.004, 1.041)	1.007 (0.974, 1.041)	1.049* (1.015, 1.083)
Coal combustion	1.004 (0.979, 1.029)	1.017 (0.972, 1.061)	1.001 (0.951, 1.052)
Mobile	1.022* (1.003, 1.041)	1.023 (0.987, 1.059)	1.056* (1.019, 1.094)
Biomass burning	1.002 (0.990, 1.014)	1.013 (0.994, 1.033)	1.006 (0.982, 1.031)
Industry	1.016 (0.999, 1.034)	1.014 (0.983, 1.045)	1.037* (1.004, 1.069)
Oil combustion	1.008 (0.994, 1.022)	1.007 (0.982, 1.033)	1.028 (0.998, 1.060)
Soil	1.007 (0.987, 1.028)	1.014 (0.977, 1.052)	1.029 (0.985, 1.075)

* : significant at 95% CI

Table 5-7 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents in Gwangju

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.022 (0) (0.989, 1.055)	1.011 (3) (0.992, 1.03)	1.032 (2) (0.993, 1.071)
NO_3^-	1.018 (2) (0.999, 1.037)	1.018 (2) (0.998, 1.037)	1.034* (2) (1.003, 1.065)
NH_4^+	1.014 (2) (0.995, 1.035)	1.014 (3) (0.997, 1.032)	1.030 (2) (0.996, 1.063)
K^+	1.016 (2) (0.998, 1.035)	1.019* (3) (1.003, 1.036)	1.026 (2) (0.996, 1.062)
OC	1.016 (3) (0.996, 1.035)	1.017 (3) (0.997, 1.038)	1.048 (0) (0.986, 1.111)
EC	1.015 (3) (0.997, 1.035)	1.023* (3) (1.003, 1.043)	1.029 (3) (0.998, 1.062)
Ti	1.005 (2) (0.993, 1.016)	1.006 (2) (0.994, 1.018)	1.010 (2) (0.991, 1.029)
V	1.011 (2) (0.991, 1.030)	1.011 (3) (0.992, 1.030)	1.021 (2) (0.985, 1.057)
Mn	1.007 (3) (0.991, 1.023)	1.012 (3) (0.994, 1.030)	1.013 (3) (0.988, 1.038)
Fe	1.007 (2) (0.991, 1.023)	1.007 (2) (0.990, 1.024)	1.015 (2) (0.988, 1.043)
Ni	1.016 (2) (0.997, 1.034)	1.013 (3) (0.996, 1.031)	1.028 (2) (0.997, 1.060)
Cu	1.008 (2) (0.991, 1.025)	1.017 (0) (0.996, 1.038)	1.018 (2) (0.989, 1.048)
Zn	1.013 (3) (0.996, 1.030)	1.017 (3) (0.999, 1.036)	1.022 (3) (0.996, 1.049)
As	1.029* (0) (1.002, 1.056)	1.010 (3) (0.992, 1.028)	1.056* (0) (1.009, 1.103)
Pb	1.015 (2) (0.994, 1.037)	1.006 (3) (0.986, 1.025)	1.025 (2) (0.987, 1.063)

* : significant at 95% CI

Table 5-8 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in source contribution in Gwangju

Source	All-cause	CVD	RD
Secondary sulfate	1.024 (0.991, 1.057)	1.012 (0.990, 1.034)	1.031 (0.986, 1.077)
Secondary nitrate	1.016 (0.996, 1.036)	1.019 (0.998, 1.039)	1.029 (0.996, 1.061)
Incinerator	1.018 (0.999, 1.037)	1.018 (0.997, 1.039)	1.024 (0.995, 1.054)
Coal combustion	1.025* (1.004, 1.046)	1.006 (0.989, 1.024)	1.044* (1.008, 1.081)
Mobile	1.026* (1.001, 1.052)	1.018 (0.994, 1.042)	1.048* (1.003, 1.094)
Biomass burning	1.014 (0.997, 1.032)	1.020* (1.005, 1.035)	1.024 (0.994, 1.054)
Industry	1.005 (0.990, 1.021)	1.012 (0.993, 1.031)	1.013 (0.989, 1.037)
Oil combustion	1.007 (0.988, 1.027)	1.011 (0.992, 1.030)	1.014 (0.979, 1.051)
Soil	1.004 (0.994, 1.014)	1.005 (0.995, 1.015)	1.011 (0.995, 1.027)
Aged sea salt	1.035* (1.011, 1.060)	1.011 (0.986, 1.038)	1.092* (1.049, 1.138)

* : significant at 95% CI

Table 5-9 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in the concentration of $PM_{2.5}$ chemical constituents in Ulsan

Constituent	All-cause	CVD	RD
SO_4^{2-}	1.023 (3) (0.996, 1.051)	1.002 (3) (0.953, 1.052)	1.054 (3) (0.999, 1.111)
NO_3^-	1.011 (2) (0.986, 1.035)	1.013 (0) (0.947, 1.081)	1.033 (2) (0.992, 1.075)
NH_4^+	1.036 (0) (0.963, 1.111)	1.038 (0) (0.912, 1.172)	1.054* (3) (1.003, 1.105)
K^+	1.005 (3) (0.994, 1.018)	1.010 (1) (0.992, 1.033)	1.015 (3) (0.994, 1.042)
OC	1.057 (0) (0.990, 1.126)	1.010 (1) (0.942, 1.080)	1.142* (0) (1.001, 1.291)
EC	1.024 (3) (0.994, 1.056)	1.010 (3) (0.956, 1.069)	1.070* (3) (1.011, 1.135)
Ti	1.001 (3) (0.984, 1.019)	1.028 (2) (0.995, 1.061)	1.015 (3) (0.982, 1.048)
V	1.014 (1) (0.994, 1.034)	1.030 (3) (0.997, 1.064)	1.045* (1) (1.003, 1.087)
Mn	1.002 (2) (0.977, 1.027)	1.022 (2) (0.974, 1.070)	1.008 (3) (0.959, 1.056)
Fe	1.006 (2) (0.978, 1.034)	1.037 (2) (0.987, 1.087)	1.009 (2) (0.956, 1.062)
Ni	1.013 (1) (0.990, 1.036)	1.029 (3) (0.992, 1.067)	1.047* (1) (1.000, 1.096)
Cu	1.009 (3) (0.984, 1.034)	1.039 (2) (0.994, 1.085)	1.052* (3) (1.001, 1.104)
Zn	1.008 (3) (0.980, 1.036)	1.028 (2) (0.975, 1.081)	1.061* (3) (1.006, 1.116)
As	1.008 (0) (0.991, 1.025)	1.036* (2) (1.008, 1.065)	1.037* (3) (1.002, 1.072)
Pb	1.024* (3) (1.001, 1.048)	1.046* (2) (1.005, 1.088)	1.086* (3) (1.042, 1.130)

* : significant at 95% CI

Table 5-10 The highest RR and 95% CI of cause-specific EDVs associated with IQR increases in source contribution in Ulsan

Source	All-cause	CVD	RD
Secondary sulfate	1.025 (0.996, 1.055)	1.008 (0.950, 1.067)	1.054 (0.996, 1.113)
Secondary nitrate	1.013 (0.980, 1.046)	1.017 (0.959, 1.077)	1.032 (0.993, 1.072)
Incinerator	0.991 (0.964, 1.019)	1.008 (0.962, 1.056)	0.997 (0.942, 1.056)
Coal combustion	1.010 (0.995, 1.026)	1.035* (1.008, 1.063)	1.044* (1.012, 1.077)
Mobile	1.030 (0.994, 1.065)	1.021 (0.965, 1.079)	1.063 (0.993, 1.133)
Biomass burning	1.004 (0.995, 1.014)	1.008 (0.993, 1.023)	1.012 (0.995, 1.029)
Industry	0.998 (0.972, 1.024)	1.019 (0.969, 1.069)	1.011 (0.959, 1.065)
Oil combustion	1.014 (0.992, 1.036)	1.031 (0.995, 1.068)	1.044 (0.998, 1.093)
Soil	1.003 (0.988, 1.018)	1.020 (0.994, 1.048)	1.007 (0.981, 1.032)
Aged sea salt	1.028 (0.998, 1.059)	1.048 (0.998, 1.102)	1.097* (1.037, 1.162)

* : significant at 95% CI

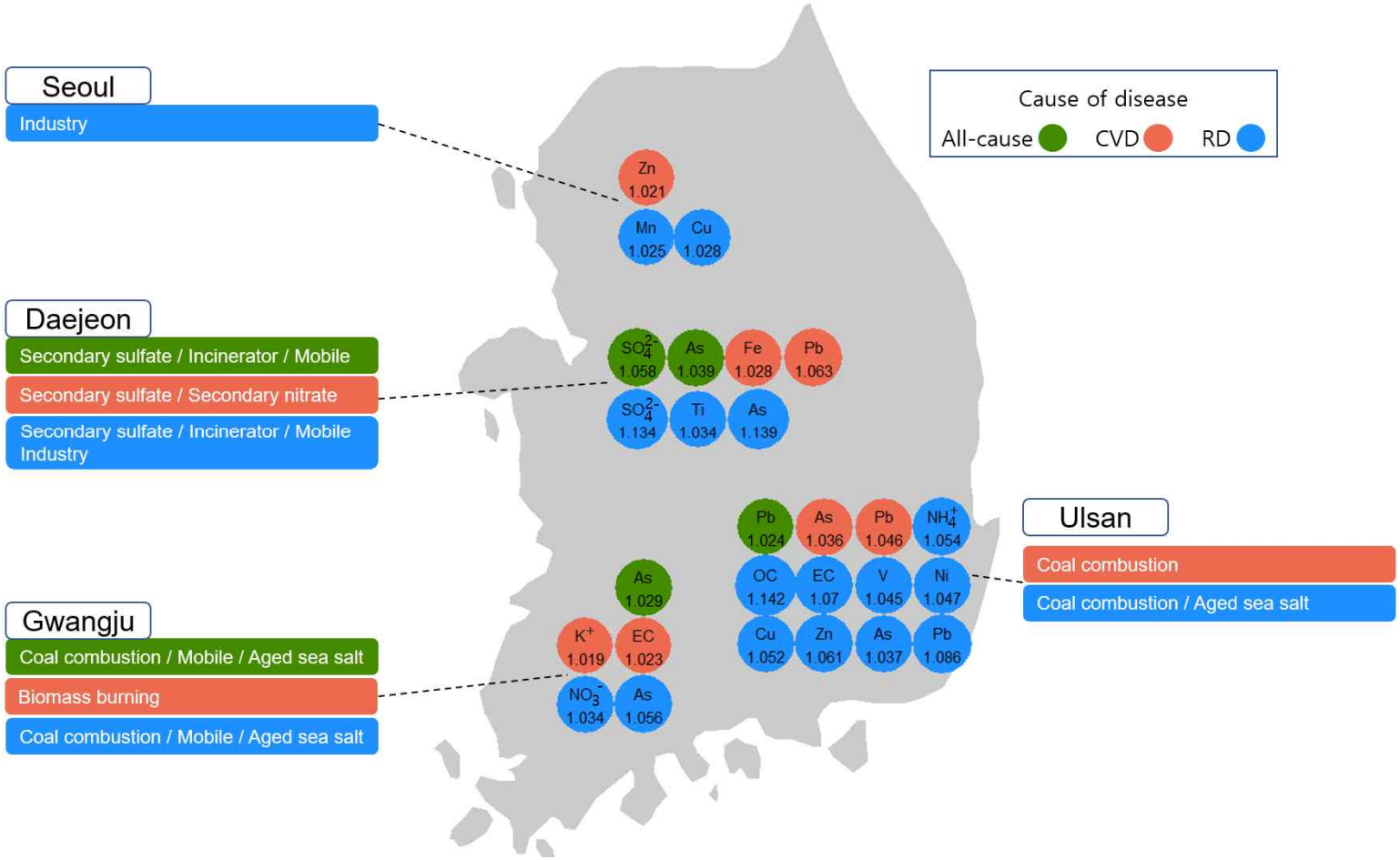


Figure 5-1 $PM_{2.5}$ constituents and sources significantly associated with EDVs in Seoul, Daejeon, Gwangju, and Ulsan

4. Conclusions

In this study, the associations of morbidity with $PM_{2.5}$ chemical constituents and source contributions in Seoul, Daejeon, Gwangju, and Ulsan were explored based on the $PM_{2.5}$ speciation data and PMF modelling results. As a parameter for morbidity, daily EDVs were selected and modeled with $PM_{2.5}$ constituent concentrations and source contributions using GLM.

The results show that both $PM_{2.5}$ chemical constituents and source contributions generally increased the cause-specific EDVs risk while components of secondary inorganic aerosols including SO_4^{2-}, NO_3^-, and NH_4^+ as well as heavy metals mostly had significant associations with the visits of emergency department, especially for respiratory diseases. For source-morbidity relationship, most of the significant associations were found for the sources of which marker species influenced the EDVs risk significantly.

However, the significance and strength of the associations were different among chemical species and sources and they also varied across the cities, which implies the heterogeneity in the chemical composition and health effects of $PM_{2.5}$ in the four cities. The findings of this study suggest region-specific effects on morbidity caused by chemical components and sources need to be assessed and taken into

consideration to establish policies for protecting public health from $PM_{2.5}$ exposure.

References

Allen, M. J. and Sheridan, S. C., 2014. High-mortality days during the winter season: comparing meteorological conditions across 5 US cities. *International journal of biometeorology*, 58(2), pp.217-225.

Bell, M. L., Ebisu, K., Leaderer, B. P., Gent, J. F., Lee, H. J., Koutrakis, P., Wang, Y., Dominici, F. and Peng, R. D. 2014. Associations of $PM_{2.5}$ constituents and sources with hospital admissions: analysis of four counties in Connecticut and Massachusetts (USA) for persons ≥ 65 years of age. *Environmental health perspectives*, 122(2), pp.138-144.

Burnett, R. T., Dales, R., Krewski, D., Vincent, R., Dann, T. and Brook, J. R., 1995. Associations between ambient particulate sulfate and admissions to Ontario hospitals for cardiac and respiratory diseases. *American journal of epidemiology*, 142(1), pp.15-22.

Campen, M. J., Nolan, J. P., Schladweiler, M. C., Kodavanti, U. P., Evansky, P. A., Costa, D. L. and Watkinson, W. P. 2001. Cardiovascular and thermoregulatory effects of inhaled PM-associated transition metals: a potential interaction between nickel and vanadium sulfate. *Toxicological Sciences*, 64(2), pp.243-252.

Cao, Z., Zhou, X., Ma, Y., Wang, L., Wu, R., Chen, B. and Wang, W., 2017. The concentrations, formations, relationships and modeling of sulfate, nitrate and ammonium (SNA) aerosols

over China. *Aerosol and Air Quality Research*, 17(1), pp.84-97.

Dabass, A., Talbott, E. O., Venkat, A., Rager, J., Marsh, G. M., Sharma, R. K. and Holguin, F., 2016. Association of exposure to particulate matter ($PM_{2.5}$) air pollution and biomarkers of cardiovascular disease risk in adult NHANES participants (2001–2008). *International journal of hygiene and environmental health*, 219(3), pp.301-310.

De Marco, A., Amoatey, P., Khaniabadi, Y. O., Sicard, P. and Hopke, P. K., 2018. Mortality and morbidity for cardiopulmonary diseases attributed to $PM_{2.5}$ exposure in the metropolis of Rome, Italy. *European journal of internal medicine*, 57, pp.49-57.

Delfino, R. J., Gong Jr, H., Linn, W. S., Pellizzari, E. D. and Hu, Y., 2003. Asthma symptoms in Hispanic children and daily ambient exposures to toxic and criteria air pollutants. *Environmental health perspectives*, 111(4), pp.647-656.

Dreher, K. L., 2000. Particulate matter physicochemistry and toxicology: In search of causality—A critical perspective. *Inhalation Toxicology*, 12(sup3), 45-57.

Feng, S., Duan, E., Shi, X., Zhang, H., Li, H., Zhao, Y., Cao, L., Zhong, X., Zhang, W., Li, R. and Yan, X., 2019. Hydrogen ameliorates lung injury in a rat model of subacute exposure to concentrated ambient $PM_{2.5}$ via Aryl hydrocarbon receptor. *International Immunopharmacology*, 77, 105939.

Fu, P., Guo, X., Cheung, F. M. H. and Yung, K. K. L., 2019. The

association between $PM_{2.5}$ exposure and neurological disorders: a systematic review and meta-analysis. *Science of the Total Environment*, 655, pp.1240-1248.

Gao, Z. X., Song, X. L., Li, S. S., Lai, X. R., Yang, Y. L., Yang, G., Li, Z. J., Cui, Y. H. and Pan, H. W., 2016. Assessment of DNA damage and cell senescence in corneal epithelial cells exposed to airborne particulate matter ($PM_{2.5}$) collected in Guangzhou, China. *Investigative ophthalmology & visual science*, 57(7), pp.3093-3102.

GBD 2019 Risk Factors Collaborators, 2020. Global burden of 87 risk factors in 204 countries and territories, 1990-2019: a systematic analysis for the Global Burden of Disease Study 2019. *The Lancet*, 396(10258), pp.1223-1249.

Godleski, J. J., 2006. Responses of the heart to ambient particle inhalation. *Clinics in occupational and environmental medicine*, 5(4), pp.849-864.

Greenwell, L. L., Moreno, T., Jones, T. P. and Richards, R. J., 2002. Particle-induced oxidative damage is ameliorated by pulmonary antioxidants. *Free Radical Biology and Medicine*, 32(9), pp.898-905.

Hamad, S. H., Schauer, J. J., Antkiewicz, D. S., Shafer, M. M. and Kadhim, A. K., 2016. ROS production and gene expression in alveolar macrophages exposed to $PM_{2.5}$ from Baghdad, Iraq: Seasonal trends and impact of chemical composition. *Science of the Total Environment*, 543, pp.739-745.

Hao, N. and Whitelaw, M. L., 2013. The emerging roles of AhR in physiology and immunity. *Biochemical pharmacology*, 86(5), pp.561-570.

He, S., Mazumdar, S. and Arena, V. C., 2006. A comparative study of the use of GAM and GLM in air pollution research. Environmetrics: *The official journal of the International Environmetrics Society*, 17(1), pp.81-93.

Jo, Y. S., Lim, M. N., Han, Y. J. and Kim, W. J., 2018. Epidemiological study of $PM_{2.5}$ and risk of COPD-related hospital visits in association with particle constituents in Chuncheon, Korea. *International journal of chronic obstructive pulmonary disease*, 13, 299.

Jones, R. R., Hogrefe, C., Fitzgerald, E. F., Hwang, S. A., Ozkaynak, H., Garcia, V. C. and Lin, S., 2015. Respiratory hospitalizations in association with fine PM and its components in New York State. *Journal of the Air & Waste Management Association*, 65(5), pp.559-569.

Kennedy, I. M., 2007. The health effects of combustion-generated aerosols. *Proceedings of the Combustion Institute*, 31(2), pp.2757-2770.

Kim, H. J., Cavanaugh, J. E., Dallas, T. A. and Fore, S. A., 2014. Model selection criteria for overdispersed data and their application to the characterization of a host-parasite relationship. *Environmental and ecological statistics*, 21(2), pp.329-350.

Kim, S. Y., Peel, J. L., Hannigan, M. P., Dutton, S. J., Sheppard, L., Clark, M. L. and Vedal, S., 2012. The temporal lag structure of short-term associations of fine particulate matter chemical constituents and cardiovascular and respiratory hospitalizations. *Environmental health perspectives*, 120(8), pp.1094-1099.

Kodavanti, U. P., Schladweiler, M. C., Gilmour, P. S., Wallenborn, J. G., Mandavilli, B. S., Ledbetter, A. D., Christiani, D. C., Runge, M. S., Karoly, E. D., Costa, D. L., Peddada, S., Jaskot, R., Richards, J. H., Thomas, R., Madamanchi, N. R. and Nyska, A., 2008. The role of particulate matter-associated zinc in cardiac injury in rats. *Environmental health perspectives*, 116(1), pp.13-20.

Liu, X., Zhu, J., Van Espen, P., Adams, F., Xiao, R., Dong, S. and Li, Y., 2005. Single particle characterization of spring and summer aerosols in Beijing: Formation of composite sulfate of calcium and potassium. *Atmospheric Environment*, 39(36), pp.6909-6918.

Liu, X., Zhao, X., Li, X., Lv, S., Ma, R., Qi, Y., Abulikemu, A., Duan, H., Guo, C., Li, Y. and Sun, Z. 2020. $PM_{2.5}$ triggered apoptosis in lung epithelial cells through the mitochondrial apoptotic way mediated by a ROS-DRP1-mitochondrial fission axis. *Journal of hazardous materials*, 397, 122608.

Martinelli, N., Olivieri, O. and Girelli, D., 2013. Air particulate matter and cardiovascular disease: a narrative review. *European*

journal of internal medicine, 24(4), pp.295-302.

Mills, N. L., Donaldson, K., Hadoke, P. W., Boon, N. A., MacNee, W., Cassee, F. R., Sandström, T., Blomberg, A. and Newby, D. E., 2009. Adverse cardiovascular effects of air pollution. *Nature clinical practice Cardiovascular medicine*, 6(1), pp.36-44.

Ostro, B., Feng, W. Y., Broadwin, R., Green, S. and Lipsett, M. 2007. The effects of components of fine particulate air pollution on mortality in California: results from CALFINE. *Environmental health perspectives*, 115(1), pp.13-19.

Park, J., Park, E. H., Schauer, J. J., Yi, S. M. and Heo, J., 2018. Reactive oxygen species (ROS) activity of ambient fine particles ($PM_{2.5}$) measured in Seoul, Korea. *Environment international*, 117, pp.276-283.

Peel, J. L., Tolbert, P. E., Klein, M., Metzger, K. B., Flanders, W. D., Todd, K., Mulholland, J. A., Ryan, P. B. and Frumkin, H., 2005. Ambient air pollution and respiratory emergency department visits. *Epidemiology*, pp.164-174.

Qiao, L., Cai, J., Wang, H., Wang, W., Zhou, M., Lou, S., Chen, R., Dai, H., Chen, C. and Kan, H., 2014. $PM_{2.5}$ constituents and hospital emergency-room visits in Shanghai, China. *Environmental science & technology*, 48(17), pp.10406-10414.

Qiu, X., Wei, Y., Wang, Y., Di, Q., Sofer, T., Awad, Y. A. and Schwartz, J., 2020. Inverse probability weighted distributed lag effects of short-term exposure to $PM_{2.5}$ and ozone on CVD hospitalizations in New England Medicare

participants-Exploring the causal effects. *Environmental research*, 182, 109095.

Risom, L., Møller, P. and Loft, S., 2005. Oxidative stress-induced DNA damage by particulate air pollution. *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, 592(1-2), pp.119-137.

Sielski, J., Kazirod-Wolski, K., Jóźwiak, M. A. and Jóźwiak, M., 2021. The influence of air pollution by $PM_{2.5}$, PM_{10} and associated heavy metals on the parameters of out-of-hospital cardiac arrest. *Science of The Total Environment*, 788, 147541.

Sinclair, A. H. and Tolsma, D., 2004. Associations and lags between air pollution and acute respiratory visits in an ambulatory care setting: 25-month results from the aerosol research and inhalation epidemiological study. *Journal of the Air & Waste Management Association*, 54(9), pp.1212-1218.

Sun, L., Lin, Z., Liao, K., Xi, Z. and Wang, D., 2015. Adverse effects of coal combustion related fine particulate matter ($PM_{2.5}$) on nematode Caenorhabditis elegans. *Science of the Total Environment*, 512, pp.251-260.

Sun, Q., Wang, A., Jin, X., Natanzon, A., Duquaine, D., Brook, R. D., Aguinaldo, J. G. S., Fayad, Z. A., Fuster, V., Lippmann, M. Chen, L. C. and Rajagopalan, S., 2005. Long-term air pollution exposure and acceleration of atherosclerosis and vascular inflammation in an animal model. *Journal of the American Medical Association*, 294(23), pp.3003-3010.

Tian, M., Zhao, J., Mi, X., Wang, K., Kong, D., Mao, H. and Wang, T., 2021. Progress in research on effect of $PM_{2.5}$ on occurrence and development of atherosclerosis. *Journal of Applied Toxicology*, 41(5), pp.668-682.

Ueda, K., Yamagami, M., Ikemori, F., Hisatsune, K. and Nitta, H., 2016. Associations between fine particulate matter components and daily mortality in Nagoya, Japan. *Journal of epidemiology*, JE20150039.

Wang, Y., Shi, Z., Shen, F., Sun, J., Huang, L., Zhang, H., Chen, C., Li, T. and Hu, J., 2019. Associations of daily mortality with short-term exposure to $PM_{2.5}$ and its constituents in Shanghai, China. Chemosphere, 233, pp.879-887.

Wu, W., Jin, Y. and Carlsten, C., 2018. Inflammatory health effects of indoor and outdoor particulate matter. *Journal of Allergy and Clinical Immunology*, 141(3), pp.833-844.

Chapter 6.

Summary, significance, and conclusions

1. Summary

1.1 Compositional characteristics and source apportionment of ambient $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018

In the present study, $PM_{2.5}$ chemical composition in Seoul, Daejeon, Gwangju, and Ulsan was investigated using $PM_{2.5}$ speciation data measured in the four cities during 2014–2018. In addition, source apportionment of $PM_{2.5}$ was conducted for identifying the sources and their relative contributions to $PM_{2.5}$. Regarding $PM_{2.5}$ mass, ionic species showed the largest proportion, followed by carbonaceous species and trace elements in common while the proportion of chemical constituents and parameters for understanding region–specific $PM_{2.5}$ characteristics such as SO_4^{2-}/NO_3^- ratio, OC/EC ratio were considerably different among the cities.

Ten identical factors were resolved from PMF modelling for Seoul, Gwangju, and Ulsan while aged sea salt, one of the ten factors, was not found for Daejeon due to its geographical location far away from the sea. In Seoul, mobile (22.3%) showed the largest contribution to $PM_{2.5}$, followed by secondary sulfate (21.8%), secondary nitrate (20.3%), coal combustion (10.7%), incinerator (8.7%), industry (4.4%), biomass burning

(4.3%), oil combustion (2.9%), soil (2.6%), and aged sea salt (2.1%). In Daejeon, sources contributing to $PM_{2.5}$ were as follows: mobile (21.7%), secondary sulfate (19.7%), secondary nitrate (19.5%), coal combustion (10.7%), incinerator (8.9%), industry (6.6%), oil combustion (6.1%), soil (4.2%), and biomass burning (2.7%). In Gwangju, the highest contributing source was secondary sulfate (21.3%), followed by mobile (20.5%), secondary nitrate (19.5%), incinerator (12.2%), coal combustion (9.7%), industry (4.3%), soil (4.2%), biomass burning (3.2%), aged sea salt (2.9%), and oil combustion (2.2%). In Ulsan, mobile (24.9%), secondary sulfate (23.9%), and secondary nitrate (18.9%) accounted for the majority of $PM_{2.5}$ mass while industry (8.8%) demonstrated higher contributions than those in other cities due to the existence of huge national industrial complexes.

The results of source apportionment in the four cities show that $PM_{2.5}$ mass concentrations mostly originated from the sources related to secondary formation (i.e. secondary nitrate, secondary sulfate) as well as mobile source, in line with $PM_{2.5}$ chemical composition. Therefore, the three sources should take priority in terms of air quality management to reduce ambient $PM_{2.5}$ mass concentration in South Korea. In addition, region-specific source management should be also implemented considering the relative source contributions to $PM_{2.5}$.

1.2 Associations of $PM_{2.5}$ chemical constituents and source contributions with mortality

In this study, health effects of $PM_{2.5}$ exposure were investigated by combining $PM_{2.5}$ speciation and source contribution data with mortality data in Seoul, Daejeon, Gwangju, and Ulsan during 2014–2018. The associations of daily death counts with IQR increases in the concentration of $PM_{2.5}$ constituents and source contribution were evaluated using generalized linear models.

Overall, $PM_{2.5}$ chemical constituents and source contributions showed positive associations with mortality. Transition metals were largely related to the mortality risk in all cities. However, the significance and strength of the associations were different among chemical species and sources. Furthermore, $PM_{2.5}$ constituents and sources of significant associations were different across the cities, which implies the heterogeneity of health effects of $PM_{2.5}$ exposure. The findings of this study suggest region-specific effects on mortality caused by chemical components and sources need to be assessed and taken into consideration to establish proper policies for protecting public health.

1.3 Associations of $PM_{2.5}$ chemical constituents and source contributions with morbidity

In this study, the associations of morbidity with $PM_{2.5}$ chemical constituents and source contributions in Seoul, Daejeon, Gwangju, and Ulsan were explored based on the $PM_{2.5}$ speciation data and PMF results. As a parameter for morbidity, daily EDVs were selected and modeled with $PM_{2.5}$ constituent concentrations. In addition, the effects of source contributions were evaluated using statistical models.

The results show that both $PM_{2.5}$ chemical constituents and source contributions generally increased the cause-specific EDVs risk. Components of secondary inorganic aerosols including SO_4^{2-}, NO_3^-, and NH_4^+ as well as heavy metals mostly had impacts on the visits of emergency department, especially on respiratory diseases. However, the significance and strength of the associations were different among chemical species and sources. Furthermore, $PM_{2.5}$ constituents and sources of significant association were different across the cities, which implies the heterogeneity in the health effects of $PM_{2.5}$ exposure. The findings of this study suggest region-specific effects on morbidity caused by $PM_{2.5}$ chemical components and sources need to be precisely assessed and taken into consideration to

mitigate the health effects of $PM_{2.5}$ pollution from a public health perspective.

2. Significance

2.1 Region-specific characteristics of the health effects of $PM_{2.5}$ exposure on mortality

The results of the health effects caused by $PM_{2.5}$ exposure in the study cities provide several implications for important constituents and sources in each region. In general, heavy metals showed significant associations with death in all cities, suggesting their high toxicity can lead to severe threat to human body. However, there are several region-specific results which need to be addressed. First of all, CVD mortality was dominantly affected in Seoul and Daejeon, whereas RD death was influenced in the southern part of the country (Gwangju and Ulsan). It is likely that $PM_{2.5}$ in the central area might have been largely affected secondary formation rather than primary emission, which resulted in finer particles. Fine particles can directly impact on cardiovascular system after they penetrate into systemic circulation (Rajagopalan et al., 2018). Secondly, the effects of secondary sources on mortality were obvious in Daejeon located in basin area. High percentage of calm

conditions during the study period might have facilitated the formation of secondary aerosols in the city. Thirdly, coal combustion source had impacts on Seoul and Gwangju relatively close to the west or south coast of Korea where coal power plants are densely located. Thus, geographical location is thought to be an important factor which can result in adverse health effects by the source. Polycyclic aromatic hydrocarbons (PAH) in the two cities were found to be closely connected with coal combustion, supporting the relationship between mortality and the source (Islam et al., 2017; Kang et al., 2020). Lastly, mobile source was significantly associated with cause-specific mortality in all cities except for Seoul. A series of policy interventions conducted since the mid-2000s to control the emissions from vehicles in the capital region seem to be important reasons for the regional difference.

2.2 Impacts of government policy interventions on $PM_{2.5}$ composition, source contribution, and health effects

Government-led policies have been conducted to control air pollutants due to the deterioration of air quality caused by the rapid industrialization and urbanization in South Korea since 1960s. In particular, a series of policy interventions started

to be strengthened in the capital region, Seoul metropolitan area, from the mid-2000s because air pollution in it was more serious. Thus, significant implications for $PM_{2.5}$ management can be acquired by comparing the $PM_{2.5}$ chemical composition and health effects in Seoul from a previous study with those of the present study. A study conducted by Heo et al. was selected to evaluated the impacts of relevant policies because there are methodological similarities between the previous and present studies. The authors had investigated $PM_{2.5}$ adverse effects on mortality using multi-pollutant models in Seoul from March 2003 to November 2007 before administrative policies and plans were intensively carried out in the city (Heo et al., 2014). In addition, they also carried out source apportionment by using PMF modelling, which also provides information on the changes of major sources and their contributions to $PM_{2.5}$. Thus, investigating the results of the previous and present studies can suggest implications to evaluate governmental interventions for $PM_{2.5}$ control.

Based on the results of the two studies, several changes in $PM_{2.5}$ chemical composition and source contribution are found. Above all, the average concentration of $PM_{2.5}$ declined considerably from 43.4 ± 24.8 $\mu g/m^3$ to 27.7 ± 17.2 $\mu g/m^3$, which might have resulted from several policies taken from since the

late 2000s. As "Special act on the improvement of air quality in Seoul Metropolitan Area" took effect from 2005, specific plans and policies were implemented to improve the air quality in the area (Han et al., 2018). One of them was "The 1st Master Plan for Metropolitan Air Quality Control" aimed at reducing the emission of primary pollutants (Han et al., 2018; Kim et al., 2018). This plan was intensively implemented from 2007 to 2014 and strengthened the regulations on the emission of PM_{10}, NOx, SOx, and VOCs. The plan included detailed policies for several emission sectors such as road transportation, non-road transportation, and point sources. Notably, road transportation emission was the main target of the plan given that it had accounted for the largest fraction of both PM_{10} (66%) and NOx (51%) emission as of 2001 (Han et al., 2017). Various policies in each emission sector led to considerable reduction of the annual emission of target air pollutants.

In addition to mass concentration, policy interventions influenced $PM_{2.5}$ chemical composition and source contribution in Seoul. It is remarkable that both the OC and EC concentrations in the $PM_{2.5}$ mass greatly decreased. OC and EC are representative pollutants largely emitted from motor vehicle exhaust (Gentner et al., 2013; Gu et al., 2010). Table 6-1 shows OC constituted the largest part of $PM_{2.5}$ mass during 2003-2007.

However, the average OC concentration dropped from 9.94 ± 5.00 ㎍/㎥ to 3.78 ± 1.90 ㎍/㎥, which resulted in significant reduction in its relative proportion. These compositional changes seem to have been affected by the intensive policy interventions on mobile sector. In a similar context, the concentration of motor-vehicle related sources was also smaller in the present study than in the previous study. As suggested in Table 6-2, the average concentration of gasoline emission, diesel emission together had been 11.10 ㎍/㎥ during 2003-2007 while that of mobile source from the present study was 7.08 ㎍/㎥. A sharp decline implies the relevant policies to control air quality worked and particularly led to the mitigation of vehicular emission. In addition, the concentration of biomass burning source decreased considerably from 4.28 ㎍/㎥ to 1.37 ㎍/㎥. This might have originated from the decrease in the agricultural areas distributed in Seoul, Incheon, and Gyeonggi. The regulation on unauthorized field burning according to the 1st master plan is also thought to be a possible reason for the change.

Furthermore, the impacts of policy interventions are also in consistent with the associations between $PM_{2.5}$ and mortality. The previous study revealed that constituents significantly associated with mortality were OC, EC, Mg, and Pb, indicating

local combustion sources including mobile were more important in terms of the adverse health effects of $PM_{2.5}$. However, vehicle-related species and sources didn't showed significant associations with mortality during 2014-2018, whereas heavy metals from natural sources mainly increased the mortality risk. Heavy metals generally exhibit high toxicity to human alveolar epithelial cells via biological mechanisms such as oxidative stress and inflammation (Chen et al., 2018; McNeilly et al., 2004).

The effects of policy interventions were more obvious in the source-mortality relationships in Seoul. Sources closely related to mortality during 2003-2007 were mainly vehicular emission and biomass burning. The estimated excess risk for respiratory mortality was 5.45 (0.49-10.66) by gasoline emission and 6.74 (0.23-13.67) by diesel emission, respectively while that of biomass burning for cardiovascular mortality was 1.86 (0.01-3.74). In contrast, mobile source didn't show significant associations with cause-specific mortality while coal combustion and soil sources were closely related to mortality during 2014-2018. These results imply that policy interventions did work considering "The 1st Master Plan for Metropolitan Air Quality Control" was focused on reducing vehicular emissions. Notably, the impacts on mortality of coal combustion source

were observed in the two studies considering the marker species of the source are As and Pb. It is likely that coal combustion and oil combustion sources were comprehensively included as industry in the previous because As and V were not separately measured. Thus, it can be inferred that coal combustion was a particularly important source for mortality in Seoul from the results.

Table 6-1 Comparison of the $PM_{2.5}$ chemical composition in Seoul from the previous and present studies

		Previous study	Present study
Constituents	unit	Avg.(S.D.)	Avg.(S.D.)
$PM_{2.5}$ mass	$\mu g/m^3$	43.4 (24.8)	27.7 (17.2)
SO_4^{2-}	$\mu g/m^3$	8.50 (7.41)	5.38 (4.74)
NO_3^-	$\mu g/m^3$	7.21 (5.82)	6.09 (5.90)
NH_4^+	$\mu g/m^3$	5.50 (4.35)	3.92 (3.19)
OC	$\mu g/m^3$	9.94 (5.00)	3.78 (1.90)
EC	$\mu g/m^3$	3.25 (2.04)	1.27 (0.64)
K	$\mu g/m^3$	0.40 (0.31)	0.31 (0.22)
K^+	$\mu g/m^3$	-	0.16 (0.15)
Ca	$\mu g/m^3$	0.19 (0.19)	0.07 (0.07)
Ti	$\mu g/m^3$	0.02 (0.03)	0.01 (0.01)
Mn	$\mu g/m^3$	0.02 (0.02)	0.01 (0.01)
Fe	$\mu g/m^3$	0.36 (0.31)	0.20 (0.11)
Ni	ng/m^3	1.91 (2.28)	1.57 (1.63)
Cu	$\mu g/m^3$	0.02 (0.01)	0.01 (0.01)
Zn	$\mu g/m^3$	0.11 (0.08)	0.07 (0.04)
Br	$\mu g/m^3$	0.01 (0.01)	0.01 (0.01)
Pb	$\mu g/m^3$	0.05 (0.04)	0.02 (0.02)

Table 6-2 Comparison of the $PM_{2.5}$ source apportionment in Seoul from the previous and present studies

Previous study			Present study		
Source	Concentration (㎍/㎥)	Contribution (%)	Source	Concentration (㎍/㎥)	Contribution (%)
Secondary nitrate	8.04	18.7	Secondary nitrate	6.45	20.3
Secondary sulfate	7.97	18.6	Secondary sulfate	6.92	21.8
Gasoline emission	6.13	14.3	Mobile	7.08	22.3
Diesel emission	4.97	11.6	Biomass burning	1.37	4.3
Roadway emission	2.18	5.1	Incinerator	2.75	8.7
Biomass burning	4.28	10.0	Soil	0.81	2.6
Soil	3.32	7.7	Industry	1.40	4.4
Industry	5.28	12.3	Coal combustion	3.40	10.7
Aged sea salt	0.72	1.7	Oil combustion	0.92	2.9
-	-		Aged sea salt	0.66	2.1

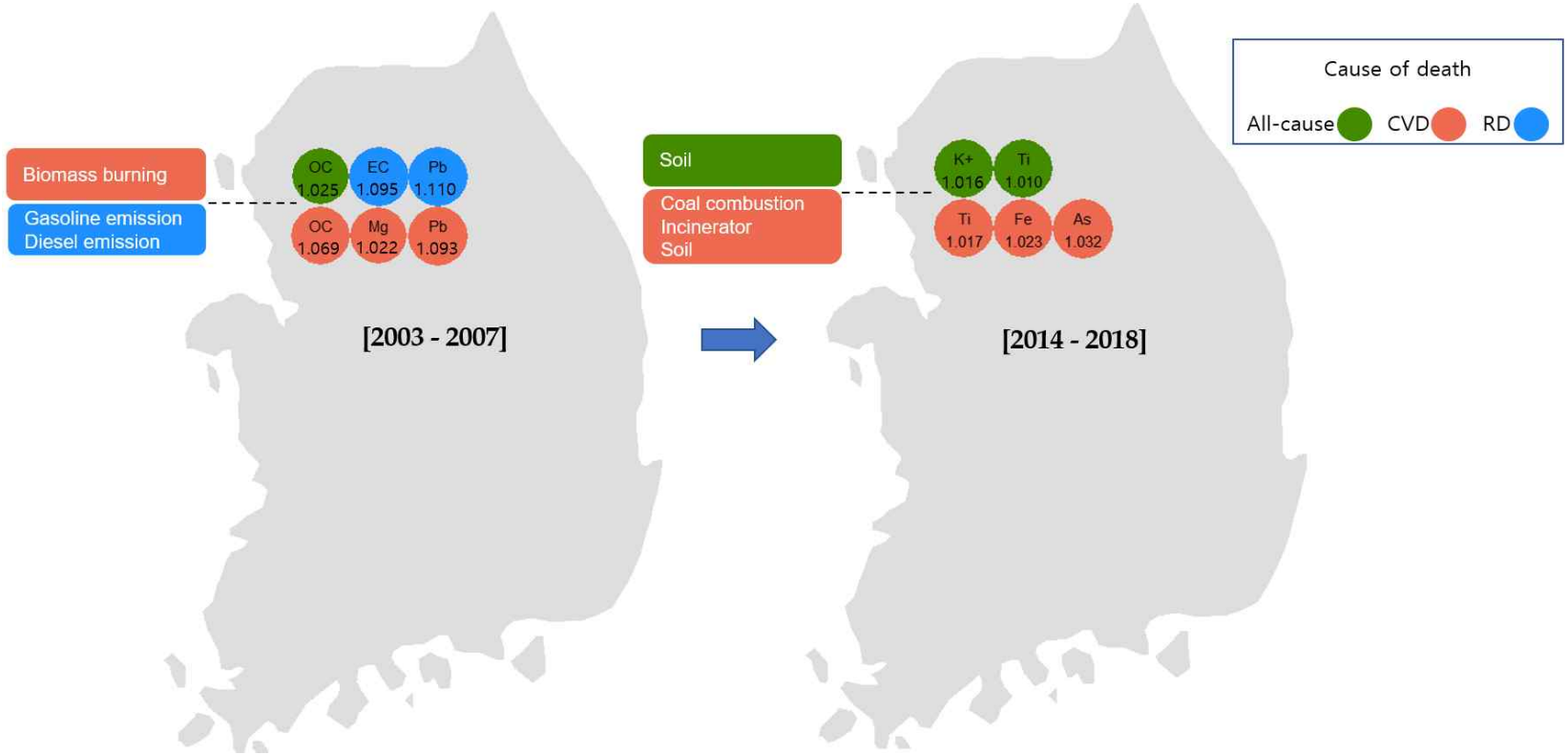


Figure 6-1 $PM_{2.5}$ constituents and sources significantly associated with mortality in Seoul from the previous and present studies using multi-pollutant models

3. Conclusions

This study investigated the compositional characteristics of $PM_{2.5}$ and sources contributing to $PM_{2.5}$ in Seoul, Daejeon, Gwangju, and Ulsan, major metropolitan cities in South Korea. $PM_{2.5}$ has been revealed as a heterogeneous mixture of numerous chemical species of which mass concentrations and relative proportion in $PM_{2.5}$ are highly region-specific due to the differences in sources, meteorological conditions, geographical locations, etc. Hence, identifying the characteristics of $PM_{2.5}$ and its sources in the region of interest is essential for reducing and managing ambient $PM_{2.5}$ efficiently.

Based on $PM_{2.5}$ the speciation data in the four cities during 2014–2018, statistical analyses and PMF modelling were conducted. The results show that the majority of $PM_{2.5}$ mass was composed of ionic compounds, carbonaceous species. Especially, ionic compounds including NH_4^+, SO_4^{2-} and NO_3^- accounted for more than 50% of $PM_{2.5}$ mass, which shows that $PM_{2.5}$ mainly originated from secondary formation by the reactions among gaseous pollutants in the atmosphere. These findings were in line with the results of PMF modelling which allocated the considerable part of $PM_{2.5}$ to secondary nitrate, secondary sulfate, and mobile source. For Seoul, Gwangju, and Ulsan, ten identical sources were found to contribute to $PM_{2.5}$

and the sources related secondary formation accounted for $PM_{2.5}$ mass concentration significantly in common. For Daejeon, PMF resolved almost similar factors while aged sea salt was not found due to the geographical location.

In addition, the adverse health effects of exposure to $PM_{2.5}$ were evaluated by combining $PM_{2.5}$ speciation data and PMF results with parameters representing mortality and morbidity. Daily death counts and daily EDVs were modeled with the mean concentration of $PM_{2.5}$ chemical constituents and source contribution to assess the effects of $PM_{2.5}$ on health outcomes. Overall, IQR increases in the concentration of $PM_{2.5}$ constituents and source contribution showed positive relation with health outcomes while the significance and strength of the associations were different depending on species and sources as well as the cause of health outcomes. Moreover, the associations between health outcomes and $PM_{2.5}$ exposure varied considerably across the cities. These findings imply that the health effects of $PM_{2.5}$ exposure might be very heterogeneous and region-specific.

The results of the study indicate that the heterogeneous and region-specific characteristics of $PM_{2.5}$ composition may result in different health effects on human body. Consequently, quantifying adverse health effects as well as identifying $PM_{2.5}$

composition and source contributions in the region of interest should be evaluated in the processes of establishing optimal policies for managing $PM_{2.5}$ from a public health perspective.

References

Chen, Y., Luo, X. S., Zhao, Z., Chen, Q., Wu, D., Sun, X., Wu, L. and Jin, L., 2018. Summer-winter differences of $PM_{2.5}$ toxicity to human alveolar epithelial cells (A549) and the roles of transition metals. *Ecotoxicology and environmental safety*, 165, pp.505-509.

Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L. C., Dallmann, T. R., Wood, E. C., Herndon, S. C., Goldstein, A. H. and Harley, R. A., 2013. Chemical composition of gas-phase organic carbon emissions from motor vehicles and implications for ozone production. *Environmental Science & Technology*, 47(20), pp.11837-11848.

Gu, J., Bai, Z., Liu, A., Wu, L., Xie, Y., Li, W., Dong, H. and Zhang, X., 2010. Characterization of atmospheric organic carbon and element carbon of $PM_{2.5}$ and PM_{10} at Tianjin, China. *Aerosol and Air Quality Research*, 10(2), pp.167-176.

Han, C., Lim, Y. H., Yorifuji, T. and Hong, Y. C., 2018. Air quality management policy and reduced mortality rates in Seoul Metropolitan Area: A quasi-experimental study. *Environment international*, 121, pp.600-609.

Han, H., Jung, C. H., Kum H. S. and Kim, Y. P., 2017. The Revisit on the PM_{10} reduction policy in Korea: focusing on policy target, tools and effect of 1st Air Quality Management Plan in Seoul Metropolitan Area. *Journal of Environmental Policy and Administration*, 25(1), pp.49-79

Heo, J., Schauer, J. J., Yi, O., Paek, D., Kim, H. and Yi, S. M., 2014. Fine particle air pollution and mortality: importance of specific sources and chemical species. *Epidemiology*, pp.379-388.

Islam, M. N., Park, M., Jo, Y. T., Nguyen, X. P., Park, S. S., Chung, S. Y. and Park, J. H., 2017. Distribution, sources, and toxicity assessment of polycyclic aromatic hydrocarbons in surface soils of the Gwangju City, Korea. *Journal of Geochemical Exploration*, 180, pp.52-60.

Kang, M., Kim, K., Choi, N., Kim, Y. P. and Lee, J. Y., 2020. Recent occurrence of PAHs and n-Alkanes in $PM_{2.5}$ in Seoul, Korea and characteristics of their sources and toxicity. *International Journal of Environmental Research and Public Health*, 17(4), 1397.

Kim, E., Bae, C., Yoo, C., Kim, B.-U., Kim, H. C. and Kim, S., 2018. Evaluation of the effectiveness of emission eontrol measures to improve $PM_{2.5}$ concentration in South Korea. *Journal of Korean Society for Atmospheric Environment*, 34(3), pp.469-485.

McNeilly, J. D., Heal, M. R., Beverland, I. J., Howe, A., Gibson, M. D., Hibbs, L. R., MacNee, W. and Donaldson, K., 2004. Soluble transition metals cause the pro-inflammatory effects of welding fumes in vitro. *Toxicology and applied pharmacology*, 196(1), pp.95-107.

Rajagopalan, S., Al-Kindi, S. G. and Brook, R. D., 2018. Air pollution and cardiovascular disease: JACC state-of-the-art review. *Journal of the American College of Cardiology*, 72(17), pp.2054-2070.

국문 초록

우리나라 주요 대도시(서울, 대전, 광주, 울산)의 $PM_{2.5}$ 구성성분 및 오염원 기여도에 의한 건강영향 분석

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$PM_{2.5}$에 대한 노출은 전 세계적으로 사람의 건강에 심각한 위협이 되고 있으며, 사망과 장애에 영향을 미치는 대표적인 위험 인자(risk factor)이다. 우리나라 역시 급속한 산업화 및 도시화에 따라 $PM_{2.5}$에 의한 심각한 대기질 문제를 겪고 있으며, 대기 중 $PM_{2.5}$ 농도 저감을 위해 다양한 정책이 추진되고 있다. $PM_{2.5}$는 불균일 혼합물(heterogeneous mixture)로 황산염, 질산염, 유기탄소, 원소탄소 및 비소, 크롬과 같은 중금속 등의 매우 다양한 화학물질로 구성되는데, $PM_{2.5}$의 화학적 조성은 지역에 따라 다른 (region- specific) 특성이 있다. 이는 $PM_{2.5}$가 배출원에서의 직접 배출(primary emission) 보다 황산화물(SOx), 질소산화물(NOx), 휘발성 유기화합물(VOCs) 등 가스상 전구물질의 대기 중 화학반응에 의한

2차 생성(secondary formation)을 통해 주로 대기 중에 존재하기 때문이다. 즉, 대상지역 및 인근지역의 전구물질 배출량, 대기 중 전구물질의 농도, 기상조건, 오염원의 위치, 지리적 특성 등 매우 다양한 인자들에 의해 $PM_{2.5}$ 조성이 결정된다.

$PM_{2.5}$ 화학적 조성은 대상 지역의 $PM_{2.5}$에 영향을 나타내는 주요 오염원을 규명하고, 각 오염원의 기여도를 산정함에 있어 매우 중요한 요소이다. 또한, 화학적 조성은 궁극적으로 $PM_{2.5}$ 노출이 인체에 유발하는 건강영향과도 밀접하게 연관되어 있기 때문에 보건학적 측면에서의 $PM_{2.5}$ 관리를 위해서는 대상 지역에서의 $PM_{2.5}$의 구성성분 및 오염원에 의한 건강영향을 정량적으로 산정할 필요가 있다.

본 연구에서는 "대기관리권역의 대기환경개선에 관한 특별법"에 따라 지정된 4개 대기관리권역을 대표하는 대도시인 서울, 대전, 광주, 울산에서 2014년부터 5년간 분석된 일별 $PM_{2.5}$ 질량농도 및 구성성분 농도를 이용하여 도시별 오염원을 규명하고, 각 오염원의 기여도를 산정하였다. 또한, 같은 기간 $PM_{2.5}$ 구성성분 농도 및 오염원 기여도와 일별 사망자 수 및 응급실 내원환자 수의 연관성을 분석함으로써 $PM_{2.5}$ 노출이 사망과 질병에 미치는 건강영향을 산정하여 건강영향 측면에서 도시별 오염원 관리의 우선순위 선정을 위한 기초자료를 구축하였다.

PMF 모델링을 통해 확인된 오염원은 서울, 광주, 울산의 경우 총 10개로 이차 질산염, 이차 황산염, 자동차, 생물성 연소, 소각시설, 토양, 산업, 석탄 연소, 석유 연소, 노후 해염입자 오염원으로 나타났다. 대전의 경우 지리적 위치로 인해 노후 해염입자

오염원은 확인되지 않았고, 나머지 9개 오염원은 다른 도시들과 동일한 것으로 확인되었다. 오염원 기여도에 있어서는 4개 도시 모두에서 공통적으로 이차 질산염, 이차 황산염 및 자동차 오염원에 의한 기여도가 60% 이상으로 나타나 $PM_{2.5}$가 주로 대기 중 이차생성 및 자동차에 기인하는 것을 확인하였다. 하지만 다른 오염원의 기여도는 도시별 특성에 따라 다르게 나타났는데 특히, 대규모 화력발전소에 인접한 서울, 광주의 경우 석탄 연소 오염원의 기여도가 10% 내외로 높게 나타나 해당 도시에서 네번째로 높은 기여도를 보였다. 반면, 가장 동쪽에 위치한 울산에서는 석탄 연소 오염원의 기여율은 상대적으로 낮았으나 대규모 중화학 공업 도시의 특성이 반영되어 산업 오염원의 기여도가 다른 도시에 비해 월등히 높게 나타났다.

$PM_{2.5}$ 구성성분 및 오염원 기여도와 건강영향의 연관성을 분석한 결과는 $PM_{2.5}$ 구성성분 농도 및 오염원 기여도의 단위(IQR) 증가가 전반적으로 사망 및 질병의 상대위험도 증가로 이어짐을 보여주었다. 그러나 구성성분 및 오염원 기여도와 건강영향 사이 연관성의 유의성 및 정도는 지역마다 다르게 나타났다. 먼저 구성성분이 사망에 미치는 영향의 경우 서울, 대전에서는 주로 심혈관계 사망에서 중금속, 유기탄소 등의 구성성분과의 유의한 연관성이 확인되었으나 광주에서는 주로 호흡기계 사망의 상대위험도가 중금속, 이온성분과 밀접한 관계가 있는 것으로 나타났다. 오염원-사망의 연관성에 있어서는 사망의 상대위험도를 증가시킨 구성성분과 밀접한 오염원의 기여도 증가가 사망과 밀접한 것으로 확인되었다. 따라서 $PM_{2.5}$ 노출로 인한 사망 영향을 줄이기 위해서는

도시별 건강영향 분석에 따라 오염원 관리의 우선순위를 마련하고, 각 오염원별 배출량 저감을 위한 정책이 수반될 필요성이 있다.

사망과 다르게 $PM_{2.5}$ 노출에 따른 질병 영향은 주로 호흡기계 질병을 중심으로 구성성분 및 오염원 기여도와 유의한 연관성이 확인되었다. 이 같은 결과는 $PM_{2.5}$의 주 노출경로가 호흡(inhalation)이고, $PM_{2.5}$가 매우 미세한 크기로 인해 매질인 공기와 유사하게 거동함에 따라 상기도 뿐만 아니라 하기도인 기관, 기관지, 폐포 등에도 쉽게 도달한 후 염증 반응, 산화스트레스 등의 메커니즘을 통해 호흡기계에 급성 영향을 나타내기 때문으로 판단된다. 상기 메커니즘에 의해 호흡기계 기관에서 생성된 염증성 사이토카인, 활성산소종 등은 다시 전신순환을 통해 심혈관계에 도달해 질병을 유발할 수 있고, 궁극적으로 사망의 위험도를 증가시킬 수 있다.

본 연구의 결과는 대기 중 질량농도 저감에 초점이 맞추어져 있는 현재의 $PM_{2.5}$ 관리정책이 지역별 조성, 오염원 기여도 및 건강영향 특성을 고려한 정책으로 확대될 필요성이 있음을 시사한다. 즉, 환경 오염물질 관리의 궁극적인 목적은 오염물질에 대한 노출이 인체에 유발하는 부정적인 영향을 최소화함으로써 국민의 건강과 안녕을 유지하는 것이기 때문에 지역 특이적인 $PM_{2.5}$의 조성과 그로 인해 다르게 나타나는 건강영향을 평가함으로써 최적의 대기관리 정책 및 계획 등을 수립하여 실행할 필요가 있다.

주요어 : $PM_{2.5}$, 구성성분, 건강영향, 일반화선형모형, PMF

학 번 : 2017-32636