Apportioning and Locating PM$_{2.5}$ sources Affecting Coastal Cities:
Ulsan in South Korea and Dalian in China

Eunhwa Choi$^1$, Kwonho Jeon$^2$, Young Su Lee$^3$, Jongbae Heo$^4$, Ilhan Ryoo$^5$,
Taeyeon Kim$^5$, Chuanlong Zhou$^6$, Philip K. Hopke$^7$, Seung-Muk Yi$^5*$

$^1$Research Institute of Industrial Science & Technology 67 Cheongam-ro, Nam-gu, Pohang-si,
Gyeongsangbuk-do, 37673, Republic of Korea
$^2$Climate and Air Quality Research Department Global Environment Research Division, National
Institute of Environmental Research, Incheon, Republic of Korea
$^3$Department of Energy and Environmental Engineering, Soonchunhyang University, 22
Soonchunhyang-ro, Asan, Republic of Korea
$^4$Busan Development Institute, Busan 47210, Republic of Korea
$^5$Department of Environmental Health Sciences, Graduate School of Public Health, Seoul
National University, 1 Gwanak-ro, Gwanak-gu, Seoul, Republic of Korea
$^6$Laboratory for Sciences of Climate and Environment, Gif-sur-Yvette, France
$^7$Center for Air Resources Engineering and Science, Clarkson University, Potsdam, New York
13699, United States; Department of Public Health Sciences, University of Rochester School of
Medicine and Dentistry, Rochester, New York 14642, United States

* Corresponding author. Tel: 82-2-880-2736
E-mail: yiseung@snu.ac.kr
Abstract

PM$_{2.5}$ mass and its constituent species were analyzed in two coastal cities (Ulsan, South Korea, and Dalian, China) between July 13, 2018, and September 20, 2019. Ten and nine sources were identified in Ulsan and Dalian, respectively, using positive matrix factorization (PMF). In Ulsan, three sources (secondary nitrate [SN], secondary sulfate [SS], and traffic) contributed ~83.0% of the PM$_{2.5}$ mass concentration (23.7 µg m$^{-3}$) during the heating period. In Dalian, four sources (SN, SS, traffic, and residential burning) accounted for ~84.3% of the total PM$_{2.5}$ mass concentration (47.8 µg m$^{-3}$). Higher contributions of residential burning in Dalian (11.7 µg m$^{-3}$) than biomass burning in Ulsan (0.22 µg m$^{-3}$) were resolved during the heating period as was a higher proportion of SS contributions in Ulsan (6.28 µg m$^{-3}$, 41.6%) than in Dalian (6.42 µg m$^{-3}$, 21.2%) during non-heating period. Squared correlation coefficients ($r^2$) of sources common to the two cities were examined for lag times from -2 days to +4 days from Dalian to Ulsan. The largest $r^2$ of PM$_{2.5}$ mass concentrations during the heating period was 0.34 on Lag day 1. The same day, largest $r^2$ during the non-heating period was 0.14 indicating, stronger, lagged PM$_{2.5}$ correlations during the heating period. The SN, SS, soil, and oil combustion sources, with $r^2$ values of 0.25, 0.20, 0.41, and 0.25, respectively, show fair correlations between the cities for these sources during the heating period.

Probable source locations were identified by simplified quantitative transport bias analysis (SQTBA) and potential source contribution function (PSCF) as a multiple site approach and a single site approach, respectively. Weaker correlations of SN ($r^2 = 0.15$) and SS ($r^2 < 0.1$) during the non-heating period were supported by the different probable source locations. This study identified the sources requiring individual national and/or joint international efforts to reduce ambient PM$_{2.5}$ in these neighboring countries.

Keywords: PM$_{2.5}$, source apportionment, positive matrix factorization, potential source contribution function, simplified quantitative transport bias analysis
1. INTRODUCTION

Air pollution is a significant cause of adverse health outcomes (WHO, 2021). The International Agency for Research on Cancer (IARC) concluded that outdoor air pollution is carcinogenic to humans, with the particulate matter (PM) component of air pollution most highly associated with increased cancer incidence (WHO, 2016). Despite various efforts to improve air quality over the past decades, PM$_{2.5}$ concentrations in many countries still exceed the PM$_{2.5}$ guideline values (5 µg m$^{-3}$ for the annual mean value; 15 µg m$^{-3}$ for the daily mean value) recommended by the WHO (2021).

Because PM$_{2.5}$ can be transported over long distances, neighboring cities and countries and even different continents can be influenced by PM$_{2.5}$ originated from regional sources or transported from distant regions (Perry et al., 1997; VanCuren and Cahill, 2002; Park et al., 2004; Vallius et al., 2005; Uno et al., 2009; Amato et al., 2016; Kim et al., 2022a; Yen et al., 2024). Comparisons of PM$_{2.5}$ concentrations, chemical compositions, and sources measured in many cities across Europe have been reported (Vallius et al., 2005; Sillanpää et al., 2006; Amato et al., 2016). In Asia, long range transport of air pollutants from the Asian continent have been reported in studies conducted in Japan and Taiwan (Lee et al. 2019; Hung et al. 2019; Griffith et al. 2020). Park et al. (2018) compared the PM$_{2.5}$ mass concentrations and its major constituents in three East Asian cities: Seoul, South Korea (hereinafter, Korea); Beijing, China; Nagasaki, Japan. Additionally, regionally transported PM$_{2.5}$ from outside of China were identified in Beijing (Wang et al. 2015). Liu et al. (2020) estimated that PM$_{2.5}$ pollution from outside China caused 100 thousand premature deaths in 2015, accounting for 9.60% of the PM$_{2.5}$ related premature deaths.

Studies performed in Korea showed that long-range transported PM$_{2.5}$ formed from secondary inorganic precursor sources, or emitted by coal combustion, and industrial sources in
China, soil dust from China and Mongolia, and biomass burning in China, Mongolia, and Russia influenced the PM$_{2.5}$ concentrations in Seoul, Incheon, or Daebudo, Korea (Heo et al. 2009; Choi et al. 2013; Kim et al. 2018; Lee et al., 2023). Kim et al. (2022a) reported that severe haze in Seoul, Korea during the winter of 2017 was influenced by transported nitrate, sulfate, and ammonium with a high proportion of the PM$_{2.5}$, transported from eastern China. Kim et al. (2022b) reported that residential coal combustion in northern China increased PM$_{2.5}$ concentrations in Seoul during the COVID-19 lockdown. Kim et al. (2020a) showed that regional transport of polluted air masses likely played an important role in the haze episodes observed in Seoul during early spring based on simultaneous measurements in Seoul (downwind) and Beijing (upwind). Nonetheless, characterization, transport, and source apportionments of atmospheric PM$_{2.5}$ mass concentrations measured during a given period using consistent methods between neighboring countries are very limited.

Most previous studies of PM$_{2.5}$ transported from outside Korea have been done in Seoul or Incheon, located in northwestern Korea and close to China. Ulsan is a city located in the southeast of Korea, and situated east of the Taebaek Mountains that divide Korea's spine from east to west and was considered less vulnerable to pollutants arriving from the northwest. However, according to the Korea Meteorological Administration, over the 30 years from 1991 to 2020, Asian dust was observed in Seoul and Incheon for 29 of those years (96.7%), and in Ulsan, located in southeastern Korea, Asian dust was observed in 26 years (86.7%). The effect of Asian dust observed in Ulsan indicates the likelihood of other transported PM$_{2.5}$ or influencing local concentrations. Korea's main wind pattern changes clearly depending on the season. In winter, cold, and dry northwest winds blow under the influence of continental high pressure. Thus, further studies were needed to determine transported pollutant impacts on southeastern coastal locations in Korea.

Dalian, located in northeastern China (upwind of Ulsan), is a city with high PM$_{2.5}$
concentrations and a moderate economic growth rate (Wang et al., 2021). The PM$_{2.5}$ concentration in Dalian is expected to increase due to fuel combustion during the cold winter. However, compared to cities with higher economic growth rates (e.g., Beijing, Shanghai, Tianjin, and Hebei) in northern China, few studies have been conducted on its atmospheric PM$_{2.5}$ concentrations or sources. Moreover, it has never been compared with the concentrations or sources of PM$_{2.5}$ in Korean cities.

Thus, this study was performed in Ulsan, Korea and Dalian, China. Both are coastal industrial cities, but they have their own characteristics, including geographic location, meteorological conditions, and local sources of PM$_{2.5}$. This study compared the PM$_{2.5}$ sources and their contributions to these two coastal cities using positive matrix factorization (PMF) and determined the likely PM$_{2.5}$ source regions related to both cities to identify the potential PM$_{2.5}$ abatement opportunities from individual and/or joint efforts. Conditional bivariate probability function (CBPF), correlation analysis of the sources common to the two cities, potential source contribution function (PSCF), and simplified quantitative transport bias analysis (SQTBA) were used to explore the local, regional, and common source locations of PM$_{2.5}$ in Ulsan and Dalian.

2 MATERIALS AND METHODS

2.1 Study sites

The locations and characteristics of the two study sites are presented in Fig. S1 and Table S1 in supplementary material (SM). The Ulsan site (35°34'52.0" N, 129°19'27.0" E) in Korea is one of intensive air pollution monitoring stations operated by the Ministry of Environment and the National Institute of Environmental Research (NIER) of Korea. Ulsan is situated in southeastern Korea. The sampling site is ~8 km and ~16 km from two large, nationally designated, industrial complexes including petrochemical, non-ferrous metal, car manufacturing, and ship building.
industries that are known PM$_{2.5}$ sources (Choi et al., 2011). The Dalian site (38°53’10.0” N 121°34’06.8” E) in China is located in the Shahekou district. It is ~7 km southwest of the center of Dalian and ~2 km from a Dalian high-tech zone (called the Dalian software park) to the east. Port and industrial complexes including machinery, petrochemical, shipbuilding, locomotive manufacturing, and automobile industries are located to the northeast of the sampling site. The two cities are approximately 800 km from each other.

2.2 Sampling and chemical analysis

There were differences in the sampling/analysis processes in the two cities. In Ulsan, hourly data were obtained using a set of in situ speciation monitors. Hourly concentrations of organic carbon (OC) and elemental carbon (EC) were collected on a quartz filter and measured by thermal-optical transmittance method (Model-4 Semi-Continuous OC-EC Field Analyzer, Sunset Laboratory Inc., USA). Ionic species ($\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{Na}^+$, $\text{K}^+$, and $\text{NH}_4^+$) were measured by Dionex® Ion Chromatography (URG-9000D ambient ion monitor, URG Corp., USA). Elements with atomic numbers ≥12 were measured by X-ray fluorescence spectrometry (XRF) (XactTM 620, Cooper Environmental Services, USA). PM$_{2.5}$ mass concentration was measured using a MetOne 1020 Beta attenuation monitor (BAM) that has been designated as a PM$_{2.5}$ Federal Equivalent Method (US Federal Register, EQPM-0308-170). In Dalian, multiple integrated filter samples were collected using a PM2.5 sampler with three parallel channels at a flow rate of 16.7 L/min. The filters were analyzed off-line using the gravimetric method (40 CFR 53) for mass and for chemical species as described in Text S1 of the SM.

2.3 Positive matrix factorization

PMF is the most widely used source apportionment tool (Paatero and Tapper 1994; Hopke et al. 2020). EPA PMF 5.0 was applied to the PM$_{2.5}$ mass concentrations and constituents to identify and apportion PM$_{2.5}$ sources (Text S1.2; Table S2). If the concentration were greater than the method
detection limit (MDL), associated uncertainties were prepared according to the equation

\[ \text{Uncertainty} = \sqrt{(0.1 \times \text{concentration})^2 + (0.5 \times \text{MDL})^2} \]

in the EPA PMF 5.0 user’s guide (Norris et al., 2014). The concentration values below the MDL were replaced by half of the MDL, and their uncertainties were set at 5/6 of the MDL. For missing constituent data, the respective geometric mean was used as the mass concentration and four times the geometric mean was used as its uncertainty. The PM$_{2.5}$ mass concentrations were used as the total variable. The total mass concentrations of PM$_{2.5}$ were down-weighted with an uncertainty of four times the mass concentration to ensure that the results of the PMF models were not considerably affected by the PM$_{2.5}$ total mass itself. PM$_{2.5}$ mass closure and ion charge balance were calculated as data screening steps (Lewis et al. 2003; Maxwell-Meier et al. 2004; Sillanpää et al. 2006). In the initial PMF run, all species were included, and in subsequent runs, poorly fitted species or species with low signal-to-noise ratios (S/N) were removed by setting to “bad” or downweighted as “weak” (Table S2) (Paatero and Hopke, 2003). As a result, 20 species including total variable PM$_{2.5}$ in 7471 hourly samples in Ulsan and 24 species from 217 23 h integrated samples in Dalian were included in the respective PMF analyses. Because shorter sampling duration provides better factor resolution and increases the number of sources resolved (Lioy et al. 1989), the hourly Ulsan data were used in the PMF analysis.

Source contributions resolved by PMF in Ulsan and Dalian were compared using daily mean values in Ulsan and 23h-integrated values in Dalian by averaging the hourly source contributions in Ulsan to daily mean values (a total of 369 values). PM$_{2.5}$ mass concentrations increased and PM$_{2.5}$ source contributions changed during the cold season when building heating was implemented. Thus, the analysis of PM$_{2.5}$ mass concentrations and PM$_{2.5}$ source contributions, and the tracing of PM$_{2.5}$ source locations was examined separately for the heating and non-heating periods after the PMF analyses for the entire period. The heating period in Dalian, China was between November 5
and March 31 of the following year. A similar heating season occurred in Ulsan, Korea.

2.4 Statistical analysis

Data analysis was performed using the Statistical Package for Social Sciences (version 21; IBM Corp., Armonk, NY, USA). The strength of relationships between sources resolved by PMF in Ulsan and Dalian were assessed using squared Pearson’s correlation coefficients. High correlations due to similar seasonal pattern in source contributions was minimized by separately analyzing the correlations for the heating period and non-heating period rather than for the entire period. Lag times from Dalian to Ulsan between -2 days and +4 days were used in the correlation analysis. The statistical differences in the contribution of PM$_{2.5}$ sources between heating and non-heating periods were found not to follow a normal distribution. Thus, the differences were assessed using the Mann Whitney U test for pairwise comparisons.

2.5 Conditional bivariate probability function

CBPF analysis (Uria-Tellaetxe and Carslaw 2014) was applied to the PMF resolved contributions using surface wind directions and speeds (KMA 2021; Raspisaniye Pogodi Ltd., 2021) to help identity the factors and investigate source directionality (Text S1.3). In this study, 12 sectors ($\Delta \theta = 30^\circ$) and threshold criteria of the upper 25th percentile for each source contributions were applied. CBPF values were down-weighted by multiplying 0.25, 0.5, and 0.75 when the total numbers of occurrences in particular wind direction-speed interval were 1, 2, and 3, respectively (Carslaw, 2019).

2.6 Potential source contribution function and simplified quantitative transport bias analysis

In this study, PSCF analysis was applied to locate possible source areas in the respective city, and SQTBA was applied to explore common regions of the sources extracted in Ulsan and Dalian. PSCF (Ashbaugh et al., 1985) was used to identify PM$_{2.5}$ source regions for each site. PSCF is based on the concept that the regions frequently traversed by high-concentration trajectories are
source regions or pathways. Quantitative transport bias analysis (QTBA) was developed by Keeler 1987 as a multiple site approach (Hopke 2016). QTBA has sophisticated features because normal
distribution by atmospheric dispersion is approximated along the trajectory centerline and the
standard deviation increases linearly with backward time (Han 2005; Hopke 2016). However, it is
very difficult to implement. Thus, a practical approach, SQTBA, has been applied using basic

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 5.1) model (Stein et al., 2015) and gridded meteorological data (GDAS1) from the US National Oceanic and
Atmospheric Administration were used to calculate air parcel backward trajectories using 0.9
planetary boundary layer (PBL) as starting heights. The GDAS 1 data were selected because of the
availability for the study period and its better performance in retrieving contributions from various
directions (Su et al., 2015; Park et al., 2022). Source contributions were used as input data in the
PSCF and SQTBA analyses. Four-day backward time was selected to explore regional source areas
of PM$_{2.5}$ in Ulsan and Dalian. For PSCF analysis of soil sources, upper 5$^{th}$–10$^{th}$ percentile
concentration criteria were used to locate probable source areas. For the other sources, an upper
25$^{th}$ percentile criterion was applied. Details of the PSCF and SQTBA calculations are presented
in Text S1.4 and S1.5. SQTBA used an open-source web application, Trajectory based source
apportionment (TraPSA) (Zhou et al. 2024).

3 RESULTS AND DISCUSSION

3.1 Overview of the observations
PM$_{2.5}$ mass concentrations and constituents (µg m$^{-3}$) measured in Ulsan and Dalian between July
13, 2018 and September 20, 2019 were compared. In Ulsan, daily mean mass concentration of
PM$_{2.5}$ during the entire period was 19.0 ± 12.6 µg m$^{-3}$, with a range of 2.3–73.0 µg m$^{-3}$. In Dalian,
the 23h mean PM$_{2.5}$ mass concentration during the entire period was 38.1 ± 28.1 µg m$^{-3}$, with a
range of 8.2 to 188 µg m$^{-3}$ indicating the PM$_{2.5}$ concentration in Dalian was approximately twice
that in Ulsan. The 23 h mean value of PM$_{2.5}$ (38.1 µg m$^{-3}$) measured in Dalian was similar with
daily mean value (35.9 µg m$^{-3}$) measured at the nearest monitoring station for the same
measurement period (Fig. S2).

The heating and non-heating seasonal average PM$_{2.5}$ concentrations were 24.8 ± 14.3 µg m$^{-3}$
and 16.0 ± 10.5 µg m$^{-3}$, respectively, in Ulsan, and 49.6 ± 37.3 µg m$^{-3}$, 30.4 ± 15.6 µg m$^{-3}$,
respectively, in Dalian (Fig. S2). Therefore, the average PM$_{2.5}$ concentration during the heating
period was more than 1.5 times the average PM$_{2.5}$ concentration during the non-heating period in
both cities. Higher PM$_{2.5}$ concentrations during the heating period are due to elevated emissions
from fossil fuel and biomass burning for heating, poorer atmospheric dispersion, and increased
condensation of semi-volatile organic compounds on pre-existing aerosols (Lee and Hieu 2011;
Xie et al. 2019; Dai et al. 2021). Mass concentrations of PM$_{2.5}$ and its chemical composition in
Ulsan and Dalian are shown in the Table S2. The PM$_{2.5}$ pollution in both cities are further
characterized using PMF in section 3.2.
3.2 Source apportionment

PMF solutions were explored from eight to eleven factors for Ulsan and six to ten factors for Dalian. The best fits to the data were chosen by examining the model performance including the distributions of scaled residuals and the interpretability of factors (Paatero et al. 2005) (Table S3). In Ulsan, the number of scaled residuals beyond $3 \sigma$ decreased from 158 to seven when factor size increased from nine to ten. In Dalian, the number of scaled residuals beyond $3 \sigma$ decreased from ten to three when factor size increased from seven to eight and decreased from three to one when factor size changed from eight to nine. However, the source profiles of vehicle exhaust mixed with industry sources in the eight factor models and there was slight increase in the $r^2$ between observed and modeled PM$_{2.5}$ in the nine factor model (Table S4). Thus, ten- and nine-factor models were chosen as the optimal fits in Ulsan and Dalian, respectively. The uncertainty of PMF solution associated with the change of source profile were assessed using the displacement (DISP) analysis. Although DISP is very sensitive to higher data uncertainties (Paatero et al., 2014; Brown et al., 2015), the DISP range were distinctly shorter for the marker species for each specific source, indicating little rotational ambiguity in the solutions (Fig. 1). There were no swaps and the bootstrap results conformed with the 80% requirement for correlation with the base run results.

The time series of PMF factor contribution are shown in Fig. 2. The model predicted PM$_{2.5}$ mass concentrations correlated with the observed values with squared correlation coefficients ($r^2$) of 0.939 and 0.960 for Ulsan and Dalian, respectively.

Secondary nitrate was characterized by the highest fraction of NO$_3^-$ and NH$_4^+$ with tight DISP intervals and accounted for 30.9% and 30.5% of total PM$_{2.5}$ in Ulsan and Dalian respectively (Fig. 1; Table S5). Higher contribution of SN sources during heating period at both sites may be explained by the formation of particle-phase ammonium nitrate facilitated by low temperature in winter (Peng et al. 2021).
Secondary sulfate comprised the highest fraction of $\text{SO}_4^{2-}$ and $\text{NH}_4^+$ occupied the largest portion (33.4%) and the second largest portion (19.3%) of total PM$_{2.5}$ in Ulsan and Dalian, respectively (Table S5). It is known that sulfate concentration is generally high in warm season due to increased photochemical activity (Miyakawa et al. 2007). However, in Dalian, the SS source contribution was higher during heating period although the difference was not statistically significant (Fig. 2). Many studies have reported higher sulfate concentrations during heating period due to domestic coal and biomass burning for heating purpose in Chinese cities (Dai et al. 2019, 2021) and indicated the primary or secondary sulfate as a cause of the severe haze during winter (Wang et al. 2016; Dai et al. 2021). Higher concentrations of SO$_2$ and NO$_2$ in Dalian during heating period were observed compared to the non-heating period (Fig. S2) implying the possibility of an elevated secondary sulfate concentration downwind and primary sulfate emissions from local residential heating (Dai et al. 2019).
Fig. 1 Profiles of the source factors extracted by PMF: (a) Ulsan; (b) Dalian.

The bars represent the concentrations of respective species apportioned to each factor (left axis). The open circles are the mean DISP values and the error bars provide the minimum and maximum DISP values. The filled circles are the percent explained variations (right axis).
Fig. 2. Daily mean PM$_{2.5}$ mass concentration by source at study sites.

Daily mean PM$_{2.5}$ mass concentration in Ulsan and 23h integrated PM$_{2.5}$ mass concentration in Dalian were used. H and NH denote heating and non-heating period, respectively.

Mann Whitney test $p$-values: *$p$ < .05; **$p$ < .01; ***$p$ < .001.
The traffic related sources, including both exhaust and non-exhaust emissions, contained high concentrations of OC, EC, Fe, Zn, Pb, Ti (Liu et al. 2014; Zannoni et al. 2016). Brake pads and tire wear are known sources of Mn, Zn, Fe, and Ti (Apeagyei et al. 2011; Zannoni et al. 2016). The presence of Pb and Ti is attributed to the ablation of road paint (Yu et al. 2016; Zannoni et al. 2016). Ba, Ca, and Mg shown in Dalian’s source profile are used in lubricating oil additives (Whisman et al. 1974). This source made up 13.1% and 12.9% of total PM$_{2.5}$ mass concentration in Ulsan and Dalian respectively.

The soil source was dominated by typical crustal components such as Si, Fe, Ca, Al, Mg, and Ti (Vouk and Piver 1983). Higher contribution of soil source during heating period was observed in both cities and statistically significant in Ulsan (p < 0.01) and in Dalian (p < 0.001). Ulsan was affected by Asian dust events between November 28 and 30, 2018 (Korea Meteorological Administration). A severe haze-fog episode was reported over North China between November 23–26 (Tang et al., 2020). The daily mean PM$_{2.5}$ concentrations in Ulsan were 29–54 µg m$^{-3}$ (November 28 to 30) and that in Dalian was 122.6 µg m$^{-3}$ (November 26) (Fig. 2). The PM$_{2.5}$ mass concentration of the soil source resolved with PMF was 9.4–16.4 µg m$^{-3}$ in Ulsan (November 28 to 30) and 19.4 µg m$^{-3}$ in Dalian (November 26) (Fig.S3). In addition to the days recorded as Asian dust events in Ulsan, there were days when the soil source contributions in Ulsan increased after those in Dalian increased.

The sea salt source was identified by Na$^+$, Ca, Cl$^-$, or Mg/Mg$^{2+}$ (Enghag 2008). This source comprised 0.49 µg m$^{-3}$ in Ulsan and 1.21 µg m$^{-3}$ in Dalian for the entire period (Table S5). The higher contribution in Dalian can be due to the sampling site being closer to the sea (approximately 1 km) compared to Ulsan site (11 km) (Fig.S1).

The oil combustion source was indicated by high explained variations and tight DISP intervals of V and Ni, elements characteristic of heavy fuel or residual oil combustion (Vouk and
Piver 1983; Jang et al., 2007; Anastasopolos et al. 2023). This source can be attributed to marine
diesel emissions from ships in the ports, or in nearby shipping lanes (Agrawahl et al., 2008a,b;
2009; 2010; Shanavas et al., 2020) as well as emissions from petrochemical plants, refineries, or
oil-fired industrial boilers in Ulsan and Dalian (Choi et al., 2021; Zhao et al., 2021). The higher
ccontributions during the non-heating period suggest that this source is more influenced by ship
emissions than point sources. The PM$_{2.5}$ concentration from oil combustion was significantly
higher (p<0.001) during non-heating period than during heating period in both cities. While
petrochemical production is relatively constant throughout the year, ship entries and departures in
Korea during non-heating period was distinctly higher between 2015 and 2019 (Statistics Korea
2022). Similarly, the volume of freight handled in coastal ports in China was larger during non-
heating period between Mar. 2021 and Feb.2022 (National Bureau of Statistics of China 2022) and
these were compatible with automatic identification system maritime data (UCL Energy Institute
2021).

The next sources were related to the metal related industrial activities. The profiles in Ulsan
were characterized by high contributions of OC and narrow DISP intervals of Fe, Zn, Mn, Cu, and
Pb whose dominant sources are ferrous and non-ferrous metal industries (Dai et al. 2015). The
profile of the metal industry in Dalian was dominated by Fe, Zn, Mg, Ca, Pb, Mn, and Cu with
small contributions of OC or SO$_4^{2-}$, and NO$_3^{-}$ indicating the impact of metal processing industries
rather than metal production or smelting (Figs. 1 and S1).

The coal combustion source featured high loadings of SO$_4^{2-}$ and NH$_4^{+}$ and high explained
variations of As and Pb (Tian et al. 2014; Yu et al. 2016). While coal is used mostly in coal fired
power plants or industrial plants for metal smelting in Korea, coal consumption for residential
heating/cooking purposes is still widely used (Kim et al., 2020b) and is very common in China
(Tian et al. 2015; Li et al., 2019a; Hopke et al. 2020; Dai et al., 2021; 2023). However, higher
emissions of As and Pb from coal consumption was attributed to coal fired power plants or
industrial boilers rather than residential sectors in China (Tian et al. 2015). Additionally, increase
in the contribution of this source in Dalian from March to September (Fig. 2) suggested that this
was attributed to not only electricity generation for district heating or industrial boilers but also to
electricity generation for space cooling. Rapid rise in space cooling demands in China (IEA, 2019)
explain the higher proportion of this sources during non-heating period.

The next factor in Ulsan was interpreted as biomass burning because it featured high
explained variations of K⁺ and high loadings of OC, EC, and SO₄²⁻ (Hopke et al. 2020). The waste
combustion source in Ulsan was indicated by OC, Cl⁻, NO₃⁻, Si, Zn, and Pb (Jayarathne et al. 2018;
Kumar et al. 2018; Moffet et al., 2008; Yang et al., 2016). The amount of municipal solid waste
combusted nationwide in Korea is usually larger during non-heating period than heating period
(Korea Environment Corporation 2017), but the increase in the contribution of waste combustion
source during heating period could be due to industrial incineration and greater partitioning of gas-
phase HCl to particulate matter in colder season (Gunthe et al. 2021).

The last factor in Dalian was interpreted as residential burning sources because of high
loadings of OC, EC, NO₃⁻, K⁺, NH₄⁺, and Cl⁻. The profile was characterized by high explained
variations of OC, EC, K⁺, which are dominant markers of biomass burning, as well as high
variations in As and Pb, coupled with high contributions of Cl⁻, a strong marker for coal combustion
in China (Yu et al. 2013; Liu et al. 2018). Increased emissions from residential biomass and coal
burning during heating period in China has been reported in many previous studies (Li et al, 2019;
produces primary sulfate (Dai et al., 2019) and significant quantities of OC including humic-like
substances (HULIS) (Li et al., 2019). Meanwhile, Cl⁻ also is a marker of waste combustion
(Jayarathne et al. 2018; Li et al., 2012) because of wastes containing plastics made of polyvinyl
chloride and the salt in kitchen waste (Yang et al., 2016), and chloride was most associated with
district coal combustion in China (Liu et al., 2018; Li et al., 2019). It indicated the possibility of
mixed residential burning of coal/biomass/waste and district coal combustion during the heating
season. The contribution of this source to PM$_{2.5}$ concentrations in Dalian during the heating period
(11.7 $\mu$g m$^{-3}$, 24.4% of PM$_{2.5}$ mass concentration) was significantly higher ($p<0.001$) compared to
that during non-heating period (2.21 $\mu$g m$^{-3}$, 7.3 % of PM$_{2.5}$), and markedly higher than biomass
burning sources in Ulsan during heating period (0.22 $\mu$g m$^{-3}$, 0.9 % of PM$_{2.5}$).

In Ulsan, three sources (SN, SS, and traffic) accounted for approximately 83.0% of PM$_{2.5}$
concentration during the heating period. In Dalian, four sources (SN, SS, traffic, and residential
burning) constituted approximately 84.3% of PM$_{2.5}$ concentration during the heating period. SS
was a large fraction of PM$_{2.5}$ in Ulsan (33.4%) compared to Dalian (19.3%) during the study period.
Thus, there is a need for SS precursor reductions in the Ulsan source areas. During the heating
period, the contributions of residential burning sources accounted for 24.4% in Dalian, becoming
the second largest source of PM$_{2.5}$ in Dalian.

### 3.3 Correlations of PM$_{2.5}$ sources common to Ulsan and Dalian

PM$_{2.5}$ sources can be local, regional, or both. To identify the local and regional sources that likely
influenced the PM$_{2.5}$ mass concentrations in both cities, correlations between the contributions from
the sources common to Ulsan and Dalian were analyzed. For residential burning sources in Dalian,
correlations with Ulsan’s biomass burning, coal combustion, and waste combustion were analyzed.
Because there was no notable difference in the correlation coefficients, the correlation with the
biomass burning sources in Ulsan is shown (Fig. 4).

The $r^2$ value indicates the variance of one variable that can be explained by the other variable.
During the heating period, the largest $r^2$ for PM$_{2.5}$ concentrations between the two cities for a $+1$
day lag was 0.34. Thus, 34% of the variance in PM$_{2.5}$ concentration in Ulsan can be explained by the changes in PM$_{2.5}$ concentration in Dalian with a one-day transport period. However, during the non-heating period, the largest $r^2$ of PM$_{2.5}$ concentration was 0.14 on the same day, indicating a weak correlation during the non-heating period. The $r^2$ of SN (0.25), SS (0.20), soil (0.41), and oil combustion (0.25) sources were $>0.2$ during the heating period. However, the $r^2$ of SN (0.15), SS (0.08), and oil combustion (0.18) were $<0.2$ during the non-heating period. Soil had a $r^2$ of 0.25 during the non-heating season. The relatively higher $r^2$ of soil sources is probably due to when a combination of wind erosion of cultivated soil and dust storms would affect both cities. A dust storm in the Gobi Desert on April 28, 2019 was reported, and Asian dust events were recorded in six cities (or islands) in Korea between May 1 to 2 (Kai et al., 2021; Korea Meteorological Administration).

Given that the relatively higher correlations between sources common to Ulsan and Dalian (SN, SS, soil, and oil combustion sources) can be due to transport on a regional scale as well as local sources, the correlation coefficients may be somewhat underestimated or overestimated. This possibility arises because PM$_{2.5}$ undergoes various physical and chemical interactions and transformations including phase transitions, gas uptake, and chemical reactions (Monks et al., 2009). There also can be sufficient local source contributions to distort the covariances.

The SN, SS, soil, and oil combustion sources with relatively higher correlation coefficients between Ulsan and Dalian had similar fractions of key indicator elements with tight DISP intervals (Fig.1). In contrast, the sources (traffic, sea salt, and industry) with relatively lower correlation coefficients between the two cities showed respective profile characteristics as explained in 3.2. The coal combustion sources in Ulsan and Dalian showed different Zn, As, and Pb concentrations, suggesting the differences in coal fuel or burning conditions in the respective cities.
Fig. 3 Squared correlation coefficients ($r^2$) between common sources to Ulsan and Dalian during heating period and non-heating period. $r^2$ values larger than 0.1 are presented for each source.

3.4 Local characteristics of PM$_{2.5}$ sources

Wind roses, CBPF plots, and Pearson’s correlations between secondary and primary sources at Ulsan and Dalian, respectively, are presented in Figs. S4–S7. The CBPF plots for SN and SS sources and high correlations with primary sources in Ulsan compared to in Dalian suggested that SN and SS in Ulsan were more influenced by local sources (Figs. S5–S7). The probable source directions in the SN CBPF plots in Ulsan during the heating and non-heating periods were similar to the four combustion sources (oil, coal, waste, and biomass burning sources), industry, and traffic.
sources. This directionality indicated the possibility of multiple collocated sources or nitrate formation by the oxidation of NO\textsubscript{x}, which is mainly emitted from the combustion sources. The CBPF results in Dalian showed that wind from the southwest direction primarily affected the increase in SN source contributions. Relatively high correlations with coal combustion and residential burning were identified. Such correlations are reasonable given that they would all be NO\textsubscript{x} sources that can be rapidly converted to nitrate.

The CBPF results for SS sources showed that the Ulsan site during non-heating period was primarily affected from the southeast where ports and industrial complexes are located. Marine diesel engines are a source of primary sulfate as well as SO\textsubscript{2} (Kim and Hopke, 2008). Higher CPF values under southeasterly winds of 2–4 m/s during the non-heating period suggested local sources such as emissions from ships ($r^2 = 0.31$) in the ports and from cargo loading vehicles ($r^2 = 0.35$) to and from industrial complexes and ports (Figs. S5–S7). In Dalian, the port and most of local industrial sources are northeast of the sampling site (Fig.S1). The elevation in PM\textsubscript{2.5} mass concentrations during heating period, influenced by SS sources, may be attributed to the port of Dalian and the extensive shipping in the Bohai Sea when the northeasterly wind is strong, at approximately 10 m/s (Fig. S5). Additionally, an $r^2$ of 0.32 between SS and residential burning sources suggested that local residential heating contributed to the elevation of SS source contributions during the heating period (Fig. S7). Similarly, the source directions of SS and $r^2 = 0.51$ with biomass burning at the Ulsan site during heating period indicated that primary sulfate from local burning of biomass could be sources of SS (Dai et al., 2019; Song et al., 2024) (Fig. S5).

The traffic sources affected by ubiquitous local emissions were seen in the Ulsan CBPF plots. Dominant directions of traffic sources were not found because high CBPF values were in the center of the CBPF plots with 0–4 m/s wind speeds. The ancillary directions of traffic sources were found to be junctions of highways to the east, southwest, and west of the Ulsan site. For Dalian,
the CBPF plot showed traffic sources in all directions except to the south and southeast toward the
sea.

The CBPF plots, which indicate the direction of relatively local soil sources, pointed
southwest of the Ulsan site with wind speed of 7–8 m/s during the heating period. It was inferred
that the site was affected by agricultural activities such as clearing fields or preparing the soil for
planting crops in small farmlands to the southwest of the sampling site. The CBPF results for soil
at Dalian site during heating period showed that prevailing directions were north and northeast,
under strong wind speeds (> 8 m/s). It appears to be due to agricultural areas in the Ganjingzi
district in Dalian.

At both sites, the easterly wind in Ulsan and the southerly wind in Dalian coinciding with
the sea direction, prevailed during non-heating period compared to heating period (Fig. S4). This
appears to have influenced that the potential source direction of sea salt and oil combustion sources
more pronounced during the non-heating period (Fig. S5). The CBPF plots for oil combustion
sources at Ulsan showed that prevailing directions was southeast with 0–5 m/s wind speed. In Ulsan,
two ports located at 7.5 km and 13.5 km southeast of the sampling site and the second largest
petrochemical complex in Korea to the southeast of the sampling site likely contributed to the oil
combustion sources. For Dalian, the CBPF results suggest that oil combustion contributions were
from south toward the sea (Fig. S5). The direct southerly and southeasterly directions in both
seasons suggest the influence of the major marine shipping lanes that run to Tianjin and Dalian.

Industrial sources were identified near the Ulsan sites to the southeast where Mipo and
Onsan industrial complexes are located. In Dalian, the north and northeast where multiple metal
processing plants were located, were dominant source directions with 0–8 m/s wind speeds.

The CBPF results for coal combustion at Ulsan demonstrated southeasterly sources where
the industrial complexes including non-ferrous metal manufacturing plants using coal for smelting, are located. For Dalian, the direction of coal combustion sources during non-heating period included the north and northeast where coal fired power plants are located (Global Energy Monitor 2022). Additionally, CBPF plots show areas to the south. District space heating or cooling in nearby large residential districts and the Xinghai park is likely influence high CPF values during heating and non-heating periods (Fig.S5).

Biomass burning sources in Ulsan during heating period were identified in the east to northeast where vegetable and horticultural farms are located. In Korea, burning crop residues or weeds on farmland is legally prohibited. From December 1 to March 31 each year, the collection and disposal of agricultural waste has been enhanced as part of the seasonal intensive management program for PM$_{2.5}$. However, there are still some areas where the practice of open burning continues. Households where biomass is used for heating or cooking are rarely found in Korea. As of 2019, the number of households using briquettes in Ulsan is 0.026% of the total number of households (Babsang Community Briquette Bandk and Briquette Bank National Council, 2022). Residential burning sources were only identified at Dalian. During heating period, this source is affected by a very localized emissions as it has high CBPF values in most directions including the center of the plot (low wind speeds) and from the west where the nearest residential district is located.

3.5 Probable source region located by PSCF and SQTBA

The PSCF plots suggest the probable PM$_{2.5}$ source regions for Ulsan and Dalian sites. The sources that were commonly interpretable by the PSCF plots for Ulsan and Dalian were coal combustion, SN, SS, soil, and oil combustion sources (Figs. S8–S9). Among them, probable areas of coal combustion sources for Ulsan and Dalian were not close to each other. In Ulsan, a probable source area of coal combustion was identified along the east coast of Korea including Donghae, Samchok, and Yeongdong where coal-fired power plants are located (Global Energy Monitor 2022). In Dalian,
a probable source area was between southern Shandong Province and Shanghai along the Chinese coast.

Because the PSCF plots showed similar source locations (Figs. S8–S9) for the SN, SS, soil, and oil combustion sources with $r^2 > 0.14$, these joint sources were further assessed using the SQTBA plots (Fig. 4). The SN source areas common to Ulsan and Dalian were in Shandong, Hebei, Henan, and Jiangsu Provinces. Ammonium nitrate is formed in areas characterized by high ammonia and nitric acid concentrations (Lee et al., 2006). Regional transport of high ammonia emissions from agricultural areas in Shandong, Anhui, Jiangsu, Henan, and Hebei (Kim et al., 2006; Lee et al., 2006) and $NO_x$ emissions from high vehicle populations or industrial activities in Shandong, Henan, Hebei, and Jiangsu (Park et al., 2022) likely contribute to NH$_4$NO$_3$ concentration in Ulsan and Dalian. In addition, high nitric acid from atmospheric processing of local emissions of $NO_x$ from traffic emissions and industrial facilities in Ulsan and Dalian contribute.
Fig. 4 Likely common source areas identified using SQTBA plots, 96 h backward time during heating and non-heating period: (a) Secondary nitrate; (b) Secondary sulfate; (c) Soil; (d) Oil combustion. (The units of the numbers in the color bar are the weighted SQTBA values.)
The SQTBA plots show probable common source locations for SN and SS during the heating period and SN during the non-heating period (e.g., Shandong, Hebei, Henan, and Jiangsu) (Fig.4). The PSCF plots suggest SN and SS in Ulsan were less influenced by China during the non-heating period (Figs. S8–S9). The differences in common source location between heating and non-heating period were greater for SS than SN consistent with lower maximum $r^2$ values for SN (0.15) and SS (0.08) sources during the non-heating period compared to heating period values (0.25 for SN; 0.20 for SS) (Fig. 3). Lower $r^2$ values (0.08) of SS sources during the non-heating period support the spread of probable common source regions in Fig. 4 by including the Yellow Sea and the East China Sea. The probable location of SS sources in the sea may represent the oxidation of dimethyl sulfide, ship emissions, and power plants and industrial emissions located along China’s coast (Kim and Hopke 2008; Heo et al. 2009). During the heating period, pollutant emissions from combustion in China may contribute to secondary aerosol formation (Liu et al., 2018; Dai et al. 2019, 2021), resulting in the higher correlations of the SN and SS sources between Ulsan and Dalian, and the common source areas in China identified by SQTBA. Higher correlation of SN and SS on the same days in Ulsan and Dalian (Fig.3) may be attributed to seasonal variation or meteorological conditions in part (Peng et al., 2021; Miyakawa et al., 2007). Other previous studies (Li et al., 2019; Islam et al., 2023; Chen et al., 2020) also suggested that factors such as geographic location, similar emission characteristics, or seasonal variations in human activities may affect PM variations.

The PSCF plots for the upper 10th percentile of soil source concentration during the heating period in Ulsan and Dalian indicated Mongolia to northern/northeastern China as probable source areas. Asian dust storms occur in dry late winter and spring as air masses move from Mongolia or northern China to the East China Sea (Tan et al. 2017), affecting Chinese and Korean cities (Heo et al. 2009; Choi et al. 2013; Korea Meteorological Administration). Trajectories associated with the upper two percentile of hourly soil source concentration in Ulsan showed air parcels (Fig. S11) passing...
through the Gobi Desert, southern Mongolia, northern China, and Inner Mongolia. The SQTBA plots identified soil sources in similar areas and Shandong province as probable common source areas. A review of 39 studies in Shandong reported dust sources as the second largest PM source accounting for 18.4% of total PM$_{2.5}$ concentration among secondary aerosols, dust, coal combustion, and vehicle emissions (Zhou et al. 2021). Soil and construction dust contributed 11.5% and 7.7%, respectively, to total PM$_{2.5}$ mass concentration (100.9 µg m$^{-3}$) in Heze, Shandong (Liu et al. 2017). The PSCF plots for soil sources showed the influence of Shandong province on Ulsan and Dalian (Figs. S8–S9).

The PSCF results for oil combustion at Ulsan showed that during heating period, areas near the Yellow Sea contributed marine diesel oil combustion emissions from the extensive shipping in this area. During non-heating period, southerly winds were prevalent such that the probable source region was the East China Sea (Figs. S8–S9). For Dalian, potential source regions identified by PSCF plots were the Yellow Sea during non-heating period and during heating period, were the areas between Shanghai and Qingdao where the world’s largest and the seventh largest port, respectively, are located (World Shipping Council 2020). Joint source areas of oil combustion identified by SQTBA were similar to those identified by the PSCF at Ulsan. Oil combustion was attributable in part to local petrochemical plants, but also from emissions from maritime transport.

4 CONCLUSIONS

Using the PM$_{2.5}$ mass concentration and chemical constituents from Ulsan and Dalian, PMF resolved ten sources in Ulsan and nine sources in Dalian. Similar source types were resolved in both countries. The high emissions and the transport patterns during the heating period led to higher lagged correlations between the cities for the SN, SS, soil, and oil combustion sources implying the PM$_{2.5}$ transport from China to Ulsan in Korea. Comparisons of the $r^2$ of these common sources
and the potential source locations using PSCF and SQTBA plots suggested that the sources with higher correlations (SN, oil combustion, and soil during both heating and non-heating period; SS during heating period) had similar potential source regions. During the non-heating period, scattered potential SS source regions in the SQTBA plots were consistent with the smaller $r^2$ values. The Ulsan SS source had a common source area with Dalian in China during heating period. The high fractional SS contributions (41.6%) in Ulsan during the non-heating period compared to heating period (23.5%) in Ulsan, and relatively higher correlations among the primary sources (oil combustion and traffic) in Ulsan than those in Dalian suggested the local source management could reduce the Ulsan sulfate concentrations during the non-heating period.

In Dalian, higher SS concentrations (8.4 µg m$^{-3}$) during the heating period compared to the non-heating period (6.4 µg m$^{-3}$), and higher $r^2$ values (0.32) with residential burning sources compared with other primary sources during the heating period were identified. During the heating period in Dalian, residential burning sources and SS sources showed a concentration of 11.7 µg m$^{-3}$ and 8.4 µg m$^{-3}$, respectively, thus management of residential burning sources could be an effective tool for local and regional air quality management.

The PM$_{2.5}$ source apportionments and the relationships among the two cities common sources showed when and which sources require local national and/or joint international efforts to reduce PM$_{2.5}$ concentrations in these neighboring countries.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Institute of Environmental Research (NIER), funded by the Ministry of Environment (ME) of the Republic of Korea (No. NIER-2020-04-02-086).

DISCLAIMER
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data
Supplementary data to this article can be found in online.

REFERENCES


Apeagyei E, Bank MS, Spengler JD (2011) Distribution of heavy metals in road dust along an urban-rural gradient in Massachusetts. Atmos Environ 45:2310–2323


Hopke PK, Dai Q, Li L, Feng Y (2020) Global review of recent source apportionments for

PM2.5 events over Northern Taiwan during 2005–2015 winter seasons. Atmospheric


Testing Experiment (NAMaSTE): emissions of particulate matter from woodland dung-
fueled cooking fires, garbage and crop residue burning, brick kilns, and other sources.

Atmos Chem Phys 18:2259–2286

Junri Zhao, Yan Zhang, Haoran Xu, Shu Tao, Rong Wang, Qi Yu, Ying Chen, Zhong Zou, and
Weichun Ma (2021) Trace Elements From Ocean-Going Vessels in East Asia: Vanadium
and Nickel Emissions and Their Impacts on Air Quality. JGR Atmosphere.

10.1029/2020JD033984.

Survey in April 2019. Sola 17:130-133

Northeastern United States. Thesis


Kim E, Hopke PK (2008) Source characterization of ambient fine particles at multiple sites in the

factorization (PMF) at a rural site in Korea. Journal of Environmental Management

episodes and influences of long-range transport in the Seoul metropolitan area in March


Kim, Y, Kim H, Kang H, de Foy, B, Zhang, Q (2022a) Impacts of secondary aerosol formation
and long range transport on severe haze during the winter of 2017 in the Seoul

transboundary impacts of PM2.5 sources identified in Seoul during the early stage of the
COVID-19 outbreak, Atmospheric Pollution Research (in press).

https://data.kma.go.kr/data/grnd/selectAwsRltmList.do?pgmNo=56


Korea Meteorological Administration. Observation days of Asian dust.
https://www.weather.go.kr/w/dust/dust-obs-days.do?type=1&stnId=152. Accessed 5 Dec
2022.


of Mexico City. Environmental science & technology 42, 7091–7.


Wang Y, Gong Y, Bai C, Yan H, Yi X (2021) Exploring the convergence patterns of PM2.5 in
Chinese cities. Environment, Development and Sustainability.


WHO (2021) WHO global air quality guidelines: particulate matter (PM2.5 and PM10), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide. World Health Organization


